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The *ab initio* model potential method: Lanthanide and actinide elements

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In this paper we present relativistic core *ab initio* model potentials based on atomic Cowan–Griffin calculations, together with Wood–Boring spin-orbit operators and optimized Gaussian valence basis sets, for the lanthanide elements Ce to Lu and for the actinide elements Th to Lr. This completes the chemically relevant part of the Periodic Table. A [Kr,$4d$] core was chosen for Ce–Lu and a [Xe,$4f$,$5d$] core was chosen for Th–Lr. Minimal $(14s10p9d8f)/[2s1p1d1f]$ and $(14s10p11d9f)/[2s1p1d1f]$ valence basis sets were, respectively, optimized for Ce–Lu and Th–Lr, and a $[6s5p5d4f]$ contraction is recommended for all these 28 elements in molecular calculations. The atomic and molecular results show the same good quality already observed for the main-group elements and the transition metal elements.
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I. INTRODUCTION

Effective core potential methods (ECP) are accepted as efficient tools to carry out spin-free and spin-orbit relativistic *ab initio* calculations in molecules and crystals. They are especially indicated when heavy elements are involved.

Two families of relativistic ECP methods exist: those relying on the pseudo-orbital transformation,[1] which produce nodeless valence pseudo-orbitals and are known as *pseudopotential* methods, and those based on the Huzinaga–Cantu equation,[2] which lead to valence orbitals with the same nodal structure as the all-electron orbitals and are know as *model potential* methods. Within the latter kind, the *ab initio* model potential method (AIMP)[3] resulted from the implementation of two ideas:[4] (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. Spin-free relativistic core AIMPs derived from atomic Cowan–Griffin calculations[5] and extended to include spin-orbit coupling effects according to Wood and Boring suggestions[6] constitute the so-called relativistic WB-AIMPs,[7] which are used with optimized valence basis sets. In addition to the nonrelativistic ones, the ingredients of the WB-AIMP method have been produced, successfully monitored, and used for the main-group elements and for the three series of transition metal elements.[4,7–11] The quality of the one-electron effective spin-orbit Wood–Boring operators was shown to be very high in atomic and molecular calculations.[12,13] Also, the expected good performance of this method for f elements has been confirmed in relativistic spin-orbit calculations on Ce and spin-free calculations on CeO (Ref. 14) (Ce is recognized as a difficult case[15,16]) and taken as an indication that one could safely proceed with the lanthanide and actinide series.

In order to complete the chemically relevant part of the Periodic Table, we produced and present here the ingredients of the WB-AIMP method for the lanthanide elements Ce to Lu and for the actinide elements Th to Lr. (For these elements, several sets of relativistic pseudopotentials are available in the literature.[16–20]) We present [Kr,$4d$] core AIMPs together with $5s$,$5p$,$4f$,$5d$,$6s$ optimized valence basis sets and Wood–Boring spin-orbit operators for Ce–Lu, and [Xe,$4f$,$5d$] core AIMPs with $6s$,$6p$,$5f$,$6d$,$7s$ optimized valence basis sets and Wood–Boring spin-orbit operators for Th–Lr. It is worth noticing that the Gaussian primitive functions that have been optimized here with the Cowan–Griffin relativistic Hamiltonian are expected to be transferable to relativistic AIMPs based on the Douglas–Kroll–Hess Hamiltonian,[21,22] as was the case of the transition metal elements from Sc to Hg.[23,24]

II. *AB INITIO* MODEL POTENTIALS AND VALENCE BASIS SETS

We summarize here the procedure leading to (1) the spin-free relativistic core *ab initio* model potentials derived from Cowan–Griffin atomic calculations (CG-AIMP); (2) 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; and (3) the valence basis sets. The details have been fully described in Refs. 3, 4, and 7. All these data are available from the authors[25] and are presented in the Supplementary Material Section of Ref. 26 as E-PAPS document files.

A. WB-AIMP Hamiltonian

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

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TABLE I. Core/valence partitions and valence basis sets used for the lanthanide and actinide elements.

	Label	Core orbitals	Valence orbitals	Minimal valence basis set
Ce–Lu	[Kr,4*d*]	K,L,M,4*s*,4*p*,4*d*	5*s*,5*p*,4*f*,5*d*,6*s*	(14*s*10*p*9*d*8*f*)/[2*s*1*p*1*d*1*f*]
Th–Lr	[Xe,4*f*,5*d*]	K,L,M,N,5*s*,5*p*,5*d*	6*s*,6*p*,5*f*,6*d*,7*s*	(14*s*10*p*11*d*9*f*)/[2*s*1*p*1*d*1*f*]

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

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

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

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

$$\begin{aligned}\hat{h}^{\text{CG-AIMP}}(i)={}&-\frac{1}{2}\hat{\nabla}_i^2+\sum_I^{N_{\text{nuc}}}\Bigg[-\frac{Z^I-Z^I_{\text{core}}}{r_i}\\&+\sum_k\frac{C^I_k\exp(-\alpha^I_k r_i^2)}{r_i}\\&+\sum_l\sum_{m=-l}^{+l}\sum_{a,b}|\chi^I_{alm}\rangle A^{I,MP}_{l;ab}\langle\chi^I_{blm}|\\&+\sum_{c\in\text{core}}(-2\varepsilon^I_c)|\phi^I_c\rangle\langle\phi^I_c|\Bigg].\end{aligned}\tag{3}$$

This operator is a practical, approximate representation of the corresponding frozen-core operator[27]

$$\begin{aligned}\hat{h}^{\text{CG-FC}}(i)={}&-\frac{1}{2}\hat{\nabla}_i^2+\sum_I^{N_{\text{nuc}}}\Bigg[-\frac{Z^I-Z^I_{\text{core}}}{r_i}-\frac{Z^I_{\text{core}}}{r_i}\\&+2\sum_{c\in\text{core}}\hat{J}^I_c(r_i)-\sum_{c\in\text{core}}\hat{K}^I_c+\hat{V}^I_{MV}\\&+\hat{V}^I_D+\sum_{c\in\text{core}}(-2\varepsilon^I_c)|\phi^I_c\rangle\langle\phi^I_c|\Bigg],\end{aligned}\tag{4}$$

which is made of the nonrelativistic kinetic energy operator and a sum of atomic operators that includes, for each of them, the nuclear attraction, the core Coulomb and exchange operators, the Cowan–Griffin–Wood–Boring valence mass-velocity and Darwin operators, and a final term resulting from the linear-independency conditions between core and valence orbitals.[2] In Eq. (4), $\hat{V}^I_{MV}+\hat{V}^I_D$ reads

$$\hat{V}^I_{MV}+\hat{V}^I_D=\sum_{nl\in\text{valence}}\hat{O}^I_l(V^I_{MV,nl}+V^I_{D,nl})\hat{O}^I_l,\tag{5}$$

where $V^I_{MV,nl}+V^I_{D,nl}$ are the orbital-dependent mass-velocity plus Darwin potentials of Cowan–Griffin–Wood–Woring (related to but different from Pauli's mass-velocity and Darwin operators)[5,6] and the angular projectors made of spherical harmonics

$$\hat{O}^I_l=\sum_{m=-l}^{+l}|Y^I_{lm}\rangle\langle Y^I_{lm}|,\tag{6}$$

prevent the *nl*-potentials from acting on orbitals with a different l'.

The ingredients in Eq. (3) are produced as follows: A numerical all-electron spin-free relativistic Cowan–Griffin–Hartree–Fock calculation[5] is performed on a given state of atom I (usually the ground state, see Tables IV and V). From this calculation, a set of atomic orbitals is arbitrarily defined as the *core* $\{\phi^I_c\}$ (see Table I). The core orbitals are represented by analytical Gaussian expansions which are obtained by a maximum overlap criterion[28] and they and their orbital energies ε^I_c are conveniently stored in libraries. With the numerical core orbitals, the core Coulomb potential $2\Sigma_c\hat{J}^I_c(r)$ is calculated, $-Z^I_{\text{core}}/r$ is added to it, and the result is represented with a local potential $1/r\Sigma_k C^I_k\exp(-\alpha^I_k r^2)$ by means of a least-squares fitting procedure and stored. This is the third term on the right-hand side of Eq. (3). The mass-velocity and Darwin radial operators of Cowan–Griffin–Wood–Boring corresponding to the valence orbitals are also stored: $\{V^I_{MV,nl}+V^I_{D,nl}\}_{nl\in\text{valence}}$. In a given atomic or molecular calculation, these scalar relativistic operators are added to the core exchange operator $-\Sigma_c\hat{K}^I_c$ 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 $A^{I,MP}_{l;ab}$ coefficients are the elements of the product matrix $S^{I^{-1}}V^I_{EMD}S^{I^{-1}}$; here, S^I is the overlap matrix in the basis of primitives $\{\chi^I_{alm}\}$ and V^I_{EMD} is the matrix of the operator $-\Sigma_{c\in\text{core}}\hat{K}^I_c+\hat{V}^I_{MV}+\hat{V}^I_D$ of atom I in the same basis. 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 $A^{I,MP}_{l;ab}$ coefficients, they are calculated during the input processing part of every single molecular calculation.[29] Strictly speaking, Eq. (5) holds only when one valence orbital exists for a given l, whereas a different operator corresponds when more than one valence orbital of a given l is used; the use of coupling operator techniques[30] would be indicated in the latter case, leading to an operator which causes, say, the $V_{MV,5s}$ to act on the ϕ_{5s} and the $V_{MV,6s}$ to act on the ϕ_{6s}. It has been shown, however, that using the mass-velocity and Darwin potentials of the outermost valence orbitals for the inner valence orbitals leads to very small errors, safely acceptable within an effective potential method.[14] As a consequence with this, we will use this approximation. Finally, the last term on the right-

TABLE II. Valence spin-orbit model potentials [Eq. (9)] of the lanthanide elements.

$V_{\mathrm{SO},5p}$		$V_{\mathrm{SO},5d}$		$V_{\mathrm{SO},4f}$	
β_k^{5p}	B_k^{5p}	β_k^{5d}	B_k^{5d}	β_k^{4f}	B_k^{4f}
		Cerium			
1 466 000.0	0.283 988 89	661 400.0	0.353 027 14	512 000.0	0.370 872 44
170 300.0	0.260 225 45	64 360.0	0.248 521 00	46 890.0	0.238 625 75
29 790.0	0.172 510 09	8 505.0	0.125 285 38	5 777.7	0.111 985 85
3 960.3	0.095 611 29	1 232.7	0.054 152 73	774.45	0.045 519 61
476.14	0.039 725 20	184.72	0.022 389 01	110.649	0.017 694 07
53.796	0.014 534 47	27.374	0.009 108 82	17.6163	0.006 555 51
5.7550	0.003 972 00	3.4660	0.002 633 19	2.5920	0.001 999 74
0.5772	0.000 655 78	0.4051	0.000 406 43	0.2947	0.000 313 00
		Praseodymium			
2195 000.0	0.270 541 43	668 700.0	0.349 630 49	508 000.0	0.369 194 53
201 300.0	0.295 867 13	65 730.0	0.250 028 10	46 790.0	0.239 866 20
26 790.0	0.179 891 71	8 795.0	0.127 698 19	5 801.7	0.113 388 03
3 985.8	0.096 576 45	1291.6	0.055 805 06	783.35	0.046 280 19
476.14	0.040 572 12	195.83	0.023 258 33	113.379	0.018 044 60
53.796	0.014 731 46	29.324	0.009 518 09	18.3963	0.006 741 20
5.7550	0.004 050 80	3.7640	0.002 829 17	2.7480	0.002 142 48
0.6023	0.000 659 82	0.4689	0.000 452 35	0.3224	0.000 323 61
		Neodymium			
477 000.0	0.135 862 86	632 200.0	0.351 253 70	554 000.0	0.361 018 73
267 400.0	0.275 185 20	31 820.0	0.249 434 24	52 590.0	0.244 383 79
26 790.0	0.196 835 19	8 217.0	0.126 556 90	6 762.7	0.119 877 97
3 960.3	0.095 641 56	1196.7	0.055 039 02	949.75	0.050 171 33
476.14	0.041 399 23	180.73	0.022 703 05	141.179	0.020 451 49
53.796	0.014 924 64	27.424	0.009 303 49	21.7463	0.007 840 70
5.7550	0.004 139 60	3.4460	0.002 777 12	3.0330	0.002 426 88
0.5772	0.000 653 62	0.3849	0.000 879 68	0.3174	0.000 343 14
		Promethium			
2 817 000.0	0.223 101 25	616 000.0	0.350 657 27	560 000.0	0.357 920 76
251 100.0	0.334 539 47	60 350.0	0.249 674 21	53 690.0	0.246 041 92
26 190.0	0.192 371 18	8 048.0	0.126 908 78	6 986.7	0.122 238 76
3 972.9	0.096 930 86	1 177.3	0.055 342 18	993.65	0.051 645 81
476.14	0.042 148 06	179.25	0.022 808 58	149.459	0.021 248 20
53.796	0.015 121 47	27.764	0.009 393 94	23.1463	0.008 224 37
5.7550	0.004 231 37	3.5520	0.002 878 12	3.2390	0.002 597 07
0.5792	0.000 647 80	0.4016	0.000 892 71	0.3404	0.000 366 92
		Samarium			
1 625 000.0	0.266 943 20	612 200.0	0.348 634 03	565 000.0	0.354 891 71
176 200.0	0.279 608 14	60 330.0	0.250 658 95	54 690.0	0.247 523 60
25 790.0	0.175 157 24	8 104.0	0.128 333 09	7 199.7	0.124 471 64
4 032.6	0.100 905 41	1 194.7	0.056 313 91	1 037.05	0.053 077 75
475.05	0.042 766 49	183.43	0.023 306 68	157.839	0.022 046 25
53.737	0.015 355 02	28.724	0.009 647 77	24.5663	0.008 611 54
5.7550	0.004 270 55	3.7180	0.003 018 01	3.4460	0.002 771 28
0.6112	0.000 667 89	0.4250	0.000 413 51	0.3627	0.000 389 79
		Europium			
1 462 000.0	0.272 142 71	654 800.0	0.341 012 03	559 000.0	0.353 165 61
163 400.0	0.271 187 27	65 920.0	0.253 420 86	54 390.0	0.248 413 41
25 320.0	0.172 155 32	9 093.0	0.133 624 07	7 192.7	0.125 971 54
4 016.7	0.102 014 17	1 879.9	0.059 957 08	1 041.55	0.053 800 59
473.79	0.043 366 82	216.96	0.025 434 32	160.529	0.022 297 14
53.604	0.015 658 42	33.984	0.010 719 05	25.7663	0.008 802 02
5.7550	0.004 327 86	4.5030	0.003 429 50	3.7440	0.002 951 90
0.6534	0.000 678 39	0.5805	0.000 553 85	0.4284	0.000 437 68
		Gadolinium			
1 422 000.0	0.269 557 38	604 000.0	0.344 768 08	564 000.0	0.350 198 07
162 500.0	0.269 040 54	60 180.0	0.252 140 29	55 390.0	0.249 594 13
25 410.0	0.174 177 71	8 197.0	0.131 053 94	7 421.7	0.127 856 03
4 011.6	0.103 333 87	1 226.1	0.058 187 57	1 088.75	0.055 317 91

TABLE II. (*Continued.*)

$V_{\mathrm{SO},5p}$		$V_{\mathrm{SO},5d}$		$V_{\mathrm{SO},4f}$	
β_k^{5p}	B_k^{5p}	β_k^{5d}	B_k^{5d}	β_k^{4f}	B_k^{4f}
474.99	0.043 978 59	191.44	0.024 268 52	468.789	0.023 243 48
53.963	0.015 823 77	30.654	0.010 149 23	26.6863	0.009 205 03
5.7550	0.004 444 81	4.0610	0.003 309 70	3.7780	0.003 076 51
0.6184	0.000 658 64	0.4723	0.000 454 11	0.3969	0.000 421 53
		Terbium			
409 000.0	0.268 752 47	600 400.0	0.342 750 87	559 000.0	0.348 485 93
162 500.0	0.265 185 73	60 150.0	0.252 893 45	55 190.0	0.250 250 73
25 990.0	0.177 412 81	8 249.0	0.132 423 12	7 448.7	0.129 062 27
4 024.3	0.105 599 53	1 242.9	0.059 125 79	1 100.95	0.056 161 82
473.76	0.044 630 14	195.84	0.024 759 61	172.189	0.023 988 25
53.820	0.016 000 63	31.714	0.010 415 57	27.5163	0.009 438 30
5.7550	0.004 530 73	4.2500	0.003 464 60	3.9260	0.003 216 86
0.6163	0.000 650 10	0.4990	0.000 478 12	0.4124	0.000 435 65
		Dysprosium			
1 440 000.0	0.264 889 99	596 000.0	0.340 904 83	553 000.0	0.346 837 95
166 800.0	0.264 795 30	60 010.0	0.253 545 68	54 890.0	0.250 831 21
26 280.0	0.183 967 07	8 286.0	0.133 665 07	7 455.7	0.130 178 28
3 915.7	0.106 394 08	1 257.5	0.060 034 76	1 109.45	0.056 933 61
464.34	0.044 605 45	199.72	0.025 232 20	174.969	0.024 096 00
53.359	0.016 076 89	32.694	0.010 664 77	28.2563	0.009 651 26
5.7550	0.004 603 23	4.4320	0.003 617 86	4.0680	0.003 351 58
0.6192	0.000 645 01	0.5242	0.000 500 23	0.4280	0.000 448 99
		Holmium			
1 480 000.0	0.259 699 39	593 900.0	0.338 773 09	547 000.0	0.345 413 40
171 600.0	0.266 475 73	60 130.0	0.254 308 43	54 490.0	0.251 453 41
26 420.0	0.189 419 66	8 360.0	0.135 105 71	7 440.7	0.131 197 25
3 839.7	0.107 129 48	1 277.7	0.061 064 46	1 113.15	0.057 652 78
458.45	0.044 803 87	204.41	0.025 768 13	176.679	0.024 446 15
53.097	0.016 186 89	33.764	0.010 938 77	28.8463	0.009 825 94
5.7830	0.004 684 14	4.6230	0.003 778 89	4.2000	0.003 478 49
0.627 10	0.000 644 94	0.5500	0.000 522 88	0.4431	0.000 461 15
		Erbium			
1 491 000.0	0.257 085 55	586 000.0	0.337 433 22	428 000.0	0.360 956 02
172 800.0	0.266 425 53	59 540.0	0.254 749 91	40 590.0	0.244 922 87
26 480.0	0.192 609 76	8 318.0	0.135 982 83	5 163.7	0.119 903 60
3 803.4	0.108 111 81	1 278.1	0.061 706 39	718.05	0.050 452 85
456.42	0.045 233 41	206.07	0.026 087 54	104.429	0.020 013 41
53.356	0.016 307 55	34.494	0.011 121 03	17.0263	0.007 045 62
5.9490	0.004 816 88	4.7890	0.003 922 81	2.9330	0.002 494 22
0.6519	0.000 666 98	0.5728	0.000 541 70	0.3205	0.000 302 40
		Thullium			
1 474 000.0	0.255 794 15	583 800.0	0.335 372 48	423 000.0	0.359 950 79
173 400.0	0.262 504 75	59 620.0	0.255 439 72	40 190.0	0.245 751 41
26 790.0	0.197 320 29	8 884.0	0.137 351 68	5 162.7	0.120 758 65
3 748.3	0.109 120 81	1 296.8	0.062 717 07	715.95	0.051 004 41
456.41	0.045 347 68	210.45	0.026 610 41	104.249	0.020 297 15
54.564	0.016 580 41	35.534	0.011 385 81	16.9163	0.007 120 99
6.1530	0.004 997 67	4.9830	0.004 086 61	2.9640	0.002 523 65
0.6769	0.000 689 41	0.5988	0.000 564 18	0.3243	0.000 301 97
		Ytterbium			
1 428 000.0	0.254 578 53	578 400.0	0.333 758 39	417 000.0	0.358 792 43
170 800.0	0.260 930 12	59 310.0	0.255 931 69	39 790.0	0.246 301 81
26 790.0	0.196 266 70	8 386.0	0.138 405 33	5 136.7	0.121 600 26
3 823.6	0.110 872 97	1 304.5	0.063 502 64	715.25	0.051 605 95
462.97	0.046 634 80	213.24	0.027 008 22	104.199	0.020 598 42
54.504	0.016 836 57	36.414	0.011 604 64	16.8163	0.007 204 72
6.1730	0.005 077 72	5.1670	0.004 245 07	2.9960	0.002 551 17
0.6824	0.000 685 79	0.6236	0.000 584 67	0.3278	0.000 301 58

TABLE II. (*Continued.*)

$V_{SO,5p}$		$V_{SO,5d}$		$V_{SO,4f}$	
β_k^{5p}	B_k^{5p}	β_k^{5d}	B_k^{5d}	β_k^{4f}	B_k^{4f}
Lutetium					
1 498 000.0	0.250 254 48	574 900.0	0.331 880 60	369 000.0	0.365 381 15
174 800.0	0.264 409 86	59 230.0	0.256 483 11	34 390.0	0.242 997 40
26 790.0	0.200 544 99	8 425.0	0.139 610 49	4 817.7	0.116 664 03
3 769.7	0.111 391 24	1 318.4	0.064 430 15	582.05	0.048 637 88
462.17	0.046 906 47	216.86	0.027 470 21	80.269	0.019 171 73
55.095	0.017 063 87	37.404	0.011 850 19	11.2563	0.006 898 82
6.2910	0.005 223 07	5.3620	0.004 413 03	1.9090	0.001 670 62
0.6927	0.000 690 85	0.6496	0.000 605 95	0.1905	0.000 155 26

TABLE III. Valence spin-orbit model potentials [Eq. (9)] of the actinide elements.

$V_{SO,6p}$		$V_{SO,6d}$		$V_{SO,5f}$	
β_k^{6p}	B_k^{6p}	β_k^{6d}	B_k^{6d}	β_k^{5f}	B_k^{5f}
Thorium					
2 115 500.0	0.188 073 58	397 210.0	0.322 405 93	339 700.0	0.335 315 20
239 900.0	0.258 631 46	41 795.0	0.259 889 23	34 730.0	0.256 313 60
31 155.0	0.265 768 43	6 130.4	0.145 569 45	4 901.1	0.137 768 22
3 567.40	0.134 195 29	965.42	0.071 073 08	751.77	0.063 651 93
478.251	0.056 450 98	148.737	0.030 264 20	116.351	0.027 306 31
61.526 5	0.021 708 85	23.184 0	0.012 143 38	17.097 3	0.010 636 54
8.166 90	0.007 133 23	3.643 60	0.003 376 34	2.517 90	0.002 471 25
0.756 64	0.001 091 21	0.451 63	0.000 543 79	0.299 21	0.000 350 64
Protactinium					
2 262 800.0	0.183 862 82	403 800.0	0.319 385 95	341 300.0	0.333 136 47
251 660.0	0.257 094 24	42 804.0	0.260 228 25	35 090.0	0.256 949 65
32 152.0	0.271 960 12	6 323.5	0.148 341 46	4 989.9	0.139 184 98
3 586.19	0.136 700 20	999.91	0.072 097 71	771.98	0.064 742 62
477.723	0.057 043 02	158.464	0.031 119 40	120.479	0.027 935 12
61.645 2	0.021 823 83	25.145 0	0.012 659 97	17.878 3	0.010 963 87
8.407 10	0.007 209 02	4.096 20	0.003 666 69	2.661 10	0.002 592 77
0.813 11	0.001 175 08	0.532 49	0.000 653 91	0.341 80	0.000 393 38
Uranium					
3 455 000.0	0.164 113 90	406 000.0	0.316 888 34	340 000.0	0.331 826 98
341 300.0	0.251 137 71	43 800.0	0.260 682 66	34 990.0	0.257 838 25
39 680.0	0.299 335 41	6 445.0	0.149 593 38	4 971.7	0.140 202 04
3 915.50	0.149 178 83	1 040.60	0.072 694 06	768.85	0.065 273 92
473.940	0.060 573 88	171.020	0.032 107 68	119.919	0.028 192 71
55.022 0	0.021 488 73	27.374 0	0.013 447 23	17.686 3	0.011 098 56
7.550 00	0.006 596 43	4.348 00	0.003 970 25	2.515 00	0.002 573 94
0.747 10	0.001 081 80	0.535 40	0.000 681 87	0.300 80	0.000 353 06
Neptunium					
2 684 200.0	0.166 770 19	395 030.0	0.317 142 67	334 900.0	0.331 041 87
301 410.0	0.250 701 13	42 106.0	0.260 873 49	34 620.0	0.257 625 56
36 260.0	0.290 780 23	6 259.0	0.149 123 54	4 955.5	0.140 515 41
3 743.00	0.144 900 14	1 007.84	0.072 887 59	773.35	0.065 765 44
485.113	0.058 840 13	163.647	0.031 796 86	121.664	0.028 548 76
62.354 0	0.022 453 98	26.357 0	0.013 808 57	18.107 3	0.011 318 42
8.541 10	0.007 853 35	4.165 80	0.003 842 81	2.577 00	0.002 552 09
0.836 89	0.001 236 86	0.536 11	0.000 673 54	0.317 43	0.000 871 80
Plutonium					
3 146 300.0	0.157 056 58	397 190.0	0.314 818 03	335 300.0	0.329 165 81
342 500.0	0.247 173 59	42 552.0	0.261 288 41	34 820.0	0.258 164 93
39 226.0	0.303 824 13	6 366.4	0.150 546 51	5 013.1	0.141 720 39
3 816.52	0.150 050 55	1 032.92	0.074 006 42	787.62	0.066 685 99
480.956	0.059 805 38	169.170	0.032 494 00	124.723	0.029 084 89
60.817 5	0.022 476 79	27.374 0	0.013 710 61	18.692 3	0.011 602 00
8.434 70	0.007 251 65	4.326 30	0.003 981 24	2.662 00	0.002 755 55
0.851 37	0.001 259 80	0.569 01	0.000 719 62	0.335 57	0.000 392 69

TABLE III. (*Continued.*)

$V_{\mathrm{SO},6p}$		$V_{\mathrm{SO},6d}$		$V_{\mathrm{SO},5f}$	
β_k^{6p}	B_k^{6p}	β_k^{6d}	B_k^{6d}	β_k^{5f}	B_k^{5f}
			Americium		
3 384 200.0	0.155 747 77	405 340.0	0.311 276 96	342 800.0	0.325 535 76
350 590.0	0.246 684 24	43 751.0	0.261 870 97	35 910.0	0.259 051 23
39 680.0	0.307 253 19	6 573.9	0.153 579 74	5 226.9	0.144 035 57
3 816.22	0.151 585 11	1 055.52	0.075 969 99	830.51	0.068 470 34
478.783	0.060 610 52	170.635	0.033 158 27	132.957	0.030 100 85
59.804 5	0.022 516 56	27.374 0	0.013 907 07	20.245 3	0.012 107 38
8.512 80	0.007 188 15	4.333 00	0.003 947 57	3.006 20	0.002 994 47
0.909 58	0.001 335 41	0.623 97	0.000 766 51	0.420 26	0.000 487 80
			Curium		
3 819 100.0	0.154 932 99	398 590.0	0.310 944 23	335 300.0	0.325 577 11
875 530.0	0.239 248 96	43 111.0	0.261 389 34	35 130.0	0.259 094 96
42 280.0	0.315 835 39	6 573.7	0.152 682 59	5 113.4	0.143 978 22
3 915.50	0.156 223 84	1 072.33	0.077 326 94	813.74	0.068 442 11
475.913	0.062 426 39	170.720	0.033 737 06	130.472	0.030 116 01
56.240 5	0.022 571 15	27.374 0	0.014 012 85	19.813 3	0.012 157 31
7.872 50	0.006 822 68	4.295 90	0.004 000 79	2.810 30	0.002 963 10
0.854 01	0.001 252 65	0.601 38	0.000 749 24	0.365 67	0.000 424 61
			Berkelium		
6 089 100.0	0.258 145 89	347 780.0	0.320 752 76	335 000.0	0.323 889 97
242 300.0	0.218 469 54	37 509.0	0.254 660 83	35 240.0	0.259 508 51
40 780.0	0.295 039 79	6 025.4	0.143 046 10	5 155.9	0.145 027 04
3 910.45	0.157 365 07	1 052.90	0.075 604 81	825.59	0.069 274 44
473.840	0.063 213 37	170.678	0.034 012 36	133.175	0.030 611 89
54.998 0	0.022 790 69	27.374 0	0.014 172 16	20.354 3	0.012 428 80
7.519 50	0.006 733 57	4.246 60	0.004 025 60	2.878 10	0.003 067 33
0.804 81	0.011 181 39	0.601 58	0.000 742 48	0.378 17	0.000 437 48
			Californium		
3 637 100.0	0.153 429 75	357 320.0	0.317 268 36	335 100.0	0.322 100 82
667 330.0	0.236 561 05	39 211.0	0.252 398 97	35 400.0	0.259 924 77
41 380.0	0.317 672 36	6 416.6	0.148 934 54	5 206.7	0.146 131 11
3 829.45	0.156 598 07	1 071.55	0.078 572 49	838.98	0.070 152 09
476.002	0.062 878 79	171.020	0.034 357 81	136.170	0.031 134 06
57.256 0	0.023 114 52	27.374 0	0.014 422 92	20.953 3	0.012 714 24
8.126 90	0.006 992 85	4.098 50	0.004 0.34 52	2.959 20	0.003 181 69
0.919 20	0.001 356 04	0.582 36	0.000 702 42	0.393 29	0.000 453 21
			Einstenium		
864 700.0	0.239 838 41	479 390.0	0.306 208 43	335 800.0	0.320 208 83
105 570.0	0.251 785 12	44 082.0	0.289 889 64	35 620.0	0.260 379 21
17 535.0	0.208 600 51	5 865.0	0.151 002 53	5 266.7	0.147 304 61
2 893.02	0.108 745 43	1 045.60	0.074 496 37	853.99	0.071 081 53
538.374	0.057 979 20	171.020	0.035 073 26	139.457	0.031 685 85
77.481 6	0.026 142 03	27.374 0	0.014 263 61	21.607 3	0.013 013 94
10.711 10	0.008 884 66	4.318 00	0.004 168 17	3.051 60	0.003 305 61
1.116 45	0.001 728 30	0.609 04	0.000 751 29	0.410 37	0.000 471 19
			Fermium		
877 200.0	0.236 742 49	546 370.0	0.295 232 44	336 000.0	0.318 375 39
107 680.0	0.250 574 96	48 038.0	0.304 296 66	35 800.0	0.260 730 01
17 984.0	0.210 416 91	5 875.0	0.156 617 50	5 321.8	0.148 407 93
2 978.00	0.110 582 60	1 040.60	0.074 255 66	868.42	0.071 978 88
554.814	0.059 839 57	171.020	0.035 535 03	142.703	0.032 226 96
79.657 9	0.026 790 70	27.374 0	0.014 303 83	22.267 3	0.013 312 60
11.015 40	0.009 097 60	4.348 00	0.004 249 17	3.145 30	0.003 432 27
1.162 29	0.001 806 33	0.608 16	0.000 748 72	0.427 61	0.000 489 01
			Mendelevium		
889 000.0	0.233 761 31	418 840.0	0.309 680 01	336 400.0	0.316 544 28
109 710.0	0.249 318 39	40 736.0	0.278 207 82	35 990.0	0.261 093 64
18 427.0	0.212 098 08	5 857.0	0.148 945 10	5 377.7	0.149 514 23
3 064.23	0.112 370 97	1 052.50	0.076 575 07	882.98	0.072 880 34

TABLE III. (*Continued.*)

$V_{SO,6p}$		$V_{SO,6d}$		$V_{SO,5f}$	
β_k^{6p}	B_k^{6p}	β_k^{6d}	B_k^{6d}	β_k^{5f}	B_k^{5f}
571.698	0.060 720 83	171.010	0.035 793 81	145.976	0.032 771 90
81.869 1	0.027 452 59	27.374 0	0.014 536 02	22.934 3	0.013 613 56
11.319 50	0.009 311 70	4.210 30	0.004 263 01	3.238 50	0.003 561 77
1.208 76	0.001 885 10	0.592 49	0.000 709 78	0.444 25	0.000 505 77
		Nobelium			
904 900.0	0.230 429 55	506 080.0	0.301 250 16	336 600.0	0.314 785 95
112 310.0	0.247 938 64	45 097.0	0.295 286 59	36 150.0	0.261 427 18
18 950.0	0.214 161 00	5 915.0	0.155 569 93	5 428.4	0.150 568 51
3 156.60	0.114 375 22	1 047.63	0.076 537 36	896.69	0.073 750 87
588.749	0.062 146 47	171.020	0.036 241 88	149.123	0.033 302 43
84.032 4	0.028 114 55	27.374 0	0.014 563 05	23.586 3	0.013 910 01
11.615 60	0.009 520 57	4.267 90	0.004 339 81	3.326 10	0.003 691 87
1.255 70	0.001 963 86	0.603 46	0.000 720 74	0.458 93	0.000 519 59
		Laurentium			
918 700.0	0.227 335 28	411 420.0	0.309 331 25	336 200.0	0.313 197 05
114 660.0	0.246 528 57	40 327.0	0.274 991 81	36 230.0	0.261 723 19
19 145.0	0.215 942 07	5 945.0	0.152 347 29	5 464.6	0.151 509 31
3 249.24	0.116 258 13	1 040.60	0.078 123 04	907.81	0.074 535 16
606.358	0.063 590 30	171.020	0.036 107 23	151.834	0.033 787 41
86.251 3	0.028 793 56	27.374 0	0.015 002 14	24.171 3	0.014 187 71
11.913 40	0.009 731 98	4.001 00	0.004 272 89	3.396 30	0.003 816 58
1.303 65	0.002 043 70	0.588 83	0.000 662 60	0.468 66	0.000 526 43

hand side of Eq. (3), which results from the linear-independency conditions between core and valence orbitals[2] is calculated with the core orbitals and orbital energies. All this defines the spin-free CG-AIMP Hamiltonian [Eq. (2)] which is obtained without resorting to any parametrization procedure based on the use of the valence orbitals.

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

$$\hat{H}^{\mathrm{SO}}=\sum_{i}^{N_{\mathrm{val}}}\sum_{I}^{N_{\mathrm{nuc}}}\hat{h}_{\mathrm{SO}}^{I}(i), \tag{7}$$

with the atomic one-electron spin-orbit terms

$$\hat{h}_{\mathrm{SO}}^{I}(i)=\lambda^{I}\sum_{nl\in\mathrm{valence}}V_{\mathrm{SO},nl}^{I,MP}(r_i)\hat{O}_l^{I}\hat{\mathbf{l}}^{I}\hat{\mathbf{s}}\hat{O}_l^{I}. \tag{8}$$

Herein, $\hat{\mathbf{l}}^I$ and $\hat{\mathbf{s}}$ are the usual vector angular momentum and spin operators, respectively, and the angular projectors $\hat{O}_l^I$ are used in the form proposed by Pitzer and Winter.[31] The radial components are chosen to be analytical functions

$$V_{\mathrm{SO},nl}^{I,MP}(r_i)=\sum_{k}\frac{B_k^{nl,I}\exp(-\beta_k^{nl,I}r_i^2)}{r_i^2}, \tag{9}$$

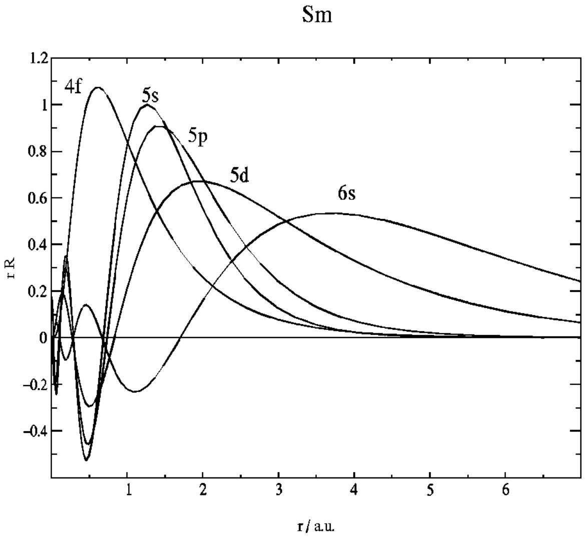

FIG. 1. Valence orbitals of Sm. Full line: numerical Cowan–Griffin all-electron results. Dashed line: analytical AIMP results of this work.

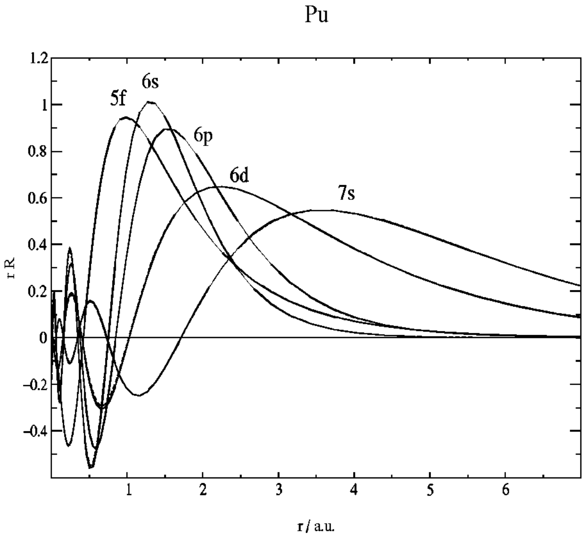

FIG. 2. Valence orbitals of Pu. Full line: numerical Cowan–Griffin all-electron results. Dashed line: analytical AIMP results of this work.

TABLE IV. Spin-free relativistic valence energy, orbital energies, radial expectation values (in atomic units), and orbital spin-orbit coupling constants ζ_{nl} (in cm^{-1}). The ζ_{nl} are calculated with the Gaussian orbitals and the analytical operators (Table II) in the CG-AIMP calculations, and with the numerical orbitals and operators [Eq. (10)] in the all-electron numerical Cowan–Griffin–Hartree–Fock calculations. The AIMP calculations correspond to a [Kr,4d] core and a 5s,5p,4f,5d,6s-valence.

	CG-AIMP			Spin-orbit corrected CG-AIMP			All-electron numerical CG-HF		
	E(val)			E(val)					
	$\epsilon(5s)$	$\langle r\rangle_{5s}$		$\epsilon(5s)$	$\langle r\rangle_{5s}$		$\epsilon(5s)$	$\langle r\rangle_{5s}$	
	$\epsilon(5p)$	$\langle r\rangle_{5p}$	ζ_{5p}	$\epsilon(5p)$	$\langle r\rangle_{5p}$	ζ_{5p}	$\epsilon(5p)$	$\langle r\rangle_{5p}$	ζ_{5p}
	$\epsilon(4f)$	$\langle r\rangle_{4f}$	ζ_{4f}	$\epsilon(4f)$	$\langle r\rangle_{4f}$	ζ_{4f}	$\epsilon(4f)$	$\langle r\rangle_{4f}$	ζ_{4f}
	$\epsilon(5d)$	$\langle r\rangle_{5d}$	ζ_{5d}	$\epsilon(5d)$	$\langle r\rangle_{5d}$	ζ_{5d}	$\epsilon(5d)$	$\langle r\rangle_{5d}$	ζ_{5d}
	$\epsilon(6s)$	$\langle r\rangle_{6s}$		$\epsilon(6s)$	$\langle r\rangle_{6s}$		$\epsilon(6s)$	$\langle r\rangle_{6s}$	
Ce $(f^1d^2s^1)^5I$	−38.368 911			−38.367 880					
	−1.8071	1.541		−1.8071	1.541		−1.8036	1.543	
	−1.0133	1.783	12 790	−1.0131	1.783	12 482	−1.0144	1.782	12 482
	−0.4581	1.090	747	−0.4581	1.090	748	−0.4571	1.091	748
	−0.2056	3.026	525	−0.2054	3.026	548	−0.2059	3.023	548
	−0.1800	4.759		−0.1800	4.759		−0.1796	4.764	
Pr $(f^3d^1s^1)^6L$	−46.931 387			−46.929 913					
	−1.7258	1.541		−1.7258	1.541		−1.7228	1.541	
	−0.9287	1.800	12 829	−0.9285	1.800	12 465	−0.9302	1.798	12 465
	−0.3275	1.099	807	−0.3274	1.099	809	−0.3271	1.100	809
	−0.1591	3.378	427	−0.1587	3.378	465	−0.1597	3.374	464
	−0.1654	5.016		−0.1654	5.016		−0.1651	5.025	
Nd $(f^3d^1s^2)^5K$	−56.625 703			−56.623 937					
	−2.0040	1.468		−2.0040	1.468		−2.0005	1.469	
	−1.1363	1.698	15 354	−1.1360	1.698	14 845	−1.1379	1.697	14 846
	−0.6949	0.947	1068	−0.6949	0.947	1072	−0.6951	0.946	1072
	−0.2592	2.658	775	−0.2592	2.658	795	−0.2600	2.655	795
	−0.1864	4.538		−0.1864	4.538		−0.1861	4.544	
Pm $(f^4d^1s^2)^6L$	−67.873 986			−67.871 695					
	−2.0603	1.438		−2.0603	1.438		−2.0574	1.439	
	−1.1614	1.666	16 586	−1.1611	1.666	15 973	−1.1630	1.665	15 974
	−0.7344	0.911	1226	−0.7344	0.910	1229	−0.7346	0.910	1230
	−0.2638	2.603	849	−0.2637	2.603	870	−0.2646	2.600	870
	−0.1885	4.483		−0.1885	4.483		−0.1884	4.489	
Sm $(f^5d^1s^2)^7K$	−80.618 805			−80.615 943					
	−2.1160	1.410		−2.1161	1.410		−2.1150	1.410	
	−1.1868	1.636	17 887	−1.1864	1.636	17 154	−1.1881	1.635	17 154
	−0.7599	0.879	1394	−0.7600	0.879	1398	−0.7597	0.879	1398
	−0.2660	2.564	918	−0.2660	2.564	926	−0.2665	2.562	926
	−0.1908	4.430		−0.1908	4.430		−0.1908	4.433	
Eu $(f^7d^1s^1)^{10}D$	−95.310 839			−95.307 573					
	−1.9421	1.421		−1.9422	1.421		−1.9459	1.417	
	−1.0258	1.666	17 549	−1.0253	1.666	16 761	−1.0269	1.665	16 760
	−0.4688	0.903	1459	−0.4689	0.903	1462	−0.4680	0.904	1462
	−0.1378	3.521	469	−0.1377	3.521	481	−0.1382	3.526	481
	−0.1811	4.682		−0.1811	4.682		−0.1812	4.685	
Gd $(f^7d^1s^2)^9D$	−111.099 477			−111.094 954					
	−2.2300	1.358		−2.2300	1.358		−2.2336	1.357	
	−1.2393	1.580	20 685	−1.2387	1.580	19 657	−1.2400	1.579	19 656
	−0.8353	0.821	1778	−0.8354	0.821	1780	−0.8339	0.822	1780
	−0.2447	2.591	952	−0.2447	2.591	950	−0.2447	2.591	950
	−0.1969	4.312		−0.1969	4.312		−0.1971	4.310	
Tb $(f^8d^1s^2)^8H$	−128.631 426			−128.625 804					
	−2.2989	1.332		−2.2989	1.332		−2.3033	1.330	
	−1.2721	1.551	22 309	−1.2712	1.551	21 104	−1.2726	1.550	21 102
	−0.8135	0.803	1974	−0.8136	0.803	1978	−0.8120	0.804	1978
	−0.2267	0.648	919	−0.2267	2.648	926	−0.2266	2.649	926
	−0.2010	4.241		−0.2010	4.241		−0.2014	4.238	
Dy $(f^9d^1s^2)^7K$	−148.052 011			−148.045 169					
	−2.3630	1.307		−2.3632	1.307		−2.3687	1.305	
	−1.3008	1.524	23 977	−1.2998	1.524	22 580	−1.3012	1.524	22 577

TABLE IV. (*Continued.*)

	CG-AIMP			Spin-orbit corrected CG-AIMP			All-electron numerical CG-HF		
	−0.8078	0.785	2189	−0.8081	0.785	2193	−0.8063	0.785	2193
	−0.2197	2.658	938	−0.2197	2.658	943	−0.2196	2.659	943
	−0.2043	4.184		−0.2043	4.184		−0.2047	4.179	
Ho $(f^{10}d^1s^2)^6L$	−169.410 279			−169.402 026					
	−2.4246	1.283		−2.4249	1.283		−2.4322	1.281	
	−1.3272	1.499	25 710	−1.3261	1.499	24 100	−1.3274	1.499	24 097
	−0.8092	0.766	2421	−0.8098	0.766	2425	−0.8076	0.766	2425
	−0.2180	2.642	984	−0.2181	2.642	981	−0.2178	2.644	981
	−0.2070	4.133		−0.2070	4.133		−0.2075	4.127	
Er $(f^{11}d^1s^2)^5L$	−192.722 449			−192.712 555					
	−2.4906	1.259		−2.4906	1.259		−2.4962	1.257	
	−1.3528	1.475	27 539	−1.3512	1.475	26 695	−1.3533	1.475	25 691
	−0.8069	0.749	2669	−0.8070	0.749	2673	−0.8058	0.749	2673
	−0.2176	2.620	1039	−0.2176	2.620	1029	−0.2175	2.622	1029
	−0.2098	4.082		−0.2098	4.082		−0.2102	4.078	
Tm $(f^{12}d^1s^2)^4K$	−218.043 452			−218.031 781					
	−2.5548	1.237		−2.5548	1.237		−2.5623	1.235	
	−1.3794	1.452	29 474	−1.3775	1.452	27 373	−1.3798	1.451	27 370
	−0.8029	0.733	2933	−0.8030	0.733	2937	−0.8022	0.733	2937
	−0.2153	2.608	1086	−0.2153	2.608	1068	−0.2153	2.610	1068
	−0.2125	4.034		−0.2125	4.034		−0.2131	4.027	
Yb $(f^{13}d^1s^2)^3H$	−245.522 441			−245.508 535					
	−2.6227	1.217		−2.6227	1.217		−2.6309	1.213	
	−1.4082	1.429	31 529	−1.4059	1.429	29 128	−1.4079	1.429	29 125
	−0.8071	0.717	3217	−0.8072	0.717	3220	−0.8052	0.717	3220
	−0.2069	2.634	1091	−0.2068	2.634	1073	−0.2069	2.636	1073
	−0.2160	3.982		−0.2160	3.982		−0.2168	3.972	
Lu $(f^{14}d^1s^2)^2D$	−275.264 284			−275.247 996					
	−2.6940	1.195		−2.6941	1.195		−2.7050	1.192	
	−1.4397	1.407	33 687	−1.4370	1.407	30 971	−1.4399	1.407	30 968
	−0.8197	0.701	3520	−0.8198	0.701	3525	−0.8189	0.702	3525
	−0.1878	2.738	1014	−0.1878	2.738	1005	−0.1877	2.743	1005
	−0.2215	3.912		−0.2215	3.912		−0.2223	3.904	

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[6]

$$V_{\mathrm{SO},nl}(r)=\frac{\alpha^2}{(2+\alpha^2[\epsilon_{nl}-V(r)])r}\,\frac{dV(r)}{dr}. \tag{10}$$

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 one-electron potential.[5] This effective one-electron spin-orbit operator includes an average of two-electron contributions through the use of the $X\alpha$ Hartree–Fock (HF) 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. (8) which was first empirically parametrized[7] and later found to be unnecessary;[12] consequently, we use $\lambda^I=1$. The $\{B_k,\beta_k\}$ parameters for the lanthanide elements and for the actinide elements have been produced here and they are presented in Tables II and III, respectively.

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

The spin-free relativistic $H^{\text{CG-AIMP}}$ Hamiltonian [Eq. (2)] is used in standard nonrelativistic methods. The spin-dependent $H^{\text{WB-AIMP}}$ Hamiltonian [Eq. (1)] is used in spin-orbit configuration interaction (CI) calculations, i.e., in a basis of double-group symmetry-adapted determinantal functions with HF or complete active space self-consistent field (CASSCF) orbitals produced with the spin-free $H^{\text{CG-AIMP}}$ Hamiltonian. In order to treat electron correlation and spin-orbit interactions simultaneously at the highest possible level, the spin-free-state-shifted (*sfss*) Hamiltonian $H_{sfss}^{\text{WB-AIMP}}$ was introduced[13]

$$H_{sfss}^{\text{WB-AIMP}}=H^{\text{WB-AIMP}}+\sum_{iSM_S\Gamma\gamma}\delta(iS\Gamma)|\Phi^{\mathcal{P}}(iSM_S\Gamma\gamma)\rangle \times\langle\Phi^{\mathcal{P}}(iSM_S\Gamma\gamma)|, \tag{11}$$

with

$$\delta(iS\Gamma)=[E^{\mathcal{G}}(iS\Gamma)-E^{\mathcal{G}}(\text{G.S.})]-[E^{\mathcal{P}}(iS\Gamma)-E^{\mathcal{P}}(\text{G.S.})]. \tag{12}$$

TABLE V. Spin-free relativistic valence energy, orbital energies, radial expectation values (in atomic units), and orbital spin-orbit coupling constants ζ_{nl} (in cm^{-1}). The ζ_{nl} are calculated with the Gaussian orbitals and the analytical operators of Table III in the CG-AIMP calculations, and with the numerical orbitals and operators [Eq. (10)] in the all-electron numerical Cowan–Griffin–Hartree–Fock calculations. The AIMP calculations correspond to a [Xe,$4f$,$5d$] core and a $6s$,$6p$,$5f$,$6d$,$7s$ valence.

	CG-AIMP			Spin-orbit corrected CG-AIMP			All-electron numerical CG-HF		
	E(val) $\epsilon(6s)$ $\epsilon(6p)$ $\epsilon(5f)$ $\epsilon(6d)$ $\epsilon(7s)$	$\langle r\rangle_{6s}$ $\langle r\rangle_{6p}$ $\langle r\rangle_{5f}$ $\langle r\rangle_{6d}$ $\langle r\rangle_{7s}$	ζ_{6p} ζ_{5f} ζ_{6d}	E(val) $\epsilon(6s)$ $\epsilon(6p)$ $\epsilon(5f)$ $\epsilon(6d)$ $\epsilon(7s)$	$\langle r\rangle_{6s}$ $\langle r\rangle_{6p}$ $\langle r\rangle_{5f}$ $\langle r\rangle_{5d}$ $\langle r\rangle_{7s}$	ζ_{6p} ζ_{5f} ζ_{6d}	$\epsilon(6s)$ $\epsilon(6p)$ $\epsilon(5f)$ $\epsilon(6d)$ $\epsilon(7s)$	$\langle r\rangle_{6s}$ $\langle r\rangle_{6p}$ $\langle r\rangle_{5f}$ $\langle r\rangle_{6d}$ $\langle r\rangle_{7s}$	ζ_{6p} ζ_{5f} ζ_{6d}
Th $(5f^1 6d^2 7s^1)^5I$	−35.551 931			−35.473 682					
	−1.9148	1.580		−1.9149	1.580		−1.9144	1.581	
	−0.9673	1.917	39 264	−0.9543	1.917	31 776	−0.9655	1.919	31 761
	−0.1842	1.904	1113	−0.1842	1.094	1107	−0.1849	1.905	1107
	−0.1901	3.400	1243	−0.1901	3.400	1276	−0.1906	3.394	1276
	−0.2050	4.484		−0.2050	4.484		−0.2050	4.481	
Pa $(5f^3 6d^1 7s^1)^6L$	−42.719 219			−42.630 610					
	−1.8981	1.556		−1.8981	1.556		−1.8990	1.555	
	−0.9216	1.900	41 342	−0.9070	1.900	33 155	−0.9198	1.903	33 136
	−0.1650	1.766	1345	−0.1651	1.766	1344	−0.1660	1.769	1344
	−0.1737	3.476	1199	−0.1729	3.476	1337	−0.1740	3.471	1337
	−0.1839	4.689		−0.1839	4.689		−0.1842	4.686	
U $(5f^3 6d^1 7s^2)^5K$	−51.057 518			−50.950 588					
	−2.1292	1.499		−2.1293	1.499		−2.1313	1.497	
	−1.0767	1.820	47 440	−1.0590	1.820	37 726	−1.0739	1.823	37 696
	−0.3869	1.440	1907	−0.3870	1.440	1899	−0.3881	1.439	1899
	−0.2250	3.003	1810	−0.2248	3.003	1882	−0.2254	2.996	1882
	−0.1971	4.392		−0.1971	4.392		−0.1973	4.389	
Np $(5f^4 6d^1 7s^2)^6L$	−60.452 972			−60.329 895					
	−2.2083	1.465		−2.2084	1.465		−2.2122	1.462	
	−1.1077	1.781	51 521	−1.0873	1.782	40 607	−1.1041	1.785	40 574
	−0.4403	1.362	2216	−0.4404	1.362	2207	−0.4413	1.361	2207
	−0.2336	2.912	2001	−0.2333	2.912	2099	−0.2338	2.907	2099
	−0.1993	4.335		−0.1993	4.335		−0.1997	4.330	
Pu $(5f^5 6d^1 7s^2)^7K$	−71.016 672			−70.875 130					
	−2.2867	1.433		−2.2868	1.433		−2.2926	1.429	
	−1.1375	1.746	55 790	−1.1140	1.746	43 560	−1.1332	1.749	43 515
	−0.4835	1.297	2538	−0.4836	1.297	2527	−0.4845	1.297	2527
	−0.2356	2.862	2159	−0.2355	2.862	2223	−0.2358	2.857	2223
	−0.2020	4.276		−0.2020	4.276		−0.2026	4.269	
Am $(5f^7 6d^1 7s^1)^{10}D$	−82.954 076			−82.800 880					
	−2.1823	1.425		−2.1824	1.425		−2.1916	1.417	
	−1.0210	1.752	56 865	−0.9955	1.752	43 907	−1.0167	1.756	43 901
	−0.3420	1.305	2671	−0.3422	1.305	2666	−0.3434	1.305	2666
	−0.1386	3.636	1295	−0.1385	3.636	1332	−0.1391	3.631	1332
	−0.1987	4.405		−0.1987	4.405		−0.1993	4.399	
Cm $(5f^7 6d^1 7s^2)^9D$	−96.003 066			−95.818 048					
	−2.4420	1.375		−2.4421	1.375		−2.4546	1.369	
	−1.1958	1.682	64 846	−1.1650	1.682	49 660	−1.1896	1.686	49 587
	−0.5894	1.190	3232	−0.5896	1.190	3221	−0.5900	1.189	3221
	−0.2110	2.904	2216	−0.2110	2.904	2216	−0.2109	2.902	2216
	−0.2097	4.148		−0.2097	4.148		−0.2107	4.124	
Bk $(5f^8 6d^1 7s^2)^8H$	−110.295 651			−110.083 976					
	−2.5310	1.347		−2.5312	1.347		−2.5483	1.339	
	−1.2326	1.649	70 023	−1.1975	1.649	53 099	−1.2252	1.654	53 012
	−0.5997	1.153	3587	−0.5999	1.154	3563	−0.5999	1.153	3564
	−0.1908	2.993	2113	−0.1908	2.993	2092	−0.1903	2.993	2092
	−0.2154	4.071		−0.2154	4.071		−0.2168	4.052	
Cf $(5f^9 6d^1 7s^2)^7K$	−126.050 792			−125.808 218					
	−2.6149	1.321		−2.6150	1.321		−2.6370	1.312	
	−1.2640	1.620	75 379	−1.2239	1.620	56 566	−1.2554	1.625	56 459

TABLE V. (*Continued.*)

	CG-AIMP			Spin-orbit corrected CG-AIMP			All-electron numerical CG-HF		
	−0.6216	1.119	3957	−0.6218	1.119	3927	−0.6212	1.119	3927
	−0.1834	3.016	2134	−0.1834	3.016	2084	−0.1826	3.018	2084
	−0.2195	4.009		−0.2195	4.009		−0.2214	3.986	
Es $(5f^{10}6d^{1}7s^{2})^{6}L$	−143.299 786			−143.024 278					
	−2.6934	1.296		−2.6936	1.296		−2.7234	1.285	
	−1.2921	1.593	80 937	−1.2466	1.593	60 000	−1.2820	1.598	59 966
	−0.6484	1.087	4348	−0.6485	1.087	4312	−0.6474	1.087	4312
	−0.1819	3.000	2220	−0.1818	3.000	2137	−0.1808	3.005	2136
	−0.2228	3.957		−0.2228	3.957		−0.2251	3.929	
Fm $(5f^{11}6d^{1}7s^{2})^{5}L$	−162.091 586			−161.780 053					
	−2.7881	1.269		−2.7883	1.269		−2.8107	1.260	
	−1.3174	1.567	86 744	−1.2659	1.567	63 631	−1.3075	1.573	63 593
	−0.6703	1.057	4753	−0.6705	1.057	4714	−0.6712	1.057	4714
	−0.1811	2.981	2314	−0.1809	2.981	2210	−0.1806	2.981	2210
	−0.2269	3.895		−0.2269	3.895		−0.2287	3.874	
Md $(5f^{12}6d^{1}7s^{2})^{4}K$	−182.428 815			−182.076 753					
	−2.8791	1.244		−2.8794	1.244		−2.9007	1.235	
	−1.3437	1.542	92 894	−1.2856	1.542	67 406	−1.3333	1.548	67 365
	−0.6921	1.030	5180	−0.6923	1.030	5135	−0.6937	1.030	5135
	−0.1785	2.974	2387	−0.1783	2.975	2258	−0.1784	2.974	2258
	−0.2310	3.837		−0.2310	3.837		−0.2326	3.819	
No $(5f^{13}6d^{1}7s^{2})^{3}H$	−204.427 555			−204.029 919					
	−2.9759	1.219		−2.9762	1.219		−2.9945	1.212	
	−1.3716	1.518	99 397	−1.3059	1.519	71 318	−1.3604	1.525	71 272
	−0.7203	1.004	5629	−0.7206	1.004	5581	−0.7226	1.003	5581
	−0.1689	3.029	2344	−0.1686	3.029	2212	−0.1695	3.022	2212
	−0.2365	3.772		−0.2365	3.772		−0.2379	3.757	
Lr $(5f^{14}6d^{1}7s^{2})^{2}D$	−228.159 302			−227.709 948					
	−3.0797	1.196		−3.0801	1.196		−3.0965	1.189	
	−1.4042	1.495	106 326	−1.3300	1.495	75 399	−1.3926	1.502	75 349
	−0.7595	0.978	6103	−0.7599	0.978	6053	−0.7630	0.978	6054
	−0.1488	3.210	2093	−0.1485	3.210	1967	−0.1492	3.207	1967
	−0.2453	3.692		−0.2453	3.692		−0.2467	3.679	

Here, $\mathcal{P}$ and $\mathcal{G}$ are two CI spaces of, respectively, small and large relative size; $\mathcal{P}$ is required 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 and G.S. 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 $H^{\text{CG-AIMP}}$ Hamiltonian using the $\mathcal{G}$ and $\mathcal{P}$ spaces and one final spin-orbit CI calculation with the $H_{sfss}^{\text{WB-AIMP}}$ 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^{+},[12] Pt,[11] and Ce.[14]

C. Atomic valence basis sets

Once the relativistic core *ab initio* model potentials have been obtained as summarized in Sec. II A, what remains is the production of the valence basis sets. In order to do so, the $H^{\text{CG-AIMP}}$ Hamiltonian [Eq. (2)] is used in atomic valence-only Hartree–Fock calculations and the exponents and coefficients of Gaussian atomic orbitals are optimized by minimization of the valence SCF energy using standard all-electron methods.[32] After this, every single p, d, and f valence atomic orbital is spin-orbit corrected:[7] The coefficient of the innermost Gaussian primitive is changed and the orbital is renormalized, in such a way that the orbital spin-orbit coupling constants calculated with the numerical Cowan–Griffin–Hartree–Fock atomic orbital and with the analytical spin-orbit-corrected valence orbital coincide. This procedure has been shown to significantly improve the spin-orbit dependent properties at a time so that the quality of the bonding related properties is maintained.[7]

Following this procedure, we obtained spin-orbit-corrected relativistic valence basis sets for the lanthanide elements Ce–Lu and for the actinide elements Th–Lr. They are presented in the Supplementary Material Section of Ref. 26 as E-PAPS document file. The radial functions of the valence orbitals of Sm and Pu are presented in Figs. 1 and 2; their similarity to the all-electron numerical orbitals is clear. The atomic valence properties that correspond to these basis

TABLE VI. Spectroscopic constants for the $^1\Sigma^+$ ground state of ThO.

	R_e/Å	ω_e/cm^{-1}	D_e/eV
Experiment[a]	1.840	896	9.0
SCF calculations			
Küechle *et al.*[b]	1.829	943	6.07
This work[c]	1.819	956	5.99
CASSCF calculations (8 electrons in 9 orbitals)			
Küechle *et al.*[b]	1.882	876	8.92
This work[c]	1.886	865	9.15

[a] Reference 35

[b] Reference 17. Relativistic energy-adjusted pseudopotential calculation corresponding to a [Kr,4d,4f] core and a (12s11p10d8f)/[8s7p6d4f] basis set.

[c] Relativistic *ab initio* model potential calculation corresponding to a [Xe,4f,5d] core and a (14s10p11d9f)/[6s5p5d4f] basis set.

sets are shown in Tables IV and V, where it is clear that they are very similar to the corresponding all-electron calculations. The basis sets are minimal valence basis sets of the size shown in Table I. When they are used in molecular calculations, their flexibility can be enhanced by adding or releasing the outermost primitives and by extension with appropriate functions, such as polarization and diffuse functions. For lanthanide elements, very stable results with respect to the basis set size are found when a number of outermost primitives are added to the minimal basis set up to a number of (14s10p9d8f)/[6s5p5d4f] basis set functions (see Ref. 14). The errors due to the use of smaller [4s3p3d3f] basis sets were 0.015 Å in bond distance, 10 cm^{-1} in vibrational frequency, and 0.2 eV in dissociation energy.[14] For actinide elements, a good performance is obtained as well with the same basis set size. The good quality of the results on the $^1\Sigma^+$ ground state of ThO using a (14s10p11d9f)/[6s5p5d4f] basis set for Th and the same basis set for O as in Ref. 14, is shown in Table VI. Although several calculations on ThO exist,[33,34] we compare our results with those of Ref. 17, which use correct choices of basis set and of core/valence partition. Our results are essentially coincident with those of the energy-adjusted pseudopotential (EAPP) calculations with a slightly smaller core,[17] as was the case of transition metals,[11] and the comparison with experimental data is good having in mind that dynamical correlation effects are missing. (These effects have been previously found to be very similar in EAPP and AIMP calculations.[11])

III. CONCLUSIONS

Starting from atomic Cowan–Griffin calculations, we produced and presented here the ingredients of the WB-AIMP method for the lanthanide elements Ce to Lu and for the actinide elements Th to Lr, what completes the chemically relevant part of the Periodic Table. These are: relativistic [Kr,4d] core AIMPs and Wood–Boring spin-orbit operators for Ce–Lu, together with optimized minimal (14s10p9d8f)/[2s1p1d1f] Gaussian valence basis sets, and relativistic [Xe,4f,5d] core AIMPs and Wood–Boring spin-orbit operators for Th–Lr, together with optimized minimal (14s10p11d9f)/[2s1p1d1f] Gaussian valence basis sets. A [6s5p5d4f] contraction is recommended for all these 28 elements in molecular calculations. The atomic and molecular results show the same good quality already observed for the main-group elements and the transition metal elements.

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[26] See AIP Document No. E-JCPSA6-114-311102 for AIMP parameters and valence basis sets. This document may be retrieved via the E-PAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.

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