Spin−Orbit Splittings in the Third-Row Transition Elements: Comparison of Effective Nuclear Charge and Full Breit−Pauli Calculations

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The spin−orbit splittings of low-lying states in third-row transition elements were calculated using both an effective core potential (ECP) method within the one-electron (Z_{eff}) approximation and all-electron (AE) methods using three different approaches. The wave functions were obtained using the multiconfiguration self consistent field (MCSCF) method followed by second-order configuration interaction (SOCI) calculations. All calculated results, except for the ones on atomic Ir, are in reasonable agreement with the corresponding experimental observations. The unsatisfactory results for atomic Ir are attributed to the poor theoretical prediction of the adiabatic energy gap between the lowest two ^{4}F states. This gap has an incorrect sign in AE calculations without scalar relativistic corrections, but the gap can be reproduced qualitatively if these corrections are added using the newly developed RESC (relativistic elimination of small components) scheme. As a result, the AE calculations with the RESC approximation give spin−orbit splittings similar to those obtained by the ECP calculations with the Z_{eff} approximation.

Introduction

Recent years have brought an increasing awareness of the importance of including spin−orbit coupling effects for accurate comparison with experimental results. For example, atomic spin−orbit splittings are included in G3 thermochemical predictions.[1] Although spin−orbit coupling is numerically larger for heavy elements than for light ones, its effects can be measured in all parts of the periodic table, as may be seen from a few recent applications. For light elements, spin−orbit effects can be observed in organic photochemistry,[2] and spin−orbit and even spin−spin couplings have been included in prediction of the methylene and silylene singlet−triplet splittings.[3] Vibrationally averaged spin−orbit couplings in CO^+ and O_2^+ agreed with high-resolution spectra from a synchotron radiation source.[4] A recent paper on HOCl[5] and earlier work on ozone indicates triplet state photochemistry is important in the stratospheric ozone problem. For intermediate weight main group elements, spin−orbit effects have recently been considered in the predissociation lifetime of the $B^3\Sigma^-{}_u$ state of S_2,[6] in the radiative lifetimes of low lying states of AsH,[7] and in photochemical branching ratios in ICl.[8] It is well-known that spin−orbit effects are large in the third row transition elements,[9] but these can play a major role in the reactivity patterns of *any* transition metal. The counterintuitive experimental observation that the reaction efficiency of $^6\Sigma^+$ FeO^+ with H_2 decreases with increasing kinetic energy of collision has been explained as this reaction occurring via a spin−orbit induced transition onto a quartet surface.[10] A study of methane activation by all neutral metal atoms indicated only Pt was reactive, because of a low energy crossing of different spin surfaces.[11] Finally, for very heavy elements, a study of the bottom row hydrides TlH to AtH predicted spin−orbit effects on potential curve shapes and concluded these could be computed in a perturbative fashion from high level L−S coupled wave functions.[12] Dirac−Fock−Breit computations on UF_6 gave good agreement with experiment for the 4d, 5d, and 4f levels.[13]

Not surprisingly, the recognition of the importance of spin−orbit coupling in chemistry has fueled continued work on methodology for its computation. An overview of recent algorithmic work will be given, but this should not be considered to be a comprehensive review.

The most fundamentally sound approach to spin−orbit coupling is based on the Dirac−Coulomb equation for four component spinors, which includes spin−orbit operator implicitly. Molecular Dirac−Hartree−Fock programs have become increasingly available,[14] and recent efforts have extended four-component calculations to MP2,[15] coupled-cluster,[16] and MCSCF[17] correlation treatments. The Breit two-electron term can be added as a perturbation or possibly included in the self-consistency optimization.[18]

However, the considerable investment in single component quantum chemistry packages has encouraged treatment of the spin−orbit coupling via the Breit−Pauli Hamiltonian, resulting from a Foldy−Wouthuysen transformation. The most frequent approach is a spin−orbit configuration interaction (CI)[19] using either configurations or L−S CI eigenstates as the basis, forming matrix elements over the Breit−Pauli operator and diagonalizing to obtain spin−orbit coupled wave functions. An alternative operator can be obtained from the Douglas−Kroll no pair transformation[20] or by other transformations of the Dirac−Coulomb equation.[21] Early on, the difficulty of calculating the two electron term in the Breit−Pauli operator led to the idea of excluding it and compensating for the error by regarding the nuclear charge in the one electron term as an effective charge.[22,23] Recently, a general program[24] in terms of including more than two spin states with an arbitrary choice of active

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space has been developed, to permit comparison of the full Breit−Pauli operator with this effective charge operator. This program also includes an option for the partial computation of the two electron term, by computing only core-active terms, omitting active−active matrix elements. Other workers have also experimented with mean field or one center approximations to the two electron term.[25−27] An alternative operator consisting of only a one electron term can be obtained from the difference of effective core potentials for different spinors, obtained from atomic calculations with the Dirac−Coulomb equation[28] or the Wood−Boring Hamiltonian.[29] Recently a gradient program has been developed for this kind of operator[30] to permit geometry optimization with spin−orbit effects. The spin−orbit interaction has been successfully incorporated into the self-consistent field optimization at the single configuration level for atoms.[31]

We have determined the effective nuclear charges (Z_{eff}) for all elements from Li−Xe.[23] For each main group element, Z_{eff} was determined in order to reproduce the splittings of energetically low-lying spectral terms of its hydride.[23a,b,d] The Z_{eff} for transition metals were chosen to optimize the agreement between the calculated splittings and those obtained from atomic spectral terms.[23e] The Z_{eff} results for main-group diatomic molecules are in good agreement with available spectral data, with errors on the order of 30% or less. On the other hand, for transition elements, especially those in the third transition row, the Z_{eff} method is more problematic.[23e] In large part, this is due to the complications arising from the large number of closely spaced low-lying states and strong spin−orbit interactions among electronic states with the same J values. Thus, it is often necessary to include a large number of low-lying excited states in the wave function in order to obtain reasonable results. Similar behavior has been observed in recent work on lanthanide ions[32] where it was found to be necessary to include interactions with all states that are close in energy to the lowest state in the spin−orbit Hamiltonian.

For the heavier elements, we have been using the SBKJC effective core potentials (ECPs) and basis sets.[33] One immediate advantage of using such a relativistic ECP is that the valence orbitals are already adjusted for spin-free relativistic orbital contractions and expansions. However, a disadvantage in using ECP basis sets is that they are generally nodeless. So, although the 3d SBKJC orbitals are qualitatively similar to correct 3d atomic orbitals, because these orbitals have no inner nodes, the 4d and 5d SBKJC orbitals are nodeless, even though they should have inner nodes. Consequently, Z_{eff} is smaller than the true nuclear charge for the first-row transition elements, whereas the incorrect nodal behavior for the second- and third-row transition elements results in rather larger Z_{eff} in order to reproduce the experimental atomic splittings.[34] Thus, Z_{eff} loses its physical meaning and becomes simply a fitted empirical parameter.

In the previous study,[23e] reasonable agreement with the experiment was reported for MCSCF-based spin−orbit splittings in low-lying electronic states for first- and second-row transition elements, whereas serious disagreement was observed for the third-row transition elements. The present study has been conducted in order to determine the origin of these errors, using larger basis sets and SOCI wave functions including more external orbitals, and by comparing predictions from the Z_{eff} and full-BP methods for the third-row transition elements.

Methods of Calculation

In the case of all-electron calculations, one may choose to use the full Breit−Pauli (full BP) Hamiltonian for spin−orbit coupling

$$H_{\text{SO}} = \frac{\alpha^2}{2}\left[\sum_{i}^{\text{electron}}\sum_{A}^{\text{nucleus}}\frac{Z(A)}{r_{iA}^3}L_{iA}S_i - \sum_{i,j}^{\text{electron}}\frac{1}{r_{iA}^3}L_{ij}(S_i + 2S_j)\right]$$

in which α is the fine structure constant, L and S are orbital and spin angular momentum operators, respectively, and the true nuclear charge $Z(A)$ is in its one-electron term. Alternatively, if only the one-electron operator is employed, Z may be replaced by Z_{eff} as discussed above:

$$H_{\text{SO}} \approx \frac{\alpha^2}{2}\left[\sum_{i}^{\text{electron}}\sum_{A}^{\text{nucleus}}\frac{Z_{\text{eff}}(A)}{r_{iA}^3}L_{iA}S_i\right]$$

For all electron calculations, the very important contraction of s and p orbitals and expansion of d and f orbitals[35] because of spin-free relativistic effects (mass−velocity and Darwin) can be incorporated using the recently developed RESC (relativistic elimination of small components) formalism.[36]

For the ECP calculations, the SBKJC potentials and basis sets[33] are employed, augmented with a set of f polarization functions[37] using only the Z_{eff} operator. The valence Gaussian functions, corresponding to 5d, 6s, and 6p orbitals, are uncontracted, (7s7p5d1f)/[4s4p5d1f], so that this basis set is referred to as uSBKJC(f). For the all-electron (AE) calculations, within either the one-electron approximation or with the full BP Hamiltonian, the MINI basis set,[38] augmented with three sets of p functions as 6p orbitals,[39] has been chosen. The valence orbitals corresponding to 5d and 6s orbitals are also uncontracted, leading to a (18s15p9d3f)/[8s7p5d1f] basis set, referred to as uMINI(3p).

The MCSCF active space includes the 5d, 6s, and 6p orbitals in both the ECP and AE calculations.[40] The MCSCF orbitals were optimized for a state of interest, with a nonzero orbital angular momentum quantum number. These orbitals were then employed to construct second-order configuration interaction (SOCI) wave functions[41] and spin−orbit coupling CI matrices. The spin−orbit CI matrix includes the state for which the MCSCF orbitals were optimized, as well as other energetically low-lying excited states with both the same and different spin multiplicities. Typically, all adiabatic states within 0.1∼0.3 hartree[42] of the ground state were included in the spin−orbit coupling matrices. The states used are shown in Table 1. The spin−orbit matrix elements were computed using the various approximations described above. All calculations reported here were carried out using the GAMESS suite of program codes.[43]

Results and Discussion

1. Z_{eff} Results Obtained Using the ECP Method. Table 2 summarizes the spin−orbit splittings of low-lying states in the third-row transition elements. The Z_{eff} values determined using MCSCF wave functions[23e] have been used to predict spin−orbit splittings at the SOCI level of theory. These predicted splittings are in better agreement with the experimental observations (error <30%) in La, Hf, Ta, W, Re, Pt, and Au than in the previous MCSCF work. In particular, excellent improvement is observed in the $^3D_2$ sublevel (114 → 0.8%) of Pt because of the use of a better wave function. As reported previously,[44−48] strong spin−orbit interaction occurs between the lowest ^1D and ^3D states. The present results show that the lowest $J = 2$ sublevel has 51% ^1D character and 47% ^3D character at the MCSCF level of theory. Dynamic correlation increases the contribution of ^1D to 58%. Thus, it appears that SOCI calculations are needed to

TABLE 1: Numbers of Configuration State Functions in SOCI Calculations and Spin States Included in SOC Matrices

atom	method[a]	mult[b]	CSFs[c]	HSO[d]	states[e]
La	ECP	2	11 992	352	S, 3P, 5D, 3F, 2G
		4	5737		3P, D, 4F, G
Hf	ECP	1	43 088	467	2S, P, 3D, F, G
		3	60 771		S, 3P, 3D, 4F, 2G, H
		5	18 106		S, P, 2D, 2F, G
	AE	1	17 215	454	S, 3D, F, 2G
		3	23 931		S, 3P, 3D, 4F, 2G
		5	6986		S, 2P, 2D, 2F, G
	RESC	1	17 215	393	2S, P, 3D, 2F, G
		3	23 931		S, 3P, 3D, 3F, G
		5	6986		S, P, 2D, 2F, G
Ta	ECP	2	285 940	714	S, 2P, 4D, 3F, 2G, H
		4	202 664		S, 3P, 4D, 3F, 3G, H
		6	40 716		P, 3D, F, G
	AE	2	55 774	292	P, D, G, H
		4	77 640		P, 2D, F
		6	15 362		2D, F, G
	RESC	2	55 774	534	S, 2P, 3D, 3F, 2G, H
		4	77 640		S, 2P, 3D, 2F, 2G
		6	15 362		P, 2D, F, G
W	ECP	1	207 964	557	S, D, F, G, I
		3	671 782		2P, 2D, 2F, G, H
		5	301 186		S, 2P, 4D, F, 2G
		7	31 625		S, P, D, F
	AE	1	112 206	531	S, G, I
		3	179 596		2P, 2D, F, 2G, H, I
		5	160 336		S, 3P, 2D, F, G
		7	16 628		S, 2P, D, F
	RESC	1	112 206	432	S, D, F, G, I
		3	179 596		P, 2D, F, H, G
		5	160 336		S, 2P, 2D, F, G
		7	16 628		S, P, D, F
Re	ECP	2	268 572	386	S, D, 2F, G, H, I
		4	219 184		2P, 2D, F, G, H
		6	132 720		S, P, 2D
		8	3211		P
	AE	2	220 200	296	P, D, F, H
		4	179 336		2P, 2D, F, 2G, H
		6	54 120		S, D
	RESC	2	220 200	224	D, F, G, I
		4	179 336		P, D, F, G
		6	54 120		S, D
		8	7830		P
Os	ECP	1	327 048	459	S, D, F, 2G, I
		3	560 940		2P, D, 2F, 2G, 2H
		5	587 604		2P, 2D, F
		7	61 644		P, D, F
	AE	1	267 542	259	D, G
		3	458 150		2P, D, 2F, G, H
		5	239 514		P, D, F
		7	50 160		D
	RESC	1	267 542	532	S, P, D, F, 2G, I
		3	458 150		3P, 2D, 2F, 2G, 2H
		5	239 514		S, P, 2D, 2F
		7	50 160		2P, D, F
Ir	ECP	2	979 720	886	2S, 3P, 6D, 5F, 4G, H
		4	860 280		S, 4P, 4D, 5F, 2G, H
		6	151 890		S, P, 3D, 2F, G
	AE	2	430 500	266	2P, 3D, F, 2G, H
		4	376 324		2P, 2F
		6	132 654		D, F
	RESC	2	430 500	280	2P, 3D, 2F, 2G, H
		4	376 324		2P, 2F
		6	132 654		D, F
Pt	ECP	1	783 696	560	2S, P, 4D, 2F, 2G
		3	1 382 920		3P, 5D, 4F, G
		5	771 040		S, P, 3D, 3F, 2G
	AE	1	595 972	550	S, 2P, 6D, 3F, 2G
		3	1 048 788		6P, 7D, 5F, G, H
		5	291 145		S, P, 2D, F, G
	RESC	1	595 972	453	2S, P, 4D, 2F, 2G
		3	1 048 788		3P, 5D, 4F, G, H
		5	291 145		S, P, 2D, F, G
Au	ECP	2	765 840	400	2S, 4P, 7D, 4F, G, H
		4	682 705		2P, 4D, 2F, G
	AE	2	521 768	372	3S, 7P, 8D, 4F
		4	461 880		2P, 4D, 3F
	RESC	2	521 768	494	3S, 6P, 7D, 6F, 2G, H
		4	461 880		S, 3P, 4D, 3F, G
Hg	ECP	1	417 400	652	5S, 8P, 8D, 4F, G
		3	732 650		3S, 11P, 9D, 6F, G
		5	405 275		2P, 2D, 2F
	AE	1	283 876	282	5S, 5P, 3D, F
		3	495 758		2S, 8P, 3D, 2F
		5	135 990		P, D, F
	RESC	1	283 876	296	3S, 3P, 2D, F, G
		3	495 758		S, 5P, 3D, 3F, G
		5	135 990		P, D, F

[a] ECP = MCSCF + SOCI/uSBKJC(f), AE = MCSCF + SOCI/uMINI(3p), and RESC = MCSCF(RESC) + SOCI/uMINI(3p). The MCSCF orbitals were optimized for the state shown in Table 2. [b] Spin multiplicity. [c] Total number of configuration state functions (CSFs) for each multiplicity. [d] Size of spin−orbit interaction matrices. [e] Space symmetries of states included for each multimplicity. 2S means two states of S symmetry, etc.

obtain reliable splittings in such states. Additionally, the lowest $J = 2$ sublevel should be assigned to $^1D_2$ rather than $^3D_2$.

Unfortunately, a large discrepancy still exists between the predicted and observed splittings in Os, even after the inclusion of dynamic correlation. Because the numerical error in the $^5D_2$ sublevel of Os is reduced to about half (90 → 46%) by the addition of dynamic correlation, it is possible that better results would be obtained for this state if improved basis sets are employed or more external orbitals were to be included in the SOCI recovery of dynamic correlation.

Note that a very large value of Z_{eff} (9040) has been used for the ^3P state of Hg because the 5d orbitals are completely filled in the main configuration of this state. As a result, the contribution of electron configurations which have unfilled 5d orbitals seems to be overestimated by using the Z_{eff} approximation. Because the $^3P_0{-}^3P_1$ energy gap is underestimated and that of $^3P_0{-}^3P_2$ is overestimated, it might be difficult to solve this problem using only one parameter. As discussed below, the Z_{eff} method may not be applicable to Group 12 atoms (see also ref 23e).

Disagreement is more severe in the ^4F state of Ir. The large discrepancy is caused by a strong interaction between the lowest two ^4F states (denoted by 1^4F and 2^4F). The main configurations of 1^4F and 2^4F states are $(5d)^7(6s)^2$ and $(5d)^8(6s)^1$, respectively. It is well-known that the lowest two ^4F states are very close to each other in energy and that the nonrelativistic Hartree−Fock method cannot predict the correct energetic order of these states.[49] Because the core potentials implicitly include spin-free relativistic effects, the energy difference (0.47 eV) obtained by the ECP method[49d] before the inclusion of spin−orbit coupling is in good agreement with the experimental estimation (0.4 eV) given by Moore.[50a] Although DHF calculations have been reported for Ir's ground level,[51−55] we have been unable to find any prior attempt to compute its excited levels, other than our own earlier work.[23e] To obtain more reliable results, state-averaged MCSCF calculations have been performed with equal weights for the 1^4F and 2^4F states.

As shown in Table 2, the SOCI results of atomic Ir using the state-averaged MCSCF orbitals are still not satisfactory. The lowest $J = {}^9/_2$ and ${}^7/_2$ sublevels (denoted by $1^4F_{9/2}$ and $1^4F_{7/2}$ in

TABLE 2: Spin−Orbit Splitting of Low-lying States in the Third-Row Transition Elements

atom	state	expt[a]	ECP[b]	err (%)	AE (1)[c]	err (%)	AE (2)[c]	err (%)	AE (3)[c]	err(%)
La	$^2D_{3/2}$	0.00	0							
	$^2D_{5/2}$	1053.20	1116	5.9						
Hf	$^3F_2$	0.00	0		0		0		0	
	$^3F_3$	2356.68	2716	15.3	2238	−5.0	2604	10.5	2232	−5.3
	$^3F_4$	4567.64	5284	15.7	4549	−0.4	5220	14.3	4504	−1.4
Ta	$^4F_{3/2}$	0.00	0		0		0		0	
	$^4F_{5/2}$	2010.10	2199	9.4	1704	−15.2	1920	−4.5	1679	−16.5
	$^4F_{7/2}$	3963.92	4411	11.3	3660	−7.7	4082	3.0	3563	−10.1
	$^4F_{9/2}$	5621.04	6369	13.3	5477	−2.6	6012	7.0	5396	−4.0
W	$^5D_0$	0.00	0		0		0		0	
	$^5D_1$	1670.30	1440	−13.8	1181	−29.3	1328	−20.5	1073	−35.8
	$^5D_2$	3325.53	3131	−5.8	2715	−18.3	3002	−9.7	2459	−26.1
	$^5D_3$	4830.00	3728	−22.8	4252	−12.0	4631	−4.1	3888	−19.5
	$^5D_4$	6219.33	6330	1.8	5711	−8.2	6142	−1.2	5344	−14.1
Re	$^6D_{9/2}$	0.00	0		0		0		0	
	$^6D_{7/2}$	2462.34	2027	−17.7	2300	−6.6	2371	−3.7	2031	−17.5
	$^6D_{5/2}$	4015.90	3473	−13.5	3510	−12.6	3604	−10.3	3518	−12.4
	$^6D_{3/2}$	4572.99	4149	−9.3	4341	−5.1	4458	−2.5	4428	−3.2
	$^6D_{1/2}$	5483.78	4963	−9.5	4908	−10.5	5048	−7.9	5672	3.4
Os	$^5D_4$	0.00	0		0		0		0	
	$^5D_3$	4159.32	3755	−9.7	3132	−24.7	3124	−24.9	3269	−21.4
	$5D_2$	2740.49	3996	45.8	2829	3.2	2841	3.7	3619	32.0
	$^5D_1$	5766.14	6024	4.5	5934	2.9	5915	2.6	5174	−10.3
	$^5D_0$	6092.79	6706	10.1	6595	8.3	6575	7.9	5633	−7.5
Ir[d]	$1^4F_{9/2}$	0.00	0		0		0		0	
	$1^4F_{7/2}$	6323.91	6564	3.8	2868	−54.7	2831	−55.2	5664	−10.4
	$1^4F_{5/2}$	5784.62	7810	35.0	6495	12.3	6414	10.9	7541	30.4
	$1^4F_{3/2}$	4078.94	6918	69.6	7316	79.3	7229	77.2	7022	72.2
	$2^4F_{9/2}$	2834.98	5447	92.1	10483	269.8	10578	273.1	5795	104.4
	$2^4F_{7/2}$	7106.61	9156	28.8	9142	28.6	8887	25.1	9212	29.6
	$2^4F_{5/2}$	9877.54	12258	24.1	9033	−8.6	8786	−11.1	12075	22.2
	$2^4F_{3/2}$	11831.09	11989	1.3	14007	18.4	17968	51.9	11114	−6.1
	$^2P_{3/2}$	10578.68	14064	32.9	17919	69.4	13727	29.8	13691	29.4
	$^2P_{1/2}$	12505.68	15464	23.7	18953	51.6	20670	65.3	14920	19.3
Pt	$^3D_3$	0.00	0		0		0		0	
	$^3D_2$	775.90	782	0.8	1407	81.4	1394	79.7	1207	55.5
	$^3D_1$	10132.00	10010	−1.2	10175	0.4	9484	−6.4	8461	−16.5
Au	$^2D_{5/2}$	0.00	0		0		0		0	
	$^2D_{3/2}$	12274.00	12032	−2.0	12658	3.1	11448	−6.7	10281	−16.2
Hg	$^3P_0$	0.00	0		0		0		0	
	$^3P_1$	1767.22	703	−60.2	1743	−1.4	1076	−39.1	837	−52.7
	$^3P_2$	6397.90	8961	40.1	6189	−3.3	3558	−44.4	2723	−57.4
Avg.				20.3		26.7		28.6		23.8

[a] Reference 50a. [b] ECP = MCSCF + SOCI/uSBKJC(f) using effective nuclear charges (Z_{eff}). Z_{eff}(La) = 803.70, Z_{eff}(Hf) = 1025.28, Z_{eff}(Ta) = 1049.74, Z_{eff}(W) = 1074.48, Z_{eff}(Re) = 1099.50, Z_{eff}(Os) = 1124.80, Z_{eff}(Ir) = 1150.38, Z_{eff}(Pt) = 1176.24, Z_{eff}(Au) = 1202.38, and Z_{eff}(Hg) = 9040.00. The equation for Z_{eff} is $Z_{\text{eff}} = Z(A)f_n$, where $f_n = 13.96 + 0.14n$ ($n = 2 \sim 9$) and $Z(A)$ is the true nuclear charge of A atom. [c] AE = MCSCF + SOCI/uMINI(3p) method, where the most outer functions corresponding to 5d and 6s orbitals were completely uncontracted and three sets of p functions were added as 6p orbitals. AE(1) = the Z_{eff} approximation was used; Z_{eff}(Hf) = 50.40, Z_{eff}(Ta) = 53.29, Z_{eff}(W) = 56.24, Z_{eff}(Re) = 59.25, Z_{eff}(Os) = 62.32, Z_{eff}(Ir) = 65.45, Z_{eff}(Pt) = 68.64, Z_{eff}(Au) = 71.89, and Z_{eff}(Hg) = 132.80. The equation for Z_{eff} is $Z_{\text{eff}} = Z(A)f_n$, where $f_n = 0.64 + 0.03n$ ($n = 2 \sim 9$) and $Z(A)$ is the true nuclear charge of A atom. AE(2) = full BP Hamiltonian was used, instead of the Z_{eff} approximation. AE(3) = MCSCF orbitals were optimized within the RESC approximation, and spin−orbit splittings were estimated using full BP Hamiltonian. [d] State-averaged MCSCF calculation was carried out for 1^4F and 2^4F states with equal weights.

Table 2) have 1^4F (i.e., $(5d)^7(6s)^2$) character of 88% and 94%, respectively, and the energy gap (6564 cm^{-1}) between these states is in good agreement with the corresponding experimental value (6323.91 cm^{-1}). However, the lowest $J = {}^5/_2$ and ${}^3/_2$ sublevels (denoted $1^4F_{5/2}$ and $1^4F_{3/2}$ in Table 2) strongly interact with higher states and have smaller 1^4F contribution. In particular, the $J = {}^3/_2$ sublevel has 45% ^2P character and only 13% 1^4F character. The next lowest $J = {}^3/_2$ sublevel has 50% 1^4F character, but its energy is about 5000 cm^{-1} higher. On the other hand, the sublevels assigned to 2^4F have relatively strong 2^4F (i.e., $(5d)^8 6(s)^1$) character, and the calculated splittings of these sublevels are in good agreement with the experimental ones; the numerical errors are 13%, 3%, and 27% for the energy gaps of $2^4F_{9/2}-2^4F_{7/2}$, $2^4F_{9/2}-2^4F_{5/2}$, and $2^4F_{9/2}-2^4F_{3/2}$, respectively. Thus, it appears that the rather large numerical errors for Ir are mainly due to inadequate estimation of the adiabatic gap between 1^4F and 2^4F and their perturbation by a nearby ^2P term.

2. Z_{eff} Results Obtained Using the AE Method. To examine the reliability of the Z_{eff} approach, the same calculations have been performed using the uMINI(3p) all-electron basis set described above. The effective nuclear charges Z_{eff} were determined as shown in the footnote of Table 2. The calculated results are in surprisingly good agreement with the experimental observations, except for Ir and Pt. Though the error for the $^3D_2$ state in Pt is 81%, the numerical difference is only 631 cm^{-1}. In the ECP calculation, the $^3D_2$ state has 58% ^1D and 42% ^3D character, but the corresponding state in the AE calculation has less singlet character (48%). Because the RESC scheme makes singlet character stronger in this state as described below, it can be said that the AE method underestimates the interaction

TABLE 3: Spin−Orbit Splittings of 1^4F and 2^4F States in Atomic Ir

state	expt[a]	ECP[b]	err (%)	AE (2)[c]	err (%)	AE (3)[d]	err (%)	WTBS[e]	err (%)	WTBS + RESC[f]	err (%)
$1^4F_{9/2}$	0.00	0		0		0		0		0	
$1^4F_{7/2}$	6323.91	6564	3.8	2831	−55.2	5664	−10.4	3096	−51.0	3526	−44.2
$1^4F_{5/2}$	5784.62	7810	35.0	6414	10.9	7541	30.4	5338	−7.7	5436	−6.0
$1^4F_{3/2}$	4078.94	6918	69.6	7229	77.2	7022	72.2	7637	87.2	5177	26.9
$2^4F_{9/2}$	2834.98	5447	92.1	10 578	273.1	5795	104.4	12 823	352.3	2251	−20.6
$2^4F_{7/2}$	7106.61	9156	28.8	8887	25.1	9212	29.6	9993	40.6	7606	7.0
$2^4F_{5/2}$	9877.54	12 258	24.1	8786	−11.1	12 075	22.2	8742	−11.5	8387	−15.1
$2^4F_{3/2}$	11 831.09	11 989	1.3	17 968	51.9	11 114	−6.1	14 738	24.6	104 42	−11.7

[a] Reference 50a. [b] MCSCF + SOCI/uSBKJC(f,p) results. [c] MCSCF + SOCI/uMINI(3p) results. [d] MCSCF(RESC) + SOCI/uMINI(3p) results. [e] MCSCF + SOCI/WTBS(3p) results, where 5d and 6s orbitals of WTBS basis set (ref 57) are split into three sets and three sets of p functions are added as 6p orbital (exponents are the same as those for uMINI(3p)). [f] MCSCF(RESC) + SOCI/WTBS results, where the outermost sets of s, p, and d functions were split into three sets and the set of f functions were split into two sets.

between the lowest ^1D and ^3D adiabatic states and/or overestimates the energy gap between the adiabatic states.

The calculated splittings in Re and Os are improved in comparison with the $Z_{\rm eff}$ results, even though the lowest state is ^5F, instead of ^5D, in Os. Results for the ^5F state of Os are not shown in Table 2, because the MCSCF orbitals have not been optimized for this state and Moore[50a] suggests ^5F is the first excited state. Serious errors remain for Ir, because the lowest ^4F state is calculated to have $(5d)^8(6s)^1$ as the main configuration in the AE calculations. This is inconsistent with the experimental observation.[50a] Thus, these results as well as those in the next subsection suggest it is necessary to incorporate spin-free relativistic effects in all-electron MCSCF calculations.

3. Full Breit−Pauli (BP) Results Obtained Using the AE Method. Full BP calculations were performed on the third-row transition elements (Table 2). The calculated results are very similar to those obtained using the AE $Z_{\rm eff}$ method. It is disappointing that no improvement is observed for Ir or Pt and that the spin−orbit splittings are underestimated by more than 30% for Hg. The splittings of the ^3P states in Hg are rather smaller than those obtained by the $Z_{\rm eff}$ approach and then those observed experimentally.

4. Full BP Results Including Spin-Free Relativistic Corrections. As noted above, serious disagreement between theory and experiment is found for the ^4F states of Ir when the AE basis set is used, because the order of adiabatic L−S states is not well described without spin-free relativistic corrections. This prompted the use of the RESC approximation in the all-electron orbital optimization. The RESC implementation in GAMESS is presently limited to spin-free (scalar) one-electron corrections and both one and two electron spin-dependent corrections (spin−orbit couplings). The inclusion of scalar relativistic effects by means of the RESC improves the energetic order of the low-lying adiabatic states, so that an improved description of the spin−orbit mixing is obtained after diagonalization of the Hamiltonian in which the off-diagonal spin−orbit perturbations have been added to these L−S energies.

A nonrelativistic MCSCF calculation gives ^5F as the ground state of Os, but inclusion of the RESC correctly predicts a ^5D ground state. The spin−orbit splittings of the ^5D state are very similar to those obtained by the ECP method: the $^5D_2$ substate is higher in energy than $^5D_3$ but the error is about 30% (Table 2). In atomic Ir, the relativistic corrections reverse the order of $(5d)^8(6s)^1$ and $(5d)^7(6s)^2$, so that the ground configuration is correctly predicted to be $(5d)^7(6s)^2$, because of strong relativistic stabilization of the 6s orbital. The spin−orbit splittings of the two ^4F states are in better agreement with the experimental ones than either the AE $Z_{\rm eff}$ or full BP method and have errors similar to those obtained by the ECP method (Table 2). The source of error could be caused by an inadequate basis set or by the fact that the basis set has been optimized only for $(5d)^7(6s)^2$. If they are optimized simultaneously for both $(5d)^7(6s)^2$ and $(5d)^8(6s)^1$, better results can be provided even by the ECP method.

5. Further Investigation on the Spin−Orbit Splittings in Atomic Ir. It is clear from the above that Ir represents a severe test of the ability to compute spin−orbit levels well. It is clearly critical to include spin-free relativistic corrections, through either a relativistic ECP or the RESC correction to AE calculations, to obtain a satisfactory splitting between the $(5d)^7(6s)^2$ and $(5d)^8(6s)^1$ ^4F terms. In addition, it is important to describe well other low-lying states, including at least the ^2P state that makes the largest contribution to the level Moore assigns as $^4F_{3/2}$. Unfortunately, multireference Møller−Plesset perturbation calculations (MRMP2)[56] prove a larger energy gap between the two ^4F terms in both cases that the SBKJC(f,p) and MINI^{3p} basis sets are used. Accordingly, better agreement would not be expected even using MRMP2 wave functions. Then, the Ir calculations in Table 2 may justly be criticized as having too small an atomic basis to be able to correctly account for these important term energies.

Thus, as a probe of basis set effects, we have done an additional calculation using the WTBS basis.[57] Because this is presented as a general contraction to a minimal basis set, additional flexibility is gained by detaching as individual Gaussians the outer 2s, 2p, and 5d primitives and adding additional diffuse s and p primitives with exponent 0.016 388. No additional f function was included. The SOCI includes nine low-lying orbitals (one s, p, and d virtual level only). Table 3 shows that the results including RESC are quite encouraging. In particular, the $2^4F_{9/2}$ level at 2834.98 cm^{-1}, which is the second level overall, is computed at 2251 cm^{-1} compared to 2834.98 cm^{-1}, a marked improvement over the results in Table 2. In addition, the irregular ordering of $1^4F_{3/2}$ and $1^4F_{5/2}$ at 4079 and 5785 cm^{-1} is more nearly quantitative than the ECP or AE^3 results in Table 2. However, the irregular order of the $1^4F_{7/2}$ level at 6323.91 cm^{-1} is not well reproduced in Table 3, which finds this to be the third rather than fifth overall level. Table 3 hints that it may be possible to obtain good spin−orbit levels, using RESC and the BP operator, with appropriate basis sets and the inclusion of sufficient dynamic correlation.

Summary

The spin−orbit splittings of low-lying states in the third-row transition elements were predicted using four methods: (i) MCSCF + SOCI/uSBKJC(f) within a one-electron ($Z_{\rm eff}$) approximation, (ii) MCSCF + SOCI/uMINI(3p) with $Z_{\rm eff}$ approximation, (iii) MCSCF + SOCI/uMINI^{3p} with full BP Hamiltonian, and (iv) MCSCF + SOCI/uMINI^{3p} with full BP Hamiltonian and the RESC approximation. It is found that both the first and fourth methods lead to acceptable predictions of spin−orbit splittings, except for the case of atomic Ir. The latter may be caused by the use of inadequate basis sets and by the need for a larger CI expansion. Thus, we conclude that for most atoms one can predict ground-state spin−orbit splittings within roughly 30% relative error by using the simple and inexpensive scheme of the effective charge approach combined with the ECP method. It is very helpful to be able to perform higher-level calculations to discover the reasons for the failure of this simple approach observed in the cases of Re, Os, and Ir. In atomic Re and Os, the splittings improved greatly when the full BP approach was used. Even though a satisfactory reproduction of Ir spin−orbit levels has not yet been obtained, the RESC results are entirely similar to the ECP results, and it can be concluded that the ECP method is reliable and has an advantage in terms of computational effort.

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References and Notes

(1) Curtiss, L. A.; Ragavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764−7776.

(2) (a) Zimmermann, H. E.; Kutateladze, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 8, 249−250. (b) Reguero, M.; Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Org. Chem.* **1997**, *62*, 6897−6902. (c) Danovitch, D.; Marian, C. M.; Neuheuser, T.; Peyerimhoff, S. D.; Shaik, S. *J. Phys. Chem. A* **1998**, *102*, 5923−5926.

(3) Havlas, Z.; Downing, J. W.; Michl, J. *J. Phys. Chem. A* **1998**, *102*, 5681−5692.

(4) Fedorov, D. G.; Evans, M.; Song, Y.; Gordon, M. S.; Ng, C. Y. *J. Chem. Phys.* **1999**, *111*, 6413−6421.

(5) Minaev, B. A.; Agren, H. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2061−2067.

(6) Wheeler, M. D.; Norman, S. M.; Orr-Ewing, A. J. *J. Chem. Phys.* **1998**, *108*, 6594−6605.

(7) Alekseyev, A. B.; Liebermann, H.-P.; Hirsch, G.; Buenker, R. J. *J. Chem. Phys.* **1998**, *108*, 2028−2040.

(8) Yabushita, S. *J. Mol. Struct. (THEOCHEM)* **1999**, *461−462*, 523−532.

(9) (a) Witek, H. A.; Nakajima, T.; Hirao, K. *J. Chem. Phys.* **2000**, *112*, 8015−8025. (b) Nakajima, T.; Koga, K.; Hirao, K. *J. Chem. Phys.* **2000**, *112*, 10142−10148.

(10) Danovich, D.; Shaik, S. *J. Am. Chem. Soc.* **1997**, *119*, 1773−1786.

(11) Wittborn, A. M. C.; Costas, M.; Blomberg, M. R. A.; Sigebahn, P. E. M. *J. Chem. Phys.* **1997**, *107*, 4318−4328.

(12) DiLabio, G. A.; Christiansen, P. A. *J. Chem. Phys.* **1998**, *108*, 7527−7533.

(13) Malli, G. L.; Styszyski, J. *J. Chem. Phys.* **1996**, *104*, 1012−1017.

(14) (a) Visscher, L.; Visser, O.; Aerts, H.; Merenga, H.; Niewpoort, W. C. *Comput. Phys. Commun.* **1989**, *50*, 375. (b) Matsuoka, O. *J. Chem. Phys.* **1992**, *97*, 2271−2275. (c) Dyall, K. G. In *Relativistic and Correlation Effects in Molecules and Solids*; Malli, G. L., Ed.; Plenum Press: New York, 1993. (d) Saue, T.; Faegri, K.; Helgaker, T.; Gropen, O. *Mol. Phys.* **1997**, *91*, 937−950. (e) Pernpointner, M.; Visscher, L.; de Jong, W. A.; Broer, R. *J. Comput. Chem.* **2000**, *21*, 1176−1186.

(15) (a) Dyall, K. G. *Chem. Phys. Lett.* **1994**, *224*, 186−194. (b) Laerdahl, J. K.; Saue, T.; Faegri, K. *Theor. Chem. Acc.* **1997**, *97*, 177−184. (c) Laerdahl, J. K.; Faegri, K.; Visscher, L.; Saue, T. *J. Chem. Phys.* **1998**, *109*, 10806−10807.

(16) (a) Eliav, E.; Kaldor, U.; Ishikawa, Y. *Chem. Phys. Lett.* **1994**, *222*, 82−87. (b) Visscher, L.; Dyall, K. G.; Lee, T. J. *Int. J. Quantum Chem.* **1995**, *S29*, 411−419. (c) Visscher, L.; Lee, T. J.; Dyall, K. G. *J. Chem. Phys.* **1996**, *105*, 8769−8776.

(17) (a) Jensen, H. J. A.; Dyall, K. G.; Saue, T.; Faegri, K. *J. Chem. Phys.* **1996**, *104*, 4083−4097. (b) Fleig, T.; Marian, C. M.; Olsen, J. *Theor. Chem. Acc.* **1997**, *97*, 125−135.

(18) (a) Visser, O.; Visscher, L.; Aerts, P. J. C.; Niewpoort, W. C. *Theor. Chim. Acta* **1992**, *81*, 405−416. (b) Baeck, K. K.; Lee, Y. S. *J. Chem. Phys.* **1994**, *100*, 2888−2895. (c) Styszynski, J.; Cao, X.; Malli, G. L.; Visscher, L. *J. Comput. Chem.* **1997**, *18*, 601−608. (d) Visscher, L.; Enevoldsen, T.; Saue, T.; Oddershede, J. *J. Chem. Phys.* **1998**, *109*, 9677−9684. (e) Ishikawa, Y.; Nakajima, T.; Hada, M.; Nakatsuji, H. *Chem. Phys. Lett.* **1998**, *283*, 119−124.

(19) (a) Havriliak, S. J.; Yarkony, D. R. *J. Chem. Phys.* **1985**, *83*, 1168−1172. (b) Yarkony, D. R. *J. Chem. Phys.* **1986**, *84*, 2075−2078. (c) Battle, J. S.; Gould, M. D. *Chem. Phys. Lett.* **1993**, *201*, 284−293. (d) Sjovall, M.; Gropen, O.; Olsen, J. *Theor. Chem. Acc.* **1997**, *97*, 301−312. (e) Mitrushenkov, A. O.; Palmieri, P. *Mol. Phys.* **1997**, *92*, 511−522. (f) Yabushita, S.; Zhang, Z.; Pitzer, R. M. *J. Phys. Chem. A* **1999**, *103*, 5791−5800. (g) Nicklass, A.; Peterson, K. A.; Berning, A.; Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **2000**, *112*, 5624−5632. (h) Tilson, J. L.; Ermler, W. C.; Pitzer, R. M. *Comput. Phys. Commun.* **2000**, *128*, 128−138.

(20) (a) Hess, B. A. *Phys. Rev. A* **1986**, *32*, 3742−3748. (b) Samzow, R.; Hess, B. A. *Chem. Phys. Lett.* **1991**, *184*, 491−496. (c) Samzow, R.; Hess, B. A.; Jansen, G. *J. Chem. Phys.* **1992**, *96*, 1227−1231. (d) Sjovall, M.; Fagerli, H.; Gropen, O.; Almlof, J.; Saue, T.; Olsen, J.; Helgaker, T. *J. Chem. Phys.* **1997**, *107*, 5496−5501. (e) Sjovall, M.; Fagerli, H.; Gropen, O.; Almlof, J.; Schimmelpfennig, B.; Wahlgren, U. *Theor. Chem. Acc.* **1998**, *99*, 1−7.

(21) Dyall, K. G. *J. Chem. Phys.* **1998**, *109*, 4201−4208.

(22) Hay, P. J.; Wadt, W. R.; Kahn, L. R.; Raffenetti, R. C.; Phillips, D. H. *J. Chem. Phys.* **1979**, *71*, 1767−1779.

(23) (a) Koseki, S.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem.* **1992**, *96*, 10768−10772. (b) Koseki, S.; Gordon, M. S.; Schmidt, M. W.; Matsunaga, N. *J. Phys. Chem.* **1995**, *99*, 12764−12722. (c) Matsunaga, N.; Koseki, S.; Gordon, M. S. *J. Chem. Phys.* **1996**, *104*, 7988−7996. (d) Koseki, S. Unpublished results for the sixth-row typical elements: Z_{eff}(Cs) = 12210, Z_{eff}(Ba) = 12432, Z_{eff}(Tl) = 9153, Z_{eff}(Pb) = 18204, Z_{eff}(Bi) = 18426, Z_{eff}(Po) = 18648, Z_{eff}(At) = 18870. (e) Koseki, S.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem. A* **1998**, *102*, 10430−10435.

(24) Fedorov, D. G.; Gordon, M. S. *J. Chem. Phys.* **2000**, *112*, 5611−5623.

(25) (a) Marian, C. M.; Wahlgren, U. *Chem. Phys. Lett.* **1996**, *251*, 357−364. (b) Hess, B. A.; Marian, C. M.; Wahlgren, U.; Gropen, O. *Chem. Phys. Lett.* **1996**, *251*, 365−371.

(26) Polly, R.; Gruber, D.; Windholz, L.; Gleichmann, M. M.; Hess, B. *J. Chem. Phys.* **1998**, *109*, 9463−9472.

(27) Berning, A.; Schweizer, M.; Werner, H.-J.; Knowles, P. J.; Palmieri, P. *Mol. Phys.* **2000**, *98*, 1823−1833.

(28) (a) Pitzer, R. M.; Winter, N. W. *J. Phys. Chem.* **1988**, *92*, 3061−3063. (b) Ermler, W. C.; Ross, R. B.; Christiansen, P. A. *Adv. Quantum Chem.* **1988**, *19*, 139.

(29) Seijo, L. *J. Chem. Phys.* **1995**, *102*, 8078−8088.

(30) Han, Y.-K.; Bae, C.; Lee, Y. S.; Lee, S. Y. *J. Comput. Chem.* **1998**, *19*, 1526−1533.

(31) Takahashi, O.; Saito, K.; Yabushita, S. *Int. J. Quantum Chem.* **1999**, *74*, 515−530.

(32) Sanoyama, E.; Kobayashi, H.; Yabushita, S. *J. Mol. Struct. (THEOCHEM)* **1998**, *451*, 189−204.

(33) (a) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026−6033. (b) Stevens, W. J.; Basch, H.; Krauss, M.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612−630. (c) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555−5565.

(34) Stevens, W. J.; Krauss, M. *Chem. Phys. Lett.* **1982**, *86*, 320−324.

(35) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563−594.

(36) (a) Nakajima, T.; Hirao, K. *Chem. Phys. Lett.* **1999**, *302*, 383−391. (b) Nakajima, T.; Koga, K.; Hirao, K. *J. Chem. Phys.* **2000**, *112*, 10142−10148. (c) Witek, H. A.; Nakajima, T.; Hirao, K. *J. Chem. Phys.* **2000**, *113*, 8015−8025. (d) Yanagisawa, S.; Nakajima, T.; Tsuneda, T.; Hirao, K. *J. Mol. Struct.* (THEOCHEM) (Fraga Special Issue) in press. (e) Fedorov, D. G.; Nakajima, T.; Hirao, K. *Chem. Phys. Lett.* Submitted.

(37) (a) Ehlers, A. W.; Boehme, M.; Dapprich, S.; Gobbi, A.; Hoellwarth, A.; Jonas, V.; Koehler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111−114. (b) Hoellwarth, A.; Boehme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Koehler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237−246.

(38) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

(39) The exponents of p functions are 0.054 (Lu), 0.059 (Hf), 0.065 (Ta), 0.069 (W), 0.073 (Re), 0.077 (Os), 0.081 (Ir), 0.086 (Pt), 0.089 (Au), and 0.093 (Hg) as the first set. The exponents for the second and third sets are those for the first set multiplied by 4.00 and 0.25, respectively.

(40) (a) Ruedenberg, K.; Schmidt, M. W.; Dombek, M. M.; Elbert, S. T. *Chem. Phys.* **1982**, *71*, 41−49, 51−64, 65−78. (b) Schmidt, M. W.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233−266.

(41) The second-order CI method is defined as a multireference CI consisting of single and double excitations from the MCSCF reference functions, in this case into external orbitals chosen to be eigenvectors of the standard MCSCF Fock operator. Only the lowest external orbitals were employed in order that the size of CI matrices is kept practical in our computer systems. Although all external orbitals were used for La, Hf, and

Ta atoms, the number of external orbitals used was 20 for Re and Os, 15 for Ir and Pt, and 11 for Au and Hg.

(42) The energy threshold depends strongly upon atoms in order to keep the size of the spin−orbit matrices practical: La = 0.11, Hf = 0.13, Ta = 0.12, W = 0.13, Re = 0.16, Os = 0.13, Ir = 0.21, Pt = 0.26, Au = 0.41, and Hg = 0.72 Hartree in the ECP calculations.

(43) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

(44) Visscher, L.; Saue, T.; Niewpoort, W. C.; Faegri, K.; Gropen, O. *J. Chem. Phys.* **1993**, *99*, 6704−6715.

(45) Dyall, K. G. *J. Chem. Phys.* **1993**, *98*, 9678−9686.

(46) (a) Heinemann, C.; Schwarz, J.; Koch, W.; Schwarz, H. *J. Chem. Phys.* **1995**, *103*, 4551−4561 and private communication. (b) Heinemann, C.; Koch, W.; Schwarz, H. *Chem. Phys. Lett.* **1995**, *245*, 509−518.

(47) Casarrubios, M.; Seijo, L. *Chem. Phys. Lett.* **1995**, *236*, 510−515.

(48) Schimmelpfennig, B.; Maron, L.; Wahlgren, U.; Teichteil, C.; Fagerli, H.; Gropen, O. *Chem. Phys. Lett.* **1998**, *286*, 261−266, 267−271.

(49) (a) Martin, R. L.; Hay, P. J. *J. Chem. Phys.* **1981**, *75*, 4539−4545. (b) Ross, R. B.; Powers, J. M.; Atashroo, T.; Ermler, W. C.; LaJohn, L. A.; Christiansen, P. A. *J. Chem. Phys.* **1990**, *93*, 6654−6670. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283. (d) According to Martin et al. (ref 49a), $(5d)^8(6s)^1$ is lower than $(5d)^7(6s)^2$ by 2.43 eV, but relativistic effects reverse the energetic order, to a gap of 0.09 eV. This splitting is re-estimated to be 0.16 eV by AREP (see ref 49b) and 0.27 eV by RECP (see ref 49c). The uSBKJC(f,p) gives 0.47 eV when the MCSCF orbitals are optimized with equal weights for both configurations. The uMINI(3p) provides a gap of −1.53 eV without RESC and of 0.54 eV with RESC.

(50) (a) Moore, C. E. *Atomic Energy Levels*; *Nat. Stand. Data Ser., Nat. Bur. Stand.* 35/V. I ∼ III (**1949**, **1952**, **1958**). (b) Hanlan, L. Ph.D. Thesis, University of Toronto, 1978. (c) Klotzbuecher, W. E. Ph.D. Thesis, University of Toronto, 1979.

(51) Desclaux, J. P. *At. Data Nucl. Data Tables* **1973**, *12*, 311−406.

(52) Grant, I. P.; McKenzie, B. J.; Norrington, P. H.; Mayers, D. F.; Pyper, N. C. *Comput. Phys. Commun.* **1980**, *21*, 207.

(53) Mohanty, A. K.; Clementi, E. *J. Chem. Phys.* **1990**, *93*, 1829−1833.

(54) Okada, S.; Shinoda, M.; Matsuoka, O. *J. Chem. Phys.* **1990**, *93*, 5013−5019.

(55) Vijayakumar, M.; Gopinathan, M. S. *J. Mol. Struct. (THEOCHEM)* **1996**, *361*, 15−19.

(56) (a) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983−7992. (b) Nakano, H. *Chem. Phys. Lett.* **1993**, *207*, 372−378.

(57) (a) Huzinaga, S.; Miguel, B. *Chem. Phys. Lett.* **1990**, *175*, 289−291. (b) Huzinaga, S.; Klobukowski, M. *Chem. Phys. Lett.* **1993**, *212*, 260−264.