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Utilizing Relativistic Effective Core Potentials for Accurate Calculations of Molecular Polarizabilities on Transition Metal Compounds

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The requirements necessary to extend an ECP basis set for the calculation of electric and linear optical properties to the transition metals are studied. Previously an augmentation of the SBK basis set for 39 elements with s and p electron only valences (H−Rn, excluding Ga, In, and Tl) [*J. Comput. Chem.*, **2005**, *26*, 1464−1471] was presented. In this work, electric dipole moments, polarizabilities, and anisotropies of selected metal hydrides, sulfides, and bromides, cisplatin, and the Fe, Ru, and Os metallocene derivatives along with many other systems are calculated and discussed. ECP calculations of molecules containing 3d and 4d metal centers among main group atoms have good agreement, often within 1−2% of the all-electron result at the time-dependent Hartree−Fock (TDHF)/Sadlej level of theory. Molecules with a 5d metal center have a large difference from and are more accurate than the all-electron results due to the inclusion of relativistic effects in the ECPs. The polarizability as calculated with and without ECPs of metallic clusters and surfaces is increasingly different as atomic number increases, again due to a lack of relativistic effects in the all-electron calculations. The augmented ECP calculations are consistent with relativistic all-electron results, while the Sadlej calculations are consistent with other nonrelativistic results. Both relativistic and basis set effects are less noticeable when the metal is in a formally positive state.

Introduction

Polarizability is a measure of the deformability of the electron density around an atomic or molecular system. It is a key element for describing electronic structure and plays an important role in governing noncovalent interactions. As such, it has been used to characterize electronic materials,[1] to characterize lead compounds in drug discovery,[2] and to develop force field parameters[3] for molecular dynamics simulations. However, those systems containing elements from the third period and beyond have computational requirements associated with treating large numbers of electrons that often make such calculations intractable. This difficulty is further complicated by the requirements of basis sets capable of describing the perturbed electronic distribution under the influence of external fields. Additional functions must be added to provide the necessary flexibility, resulting in the use of large diffuse basis sets which increase computational cost dramatically, such as the Sadlej basis sets.[4] These basis sets were designed to provide such functions in a systematic way and yield excellent dipole moments and polarizabilities when used with sufficiently correlated theory. They are well-known and provide a de facto standard for polarizability calculations.

Unfortunately, even for the second period main group elements, the Sadlej sets are quite large (10s6p4d /5s3p2d). Progressing to transition metals, the size of the basis is a far more serious concern, 21s17p11d9f4g/13s11p7d4f2g for gold, though the *g* functions are optional in molecular calculations.[5] For the mercury atom, Salek et al. have applied linear response theory with relativistic DFT.[6] Using the double-, triple-, and quadruple-ζ basis sets of Dyall,[7] they were able to find increasingly good agreement with experiment as the size of their basis set was increased. Examination of the basis sets, 22s19p12d9f, 29s24p15d11f and 34s30p19d13f, and of the systems used to test their method, Hg, AuH, and PtH_2, indicates that while when properly correlated chemical accuracy is obtainable, this is not a practical method for use on even moderately sized systems of a few heavy atoms. Clearly, an alternative to using such extensive basis sets is required if large systems are to be studied computationally.

In a previous study,[8,9] we demonstrated that effective core potentials (ECPs) could be successfully utilized for polarizability calculations of main group elements. The SBK ECPs[10] were originally optimized for computationally efficient geometry and energy applications. By effectively augmenting the standard ECP basis set with diffuse and polarization functions optimized to describe the polarizability of the remaining valence electrons, agreement of greater than 99% was found with Sadlej basis set calculations. This is unsurprising, as, in many cases, the response of the core electrons is small compared to that of the valence electrons. This augmented basis set is referred to as LFK in this work. Furthermore, work by Schwerdtfeger's group[11] has made clear that ECPs are a viable method for accurate calculations of transition metal polarizabilities. The present study, a companion to the previous study,[8] examines and reports the necessary requirements of accurately modeling the polarizability of transition metal compounds with the SBK ECPs. The approach we employ recognizes the additive nature of basis functions that reduces basis set requirements for larger molecules. To model the polarizability of a gold cation to basis set

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limits, for instance, would require significantly more functions around the cationic center than any one nuclei would require in a cluster of many atoms. In this work emphasis is placed on recognizing the minimal basis that can adequately describe the electronic properties of molecules. Very small systems such as the aforementioned cation or those with otherwise interesting electronic configurations may need a more complete description than that recommended for the closed shell neutral systems studied in this work.

We present polarizability calculations using the SBK ECP and basis set on transition metals coupled with the SBK ECP and LFK basis set on surrounding main group atoms. Basis set augmentation for modeling transition metal systems is discussed. Test calculations are completed and discussions follow indicating the appropriate use of ECPs when calculating valence electronic properties of molecules with transition metals. Time savings of one to several orders of magnitude are found. Accuracy is equivalent to or greater than that of all-electron methods at nonrelativistic theory due to the inclusion of relativistic effects in the ECPs.

Methodology and Calculations

Basis Sets. Previously, the ECP basis sets of 39 main group elements were augmented with optimized diffuse and polarization functions to introduce the ability to accurately calculate molecular electronic properties into the basis set.[8] The SBK ECPs[10] were selected for augmentation due to their wide use, ready availability (they are distributed with the GAMESS[12] and NWChem[13] electronic structure codes, and are available for download through the EMSL basis set library[14]), and good coverage of the periodic table (Li−Rn, Ce−Lu). The 2s2p SBK valence basis set was found to be severely inadequate for calculation of dipole moments and polarizabilities. Once extended to 2s3p2d with diffuse and polarization functions, however, the valence basis set proved remarkably accurate when compared to much larger basis sets. The functions were selected in the spirit of the Sadlej basis sets to improve the existing valence of the SBK sets. The important components for calculating electronic properties missing from the standard ECP basis of the main group atoms have been determined.

Cundari et al.[15] found that augmenting the basis set of the metal in RuO_4 exhibited a much smaller effect than augmenting the oxygen atoms. The positive charge on the metal localizes the electron density, and thus α is largely dependent on the description of the periphery atoms while only minimally affected by the augmenting functions on the transition metal. It is expected that this same principle applies to the majority of compounds where the metal is in a formally positive oxidation state. Additionally, with more electrons modeled in the transition metal description than the main group, larger basis sets are required. An examination of the SBK transition metal basis sets shows that several diffuse functions are already included in the basic description. In the SBK approximation, the main group elements are modeled with a 2s2p contracted valence. The LFK augmenting functions improve the basis to 2s3p2d with the addition of a diffuse *p* and diffuse and polarizing *d* functions. The SBK basis set for the metals, 4s4p3d, already has somewhat diffuse *s* and *p* functions included. At least one of the *d* functions is typically diffuse as well. Thus, the SBK metal basis set already includes many of the important components that were necessarily added for the main group elements.

Test basis sets were also developed where the valence description was further augmented with diffuse *s*, *p*, and *d* functions generated through approximate geometric progression, SBK(+spd), and linear combinations of the last few *d* functions were taken to further extend the basis and generate *f* functions, SBK(+spdf).

Methods. Molecular polarizabilities were calculated at the time-dependent Hartree−Fock (TDHF) level of theory implemented in GAMESS. All-electron calculations are contrasted with the SBK/LFK ECP calculation. The results are not compared to experiment as the correlation energy is typically important when computing quantitatively accurate values. Thus, the TDHF calculations gauge group and periodic trends, ECP, relativistic effects, and basis set effects.

Analogous relativistic all-electron Hartree−Fock polarizability calculations were completed utilizing the linear response module within the DIRAC[16] quantum chemistry program for some systems. All-electron calculations employ the Sadlej basis sets on main group atoms, and on transition metals when available (Cu−Zn, Ag−Cd, Au−Hg).[17] The well-tempered basis sets (WTBS)[18] of Huzinaga were used in the all-electron calculations of other metals.

Geometries were obtained with the SBK basis set augmented by a polarizing *d* function on heavy atoms. The calculations were performed at the B3LYP/DFT level of theory as implemented in the GAMESS quantum chemistry package. The electric dipole moments and polarizability tensors were computed using the TDHF algorithm also included in GAMESS. The α tensor was diagonalized to give a unique set of components, from which the molecular isotropic polarizabilities

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{1}$$

and polarizability anisotropies $\Delta\alpha$

$$(\Delta\alpha)^2 = \frac{1}{2}((\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{\mathrm{yy}} - \alpha_{zz})^2) \tag{2}$$

are then simple to calculate. The linear molecules studied in this work lie along the *z*-axis, so that $\alpha_{xx} = \alpha_{yy} = \alpha_{\perp}$, and $\alpha_{zz} = \alpha_{||}$. For these systems, the anisotropy is further simplified to

$$\Delta\alpha = |\alpha_{||} - \alpha_{\perp}| \tag{3}$$

The anisotropy being traditionally an unsigned quantity, for the purposes of this work the sign is included. A negative anisotropy signifies that the perpendicular components are calculated to be greater than the parallel component of the polarizability, and very likely indicates a fundamental inaccuracy in the calculation.

The compounds cover several oxidation states and a range of substituents on the metals. Dimers, tetramers, and hexamers of homonuclear systems were tested, along with a mixed metal dimer. The formal oxidation state of the metals in these clusters is neutral.

In order to differentiate the effects in the calculated polarizability from (1) the ECP and (2) the smaller basis set, additional polarizability calculations were performed with the Sadlej basis sets utilizing core potentials. This provides a direct method for assigning polarizability differences to the SBK ECP or basis set. Ideally, the two basis sets should return equivalent results when the core potentials are used, meaning the reduced basis set models polarizability as well as the larger basis. These results may be different from the all-electron results if relativistic effects are important.

Results and Discussions

Calculations on Metal−Main Group Binaries. It has been noted that atomic and small molecular systems' electronic

TABLE 1: Molecular Polarizabilities of the SBK/LFK, Sadlej, and Sadlej(ECP) Systems as Calculated in GAMESS[a]

		static polarizability						
molecule	R (Å)	SBK	LFK_{MG} SBK_{TM}	Sadlej(ECP)	uncDZ	uncTZ	Sadlej	$Sadlej^{DIRAC}$
CuH	1.47814	26.57	27.73				27.69	27.61
AgH	1.64955	31.11	33.25				33.29	33.14
AuH	1.52385	34.27	35.21	35.19	35.50	36.42	37.17	35.63
PtH_2	1.52020	36.83	38.40		37.62	38.78		

[a] All units are atomic units. Geometries and uncontracted DZ and TZ Hartree−Fock calculations are taken from Salek.[6] The PtH_2 bond angle is 88.26°. The uncDZ and uncTZ basis sets were designed by Dyall[7] and are 22s19p12d9f and 29s24p15d11f, respectively. The $Sadlej^{DIRAC}$ results utilize a relativistic wave function and were computed with the DIRAC program.

TABLE 2: Dipole Moments Obtained from Nonrelativistic TDHF Calculations Using the SBK, LFK, and Sadlej Basis Sets[a]

	electric dipole moment			
molecule	SBK	LFK	Sadlej	$Sadlej^{DIRAC}$
CuH	4.03	4.01	4.08	3.92
AgH	4.47	4.49	4.66	4.21
AuH	2.79	2.71	4.23	2.99
CuBr	6.61	6.45	6.48	
AgBr	7.74	7.53	7.56	
AuBr	5.83	5.71	7.09	5.85
ZnS	7.27	7.26	7.43	
CdS	7.92	7.97	8.85	
HgS	6.06	6.07	8.80	4.91
$PtCl_2(NH_3)_2$	15.87	12.28	12.25	

[a] Relativistic calculations are denoted by the DIRAC superscript.

properties are the most difficult to correctly model.[19] As such, the dimers included in this study provide rigorous test for the utility of the SBK/LFK basis set. The metal hydrides provide interesting examples as they are small enough to be easily studied by some all-electron methods and allow comparison to a previous study[6] that calculated polarizabilities of the molecules AuH and PtH_2 using the Dyall basis sets.[7]

The results of the hydride calculations can be found in Tables 1−3. The SBK/LFK calculations of CuH and AgH are found to be in good agreement with the Sadlej basis set when both are calculated with nonrelativistic TDHF theory. The value of the dipole moment of each system matches well with the Sadlej basis, varying the most for the AgH molecule by 0.17 D, and the results are included in Table 3. In each case, an absolute difference of 0.04 au is found in the polarizability by the addition of core electrons and larger Sadlej basis sets. The anisotropic data reported in Table 3 is also well reproduced, as for CuH the $\alpha_\perp$ and $\alpha_{||}$ components vary by less than 1% from the all-electron calculation. For AgH, only α_{zz} (the parallel component) differs by as much as 3%.

Comparisons with relativistic all-electron calculations highlight the importance of the ECPs when using nonrelativistic theory. The AgH system was also studied at the same geometry and all-electron basis set (contracted Sadlej) utilizing relativistic Hartree−Fock. Small, though important, differences are immediately noted when contrasted with the nonrelativistic (GAMESS/TDHF) treatment. The dipole moment decreases by 0.45 D. This makes the SBK/LFK calculation closer to the more accurate relativistic value than the nonrelativistic calculation with the Sadlej basis set. Concerning polarizability, it is noted that while the values of the components are close, the SBK/LFK calculated perpendicular component is lower than the nonrelativistic all-electron value, and the parallel component is higher. This results in isotropic averages ($(2\alpha_\perp + \alpha_{||})/3$) that are quite close, but anisotropies that disagree. Accounting for relativity in the all-electron calculation causes a decrease in $\alpha_\perp$, and an increase in $\alpha_{||}$, aligning the results with the ECP calculations. The ECP calculated anisotropy is nearly 70% larger than the nonrelativistic Hartree−Fock value, while only 14% larger than the relativistic Hartree−Fock results. Though this 14% difference still seems large, it is a product of the rather small anisotropy, $\approx$3.5 au. The individual components $\alpha_\perp$ and $\alpha_{||}$ calculated with the SBK/LFK ECP and basis set are only 0.3% and 1.1% different from the relativistic all-electron calculations, respectively. A similar, though exacerbated, effect is seen in the gold hydride results.

In the study by Salek et al.,[6] polarizabilities were reported at several levels of theory, including relativistic Hartree−Fock, for AuH and PtH_2. Bond lengths and angles were also reported, and these geometries were used to test the methods proposed in this study. The earlier Salek calculations and those performed for this work are reported in Table 1. All-electron basis sets were for H an uncontracted aug-cc-PVDZ and aug-cc-PVTZ,[20] and for the metal a 22s19p12d9f and 29s24p15d11f.[7] The H and metal basis sets were used in their fully uncontracted form, and are labeled uncDZ and uncTZ, respectively. This amounts

TABLE 3: Components of the Polarizability Tensor and Anisotropies Obtained through TDHF Calculations for the LFK and Sadlej Basis Sets and Reported in Atomic Units[a]

	polarizability anisotropies								
	LFK			Sadlej			$Sadlej^{DIRAC}$		
molecule	$\alpha_\perp$	$\alpha_{||}$	$\Delta\alpha$	$\alpha_\perp$	$\alpha_{||}$	$\Delta\alpha$	$\alpha_\perp$	$\alpha_{||}$	$\Delta\alpha$
CuH	26.95	29.29	2.35	26.96	29.15	2.19	26.87	29.11	2.24
AgH	31.93	35.91	3.98	32.51	34.85	2.35	32.04	35.53	3.49
AuH	34.37	36.88	2.51	37.61	36.31	−1.30	35.40	36.10	0.70
CuBr	35.28	44.99	9.71	35.04	46.05	11.01			
AgBr	38.21	51.88	13.67	38.52	52.76	14.24			
AuBr	40.94	62.31	21.36	40.24	55.14	14.90	41.43	61.70	20.27
ZnS	52.25	89.58	37.33	52.73	88.06	35.33			
CdS	61.42	116.76	55.33	65.05	115.83	50.77			
HgS	53.81	104.47	50.66	64.94	118.06	53.12	48.43	104.40	55.97

[a] Relativistic calculations are denoted by the DIRAC superscript. In angstroms, the bond lengths are $R_{CuH} = 1.47814$, $R_{AgH} = 1.64955$, $R_{AuH} = 1.56957$, $R_{CuBr} = 2.22037$, $R_{AgBr} = 2.45629$, $R_{AuBr} = 2.40133$, $R_{ZnS} = 2.08430$, $R_{CdS} = 2.29465$, and $R_{HgS} = 2.32613$.

to 310 basis functions and 80 electrons for the uncTZ AuH molecule, while the ECP basis set has only 43 functions and 20 electrons. The Sadlej basis set, a medium sized basis, has 137 functions for AuH (in its contracted form) and is also an all-electron (80) basis set. The dipole moment of the nonrelativistic Sadlej modeled AuH system was in between the moments of the copper and silver hydrides. However, when modeling with the ECP, the dipole moment is smaller than the dipole moment of the other two hydrides in the series and the all-electron result by about 1.5 D. The TDHF calculations in this work bracketed the relativistic results, as the LFK polarizability is 1% less than the uncDZ value, while the Sadlej basis set was 3% higher than the uncTZ. The most interesting data is not the small numeric differences but the values of the α tensor components with respect to one another. In the case of CuH and AgH, use of the Sadlej basis sets predicts that, as expected, the most polarizable axis is the $\alpha_{||}$ component. As these molecules lie on the *z*-axis, this is equivalent to the α_{zz} component. The ECP method faithfully reproduces this finding for both molecules, and extends the trend to AuH as well. This is in good agreement with the Salek study, where the most polarizable axis was also found to be the parallel axis. However, using the all-electron Sadlej basis set in the absence of relativistic theory, the results now break the group trend, and the $\alpha_{\perp}$ components are calculated to be the most polarizable. In order to test whether the difference could be attributed to the basis set or core electrons, the SBK ECPs were used with the Sadlej basis set. This decreases the isotropic polarizability and correctly aligns the tensor components when computed with the Sadlej basis set. It is interesting to note that the SBK/LFK basis set performs identically to the polarizability oriented Sadlej basis set in the presence of an effective core potential. Values of 35.2 au were calculated for both when each basis set modeled a 19 electron valence around the gold ECP. When the Sadlej basis set was used, however, the explicit presence of all electrons causes $\alpha_{||}$ to be calculated as the least polarizable axis. This differs from the all-electron group trend, the Salek study, and the SBK/LFK results. The explanation for this discrepancy is a lack of relativistic effects in the all-electron GAMESS/TDHF calculation. These effects are empirically included in the ECPs, and are seen in the decreased dipole moment and polarizability that characterize a relativistic contraction of the electron density. The relativistic calculations confirm the importance of relativity, as the results from the all-electron Sadlej basis calculation are again altered radically. The dipole moment decreases from 4.23 to 2.99 D, bringing it much closer to the SBK/LFK value of 2.71 D. The components $\alpha_{\perp}$ and $\alpha_{||}$ each decrease, the perpendicular component by a larger amount. This (1) brings each into closer numerical agreement with the SBK/LFK ECP calculation and (2) correctly orders the components so that $\alpha_{||}$ is greater than $\alpha_{\perp}$.

While no Sadlej basis is available for Pt, the LFK H basis and the SBK on Pt actually surpass the uncDZ system on the PtH_2 molecule. The ECP method outperforms a much larger all-electron basis set and return values within 1% of the uncTZ system for the polarizability. Thus, in the 3d and 4d metals, the Sadlej and LFK basis sets are in closest agreement at the TDHF level of theory due to the minimal relativistic effects present in the lighter elements. It can be noted, however, that the effects are more prevalent in AgH than CuH. The results are quite different however, in the gold hydride. The ECP calculation not only is 10^3 times faster than the all-electron Sadlej calculation but also includes relativistic effects that are important for an even qualitatively accurate description of the valence electronic properties. The ECP basis performs well, with a 1% difference across the metal hydrides when compared to the relativistic all-electron Sadlej calculations (or the uncTZ in the case of PtH_2). Additionally, it is more accurate and much faster than what are otherwise excellent nonrelativistic calculations. The full set of results is reported in Tables 1 through 3.

TABLE 4: Molecular Polarizabilities (au) Calculated by TDHF[a]

	static polarizability				
peripheral metal	SBK SBK	LFK SBK	LFK SBK + (spd)	LFK SBK + (spdf)	Sadlej Sadlej/WTBS
CuBr	27.69	38.52	38.87	38.89	38.71
AgBr	30.47	42.77	43.51	43.74	43.26
AuBr	37.71	48.06	48.80	48.75	45.21
$PtCl_2(NH_3)_2$	57.59	81.28	81.36	81.72	81.25
$NbCl_5$	90.81	112.83	112.98	112.74	116.78
$Hf(OSiH_3)_4$	117.99	143.76	143.68	143.55	147.30
$Zr(OSiH_3)_4$	122.94	150.63			152.51
$Ti(OSiH_3)_4$	118.36	145.01			146.24
ZnS	55.12	64.69			64.51
CdS	69.48	79.87			81.98
HgS	60.48	70.70			82.65
$Cr(CO)_6$	103.71	111.78			112.16
$Mo(CO)_6$	125.38	132.31			131.38
$W(CO)_6$	131.02	138.83			134.92
$Fe(C_5H_5)_2$	106.98	115.08			114.21
$Ru(C_5H_5)_2$	121.50	130.42			130.22
$Os(C_5H_5)_2$	122.33	131.15			131.91

[a] B3LYP/SBK geometries are used for all molecules. The metal bromide and metal sulfide dimers use Sadlej basis sets on the metals, otherwise WTBS.

Another test for the basis set is the metal bromide compounds reported in Table 4, which fair similarly to the hydrides. This is unsurprising as the electronic structure of the two is quite similar, that is, a dimer where the metal has an associated formal charge of +1. Again the Cu and Ag systems are found to be in good agreement with the nonrelativistic Sadlej calculation, averaging less than 1% different from the all-electron results in both dipoles and polarizabilities, while the AuBr molecule varies the greatest amount. Both methods set the order of increasing polarizability to be CuBr < AgBr < AuBr, and the ordering of the α tensor components is in agreement as well. The difference in the isotropic average of the tensors is again thought to be due to the inclusion of relativistic effects in ECP calculation. Utilizing the ECPs with the Sadlej basis set verifies that the ECPs cause the difference, as $\bar{\alpha}$ increases by several atomic units. To determine whether or not the ECP result, which now *increases* due to the inclusion of relativistic effects, is correct, the relativistic polarizability was computed with the Sadlej basis set and all electrons. Explicit treatment of relativity resulted in the predicted increase of the polarizability from 45.2 to 48.2 au, in remarkable agreement with the SBK/LFK result. Furthermore, the perpendicular and parallel components increased so that the agreement between the SBK/LFK calculation and the relativistic calculation for each is about 0.5−0.6 au. The parallel component of the nonrelativistic Sadlej calculation differs from the relativistic value by 6.6 au.

Zn, Cd, and Hg sulfides also pair a transition metal and main group element, though now the metals have a +2 formal charge. The 3d and 4d metals, Zn and Cd, again agree well with the nonrelativistic calculations. Augmenting only the sulfur atom with the LFK functions, and modeling the metal with the standard SBK basis, differences from the all-electron result of 0.2% and 2.6% are calculated for ZnS and CdS polarizabilities. The larger difference for cadmium is again due to the increasingly important relativistic effects. This is reflected in the dipole moment as well, as the difference between the LFK and all-electron results is 0.17, 0.88, and 2.73 D for ZnS, CdS, and HgS, respectively. For HgS, the relativistic effects are quite large, accounting for a calculated difference of about 12 au between the ECP and Sadlej values for polarizability. Using the Sadlej basis with the ECP core potential (Sadlej(ECP)) brings the dipole and polarizability in line with the LFK basis sets, indicating the influence of the ECP on the very heavy atoms (Au−Hg). Our experience with the AuH and AuBr molecules led us to predict that the lower ECP value for the HgS dipole moment and polarizability is more accurate than the all-electron case. The relativistic Sadlej calculation confirms this conclusion, as the dipole and polarizability decrease by 44% and 18%, respectively. Finally, it is noted for HgS that while the ECP calculations are more accurate, compared to the other calculations studied in this work there is still a relatively large difference from the relativistic all-electron calculations. The sulfur basis set and ECP has been found to perform well in other calculations. Furthermore, the relatively small SBK basis set returns essentially the same results as those calculated with the Sadlej(ECP) basis set, which includes several *f* functions on both mercury and sulfur. This error is therefore assigned to the mercury ECP and may require additional study to improve upon. These results are found in Tables 2 and 4.

Metal Centered Compounds. Ferrocene ($FeC_{10}H_{10}$) and its Ru and Os analogues are the first of a larger class of molecules studied which introduce distinctive electronic and molecular features, providing another interesting test for the SBK/LFK basis. The cyclopentadiene rings above and below the metal are aromatic and negatively charged. Thus, these molecules contain polarizable density in the organic intramolecular bonding, the π density above and below the rings, and the basis sets must be able to contend with the interaction of the positively charged metal with the five carbon atoms on each ring. For an all-electron reference, the Sadlej basis sets are unavailable beyond the six metals studied above (Cu−Zn, Ag−Cd, and Au−Hg), though still used for the ring atoms. The well-tempered basis set (WTBS) is employed on the metals. The ECP and nonrelativistic all-electron calculations order the polarizability of the metallocenes as $FeC_{10}H_{10} < RuC_{10}H_{10} < OsC_{10}H_{10}$. Ferrocene is calculated to be 11−12% less polarizable than when the heavier metals are present, which is explained by the slightly shorter average metal−carbon distance. This distance is ≈ 2.11, 2.26, and 2.25 Å for Fe, Ru, and Os, respectively. Despite the slightly tighter geometry around the metal, the osmium molecule is predicted to be more polarizable by both basis sets at the Hartree−Fock level, though only very slightly more so than the Ru molecule.

Silicon dioxide doped with group IVB elements also provides a unique test case and simulates a formal charge of +4 on the metal centers. The 3d and 4d systems, $Ti(OSiH_3)_4$ and $Zr(OSiH_3)_4$ are only about 1% different from the all-electron results. The results for $Hf(OSiH_3)_4$ are in good agreement with both methods, though with a difference of 2.4%, which is large enough to change the order of the all-electron trend. That is, for the all-electron result α increases as $Ti(OSiH_3)_4 < Hf(OSiH_3)_4 < Zr(OSiH_3)_4$, but when the core potential is included, it becomes $Hf(OSiH_3)_4 < Ti(OSiH_3)_4 < Zr(OSiH_3)_4$. The relativistic effects change the value only slightly, but are important in ordering the series correctly.

Neat Metal Clusters. The above systems all have a formal positive charge on the metal. Unimolecular dimers, tetramers, and hexamers have been studied with all-electron and basis set augmented ECP methods for the coinage metals. The inaccuracies due to a lack of relativistic effects in the all-electron calculations are magnified when the metals are removed from the presence of main group atoms and the formally positive oxidation state. Saue and Jensen[21] have completed relativistic and nonrelativistic calculations on the coinage metal dimers. The uncontracted all-electron basis sets they used were 18s15p9d3f, 22s18p12d3f, and 24s20p14d10f for copper, silver, and gold, respectively. Though the geometries differ, the calculations can still be compared in a semiquantitative fashion. They found the copper dimer to have a relativistic polarizability of 95.8 au, and a nonrelativistic polarizability of 101.9 au, 6.3% higher. This is reflected in our calculations with both the all-electron Sadlej basis set and the ECP. The SBK ECP basis set returns a polarizability 6.7% lower than the all-electron Sadlej basis set. The relativistic effects are increasingly more important for the silver and then gold systems. Saue and Jensen reported the nonrelativistic polarizability of the silver dimer to be 138.6 au, in good agreement with the Sadlej basis calculation we have completed. Their relativistic value of 116.7 is again very close to our SBK result. The gold dimer behaves similarly, though the relativistic effect now accounts for a roughly 60% contraction, an order of magnitude greater than that for the copper dimer. The relativistic and nonrelativistic results are 81.9 and 136.3 au,[21] which is reflected in the SBK and Sadlej calculations of 86.7 and 135.7 au, respectively. This good agreement in the dimer calculations was found with no augmentation of the SBK basis set. These results are found in Table 5.

Additionally, we have used the Sadlej basis set at the relativistic all-electron Hartree−Fock level of theory. The nonrelativistic polarizabilities for the Cu_2, Ag_2, and Au_2 molecules decreased according to the percentages noted above, in much better agreement with the SBK ECP nonrelativistic theory. It should be noted that to complete the all-electron relativistic calculations required hundreds of times longer for each dimer.

Finally, to allow for a direct comparison to the previous work, the polarizability of the dimers using the SBK basis set has also been calculated at the geometries reported by Saue and Jensen. The ECP calculations of the copper, silver, and gold dimers differ from their relativistic all-electron calculations by 1.3, 1.9, and 0.2 au, respectively.

Analogous ECP and all-electron calculations were completed for larger systems, up to six atoms for all of the metals except gold. The tetramers and hexamers behave similarly to the dimers in that the relativistic effects still account for a comparable contraction percentage. To demonstrate the usefulness of the SBK ECPs, we have without too much difficulty completed a finite field calculation on the 32 atom gold cluster reported by Wilson and Johnston.[22] $\bar{\alpha}$ is calculated to be 1106 au for the cluster, or 34.6 au per gold atom.

Computational Timing

The ECPs have the obvious advantage over the nonrelativistic all-electron calculations presented here of accounting for the relativistic contraction of electron density around high *Z* nuclei. For the metal surfaces especially, these empirically included effects are the difference between quantitatively accurate calculations and results that are, at best, semiqualitative. Two more advantages are the smaller number of electrons explicitly modeled and the smaller basis sets used. This results in substantial, though widely varying, time savings depending on the composition of the molecule. For the $M(CO)_6$ systems, the 12 second row atoms have only two electrons removed. Systems containing only second row atoms (and hydrogen) benefit the least from an ECP basis set, and require only about 3 times

TABLE 5: Molecular α Polarizabilities (au) as Calculated in GAMESS, or by the Relativistic Hartree−Fock Module of DIRAC, Indicated by the DIRAC Superscript[a]

molecule	static polarizability						
	SBK	SBK (+spd)	Sadlej(ECP)	Sadlej	Sadlej$^{\mathrm{DIRAC}}$	SBK[b]	Saue$^{\mathrm{DIRAC}}$
Cu_2	96.51	99.10	99.02	103.01	96.95	94.53	95.8
Cu_4	180.20	188.15	192.22	198.41			
Cu_6	248.76	253.57	258.34	266.65			
Ag_2	118.75	127.57	121.81	140.92	119.97	114.75	116.7
Ag_4	226.13	246.97	245.02	244.99			
Ag_6	322.04	336.37	333.81	374.48			
Au_2	86.72	89.36	86.38	135.66	84.84	82.04	81.9
Au_4	178.30	184.74	182.79	268.72			
AgAu	94.78	98.66	93.56	138.08			
	% difference						
Cu_2	−0.7	2.0	1.9	6.0		−1.3	
Ag_2	−1.0	6.3	1.5	17.5		−1.7	
Au_2	2.2	5.3	1.8	59.9		0.2	

[a] B3LYP/SBK geometries were used for calculations unless otherwise noted in the text. The percent difference is with respect to the relativistic all-electron Sadlej calculations. [b] Additionally, the metal dimers were recomputed with the SBK basis set at the geometries reported by Saue and Jensen,[21] 2.22, 2.53, and 2.472 Å for Cu_2, Ag_2, and Au_2, respectively. Calculated values are compared to their literature results (Saue) by percent difference.

longer for the all electron polarizability calculations with a Sadlej basis set instead of the LFK basis and SBK ECP. Including the lighter metal centers increases the difference to a factor of 6, and to around 15 (13 h verses 205 h) when the tungsten center is modeled, a 94% reduction in time. When a larger percentage of the molecule contains heavier atoms, the time savings benefits increase dramatically. For example, the (Cu, Ag, Au)Br series contains only atoms from the fourth period or higher. Copper has 10 electrons removed, the fewest of the atoms in this series. The time difference is now a factor of 140, 320, and 1150 (a greater than 99.9% reduction in computational time and effort), respectively.

Summary and Conclusions

The performance of the SBK/LFK basis set when used on the small and medium sized systems above is encouraging, as larger systems should perform at least as well. Due to the additive nature of basis functions in a molecular system, any deficiencies should be noticed in the dimers. However, the differences seen between all-electron calculations and the LFK calculations are explained by the lack of relativistic effects present in the all-electron case, not basis set deficiencies. While an increasing difference was found between the more costly all-electron results and the ECP, the error lies in the missing relativistic correction in the all-electron calculations. When the ECP is used with the Sadlej basis set, the results are nearly identical to the LFK/SBK values. This indicates that the reduced basis set describes the functional space necessary for electric and linear optic valence properties nearly as well as the Sadlej basis set, though more efficiently, and is more accurate when a nonrelativistic wave function is used due to the ECPs. This was confirmed when relativistic all-electron calculations with the Sadlej basis set were found to be in excellent agreement with the SBK results, not the nonrelativistic all-electron results. Augmenting functions are crucial on main group atoms, while the transition metals are adequately described with no further basis functions. Indeed, additional functions are not recommended on the metals due to minimal or no improvement of results coupled with greatly increased computational cost for even one *f* function. The description of the *s*, *p*, and *d* functional space is complete enough for quite accurate dipole and polarizability calculations.

Isotropic and tensor components of the polarizability of a broad range of molecules varying in size, geometry, atomic composition, and charge distribution have been determined and reported using both the SBK ECP and all-electron basis sets. Smaller systems such as the metal hydrides have been reported before and can be studied by very large basis sets and all-electron methods, providing a good test for the SBK ECPs and LFK basis set. In the AuH system, the ECP calculation (20 electrons, 43 basis functions) tensor components were ordered differently from the all-electron Sadlej calculation (80 electrons, 137 basis functions), though in agreement with the relativistic all-electron Dyall calculation (80 electrons, 312 basis functions) and the relativistic calculation completed using the Sadlej basis set. This is due to the contracted valence in the ECP model, which mimics the relativistic calculations in the Dyall study. Thus, when the components (α_{xx}, α_{yy}, and α_{zz}) are tightly grouped in a nonspherical system, relativity is important for a correct ordering of the values. Atoms with a high *Z* trend toward a larger difference in the ECP and nonrelativistic all-electron results. Numerically, this difference was found to be small for all of the metals studied in this work, except Au and Hg, and good results are found for the 5d metals by either method. However, as in the case of the silicon dioxide materials, if the polarizability of several systems is quite close, the ordering and trends within a group are questionable when relativity is not accounted for. Relativity affects even a qualitative description on these metals.

The metallocenes ($MC_{10}H_{10}$, M = Fe, Ru, Os), the drug cisplatin ($PtCl_2(NH_3)_2$), dielectric materials $M(OSiH_3)_4$ (M = Ti, Zr, Hf), the catalyst $NbCl_5$, and the inorganics $M(CO)_6$ (M = Cr, Mo, W) were among the largest systems tested, and all of the systems were found to be in good agreement with the all-electron basis sets. The best agreement is found between the all-electron calculations and SBK calculations with the 3d metal of a given group, as the relativistic effects are least important. Intuitively, the calculations should be in closest agreement when dealing with the lightest elements, as the relativistic effects only become important in heavier nuclei. The nonrelativistic calculations return reasonable agreement on the 4d systems, though there is no advantage to using the all-electron basis sets on the metals, as they are more difficult and costly to calculate, and less accurate than the ECP. The 5d clusters differ by 2−5% through Pt, and considerably more, 10−20%, on the Au and Hg molecules.

Small coinage metal clusters of two, four, and six atoms were examined. In the purely metallic systems, augmenting the basis affects the polarizability more so than in the molecules with a single metal. However, additional functions are computationally expensive and rarely improve the results enough to warrant inclusion of the additional functions, at least when correlation is neglected. The addition of diffuse *sp*, *d*, and *f* functions changes the calculated values by 2−6% at the HF level of theory, actually widening the difference between the SBK and relativistic all-electron calculations. This suggests that while the SBK basis set may not be a converged basis, it offers a good fit when utilizing an ECP approximation. Additional functions may prove to be important for either higher order calculations (correlated) or properties (hyperpolarizabilities). Furthermore, the contribution to the polarizability due to a relativistic contraction is found to be more pronounced when the metal is removed from the largely electron withdrawing main group atoms. Thus, when metal surfaces are modeled with nonrelativistic theory, inclusion of relativistic effects through the use of ECPs becomes necessary even for the lightest transition elements. The ECP calculated polarizability of the copper, silver, and gold dimers is found to be in good agreement with the relativistic all-electron calculations of Saue,[21] while the Sadlej calculations presented in this work are in line with their nonrelativistic calculations. Ignoring relativity causes an increase in the polarizability by ≈ 6%, 16%, and 60% for the dimers, respectively, and can be included either through very costly all-electron methods or approximately with the ECPs, and then treated with nonrelativistic theory. The ECPs are not only critical to accuracy at nonrelativistic treatments but orders of magnitude faster than all-electron calculations.

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