

# Basis Sets for Transition Metals: Optimized Outer $p$ Functions

MARC COUTY and MICHAEL B. HALL

*Department of Chemistry, Texas A & M University, College Station, Texas 77843-3255*

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## ABSTRACT

Although the  $(n + 1)p$  orbital is unoccupied in transition-metal ground-state configurations which are all  $nd^x(n + 1)s^y$ , these  $(n + 1)p$  functions play a crucial role in the structure of transition metal complexes. As we show here, the usual solution, adding one or more diffuse functions, can be insufficient to create an orbital of the correct energy. The major problem appears to be due to the incorrect placement of the  $(n + 1)p$  orbital's node. Even splitting the most diffuse component of the  $np$  orbital and adding a second diffuse function does not completely solve this problem. Although one can usually solve this deficiency by further uncontracting of the  $np$  function, here we offer a set of properly optimized  $(n + 1)p$  functions that offer a more compact and satisfactory solution to the proper placements of the node. We show an example of the common deficiencies seen in typical basis sets, including standard basis sets in GAUSSIAN94, and show that the new optimized  $(n + 1)p$  function performs well compared to a fully uncontracted basis set. © 1996 by John Wiley & Sons, Inc.

## Introduction

Over the last few years, the effective core potential (ECP) approximation has been widely used in quantum chemistry. Chemically inactive, core electrons are replaced by an effective potential that reproduces their potential on the chemically active valence electrons. The derivation of the ECPs and the associated basis sets of Gaussian-type orbitals (GTO) is usually performed by fitting the effective potential to accurate numerical relativistic Hartree–Fock or Dirac–Fock results. The use of ECP has the advantage, over all-electron

calculations, of reducing the cost of the calculation by limiting it to the valence electrons and of including atomic relativistic effects which are important to the correct state ordering and the orbital description. Their reliability has increased over the years and the latest averaged relativistic ECPs give results comparable to all-electron calculations. Users typically increase the quality of the basis sets for molecular calculations by splitting-off the outer (most diffuse) exponents (i.e., uncontracting the orbital).

Because the transition metal atoms have a large spatial overlap between the occupied  $ns$ ,  $np$  subshell and the partially occupied  $nd$  subshell, treating the  $ns$  and  $np$  electrons as part of the ECP

gives metal ligand bond distances which are too short. Thus,  $ns$  and  $np$  electrons are usually treated as valence electrons, a treatment which also enhances the transferability of the potentials to various atomic configurations. Several investigators have developed ECPs with different fits and different goals.<sup>1-4</sup> Indeed, the most recent ECPs derived by Stevens et al. are oriented toward computer efficiency. Compactness of the ECP form and the use of a  $sp$  shell contraction of the double- $\zeta$  quality basis sets simplify the standard *ab initio* techniques for geometry optimization and two electron integrals calculation. Other investigators, more concerned with the accuracy of the effective potential, derived ECPs using a larger number of fitting functions (six to seven), while giving the opportunity for the user to choose the contraction level of the basis set associated with the ECP. In this case, the user uncontracts the atomic basis set by splitting-off the outermost or the two outermost exponents from the atomic orbitals calculated for the group state of the atom to form a double- $\zeta$  or triple- $\zeta$  basis set.

In most main group atoms, there is only one low lying configuration and all the lower excited states arise from this one. Peculiar to transition metal atoms are ground state and the lower excited states, which have different configurations where the  $s$  orbital in the  $(n + 1)$  shell exhibits variable occupations:

$$ns^2 np^6 nd^x (n + 1)s^y (n + 1)p^0$$

where  $x$  and  $y$  specifies the electron distribution among these configurations. A Hartree-Fock calculation for such a state of a transition metal atom would yield  $ns$ ,  $np$ ,  $nd$ , and  $(n + 1)s$  orbitals in the optimized basis set. A natural way to form the split valence basis set is then to uncontract the most diffuse GTO to allow the atomic orbital to adapt to the molecular environment. To describe the different orbital shapes associated with a different  $d$  orbital occupancies, a triple- $\zeta$   $d$  basis set is often required. In molecular calculations, the atomic levels are rearranged by the ligand field; in particular, the  $(n + 1)p$  orbital may begin to play an important role. Since this orbital is unoccupied in the ground and lower excited states of the free atom, and thus not optimized in the development of the GTO basis, the common technique is to add one or more  $p$  GTO functions whose exponents are related to the most diffuse  $s$  or  $d$  GTO ones. These functions are left uncontracted so that, during the optimization process, orbitals have the opportunity to develop the correct  $(n + 1)p$  character. It

has been reported recently that this procedure, while increasing drastically the number of GTO functions, failed to describe properly the bonding in  $MH_2$  ( $M = \text{Pt, Os, Ir, and Re}$ ).<sup>5</sup> The correct  $s$ - $p$  hybridization was made possible by including a proper description of the contracted part of the  $(n + 1)p$  orbital, where the outermost  $p$  functions left uncontracted in order to keep the flexibility for molecular calculations.

In this work we will develop optimal  $(n + 1)p$  functions for all the transition metals. As an example, the concepts will be developed with the Christiansen et al. set of ECPs, but our method could be applied to develop  $(n + 1)p$  orbitals for other types of ECPs. In the next section, the theoretical procedure to optimize the orbitals will be described. The optimization process will be applied to the transition metals atoms in the subsequent section, and finally, an example of the reliability of the derived contractions will be illustrated on the relative stability of two isomers of the  $\text{IrBe}_2\text{H}_5$  molecule, in which proper  $6s$ - $6p$ - $5d$  hybridization plays an important role.

## Theory

The concept of split-valence basis sets is based on the transferability of nondiffuse (contracted) part of an atomic orbital from the atom to the molecule. A more general concept of orbital transferability from fragments to the whole system has been the object of a previous study by one of the authors.<sup>6</sup> In this view, a split-valence basis set optimized from atomic calculations is the simplest transferable basis set one can generate. As reported previously, the best transferability can be obtained only for the valence part of the orbitals. A necessary condition to achieve this transferability is to perform a calculation of the fragment, taking into account the effects of the outermost GTOs or, more generally, GTOs that play a different role in the fragment and the molecule. Transposed to transition metals, the previous criteria are realized by including in the calculation of the molecule, the  $(n + 1)p$  orbital of the atom with a split valence treatment of all the orbitals. This orbital plays a different role in the fragment, restricted in that case to the metal, and the molecule. The  $ns$ ,  $np$ ,  $nd$ , and  $(n + 1)s$  orbitals are extracted from the ground state of the atom, while the  $(n + 1)p$  orbital is extracted from a low-lying excited state in which the orbital is occupied. The set  $\{ns, np, nd, (n + 1)s \text{ and } (n + 1)p\}$  defines then the orbitals

involved in the valence state of the fragment. As noted in the previous study, the calculation on the fragment has to be performed on a valence state (in contrast to a spectroscopic state). This valence state has to describe the atom in the molecule, thus it should not be a Rydberg state. The description of the  $(n+1)p$  orbital for the  $d^{x+1}s^0p^1$  Rydberg configurations requires extra very diffuse functions. It has to be noted that these Rydberg states may be lower in energy than the  $d^x s^1 p^1$  valence configurations and may have a very important chemical influence, for example, in long range interactions, dissociation into atomic spectroscopic states and reactions involving a low coordination of the metal, but cannot be considered as valence states. Thus, we have chosen to optimize the atomic orbitals in the lowest energy state of the  $d^x s^1 p^1$  configurations. (Note: For Zn, Cd, and Hg the electronic configuration  $d^{10} s^1 p^1$  creates two spectroscopic states  $^3P$  and  $^1P$  relatively close in energy. However, the  $^1P$  state is considered a Rydberg state and requires diffuse functions.)

The Hamiltonian of the system can be written as:

$$H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z_{eff}}{r_i} + \sum_{i < j} \frac{1}{r_{ij}} + V(ECP)$$

where  $Z_{eff} = Z - Z_{core}$ ,  $Z_{core}$  being the number of electrons included in the ECP.  $V(ECP)$  stands for the effective potential of the core electrons, described as an operator. The problem is then to optimize orbitals for a given electron configuration and a given spin within a LCAO formalism in a given basis set. Orbitals were optimized with a quadratic convergence multiconfiguration SCF formalism (calculations performed with a quadratic convergent MCSCF code developed in the group). We use Levy's proposal<sup>7</sup> to develop the orbitals at the iteration  $(k+1)$  in the basis of the orbitals at the iteration  $(k)$  using a unitary transformation expressed as the exponential of a skew-symmetric matrix:

$$\varphi^{(k+1)} \exp(\mathbf{X}) \varphi^{(k)}$$

where  ${}^tX = -X$ . The orbital variables are the elements of the matrix  $\mathbf{X}$ . The energy is then developed in a second-order Taylor expansion of the variables  $x_1 = X_{ij}$  at the point  $\mathbf{x} = 0$ ;

$$E(\mathbf{x}) = E(0) + \mathbf{g} \cdot \mathbf{x} + 1/2 \mathbf{x} \cdot \mathbf{H} \cdot \mathbf{x}$$

where  $E(0)$  is the energy at the iteration  $(k)$  ( $E^{(k)}$ ),  $\mathbf{g}$  and  $\mathbf{H}$  are the gradient and Hessian matrix accord-

ing to the variable orbitals  $\mathbf{x}$ , respectively. Though the CI coefficients are variationally calculated, they have not been included in the optimization procedure. To obtain spherical atoms (5 equivalent  $d$  orbitals and 3 equivalent  $p$  orbitals) the following process has been used: Equivalent guess components were generated for the occupied and virtual orbitals. The equivalency of the components is then preserved during the iterations by allowing only equivalent rotations. The gradient and Hessian matrix are fully calculated; The elements of the gradient and Hessian matrix are then averaged for the equivalent orbital's pairs, reduced to eliminate the intrinsic zero eigenvalues of the Hessian matrix introduced by the averaging technique. Then, the Newton-Raphson equation  $\mathbf{H}\mathbf{x} + \mathbf{g} = 0$  is solved by standard inversion. The process is repeated until the maximum value of the gradient and  $\mathbf{x}$  is lower than  $10^{-6}$ .

The  $(n+1)p$  orbitals are optimized in the lowest energy state of the  $ns^2 np^6 nd^x (n+1)s^1 (n+1)p^1$  configuration orbitals using the fully uncontracted basis set associated with the ECP augmented, if necessary, by diffuse functions  $p$ : For the first row transition metals, the ECP derived by Hurley et al.<sup>1b</sup> were used. To develop the  $(n+1)p$  orbital, the basis sets were augmented with three GTOs created using an even-tempered progression (factor 2.55). The exponent values and the coefficients of the  $4p$  orbital are given in Table Ia. Calculations for the second row transition metals are performed using LaJohn et al.<sup>1c</sup> ECPs. The published basis sets have appropriate exponents to describe the  $(n+1)p$  orbitals. The  $5p$  orbital development in the uncontracted basis set and the exponents of the Gaussian function are reported in Table Ib (see footnote \*). The third row transition metals (ECPs) of Ross et al.<sup>1d</sup> were used to optimize the  $6p$  orbital (see footnote †). The basis sets

\* For Cd and Hg, an extra diffuse  $p$  function was added (exponent = 0.0135 and 0.071, respectively) to prove that the  $^3P$  state is not a Rydberg state.

† W.C. Ermler derived new basis sets exponents, for the  $s$  shells of Ta with six Gaussian functions to resemble the Hf and W published basis sets:

Exponents	Atomic orbitals	
	5s	6s
5.06046	0.609843	-0.194143
3.83136	-1.197724	0.406478
1.08904	0.864166	-0.400558
0.46227	0.538270	-0.356940
0.10385	0.002988	0.665454
0.03872	0.001489	0.548641

TABLE Ia.

Exponents and Coefficients of Development of  $(n + 1)p$  Orbital in Ground State of Electronic Configuration  $nd^x(n + 1)s^1(n + 1)p^1$  for First Row Transition Metals ( $n = 3$ ).

Element	Exponent	Coefficient	Element	Exponent	Coefficient
Sc	32.59	0.00198950	Fe	49.12	0.00201358
	13.22	0.00083914		20.50	0.00184532
	5.584	0.01460309		8.987	0.01400458
	2.186	-0.06319651		3.682	-0.07291822
	0.895	-0.16668364		1.522	-0.14481698
	0.352	-0.10470420		0.5927	-0.06269800
	0.1413	0.24764363		0.23081	0.23172233
	0.05667	0.62676540		0.08988	0.55944226
	0.02275	0.27457711		0.03500	0.35518791
Ti	36.37	0.00173575	Co	49.24	0.00198711
	14.78	0.00185815		20.75	0.00270811
	6.275	0.01476379		9.204	0.01175420
	2.479	-0.06662133		3.818	-0.07733078
	1.016	-0.16494878		1.588	-0.12635151
	0.3982	-0.09235636		0.6247	-0.05080611
	0.15607	0.26181982		0.2457	0.21397323
	0.06117	0.62445908		0.09666	0.52319657
	0.02397	0.26290395		0.03802	0.40531956
V	40.32	0.00231251	Ni	53.17	0.00260840
	16.46	-0.00051929		22.39	-0.00002241
	7.024	0.01564544		9.928	0.01211312
	2.790	-0.06527517		4.116	-0.07553089
	1.146	-0.16085162		1.710	-0.11958931
	0.4473	-0.08613413		0.6725	-0.05131346
	0.1746	0.24556289		0.26448	0.19960016
	0.06814	0.60777609		0.10401	0.50120903
	0.02660	0.29504409		0.04090	0.44065600
Cr	43.20	0.00231267	Cu	60.48	0.00228314
	17.78	0.00040250		25.36	0.00050299
	7.661	0.01566340		11.17	0.01147294
	3.077	-0.07232577		4.564	-0.07119115
	1.266	-0.15995210		1.884	-0.11744700
	0.4935	-0.07602042		0.7347	-0.04927176
	0.19237	0.24026686		0.28651	0.19234475
	0.07500	0.59062784		0.11173	0.49068516
	0.02923	0.31541866		0.04357	0.45800813
Mn	44.61	0.00212790	Zn ( <sup>3</sup> P)	66.08	0.00190161
	18.60	0.00113675		27.69	0.00090571
	8.138	0.01404416		12.18	0.00997383
	3.337	-0.07041591		4.988	-0.06257618
	1.379	-0.14187077		2.058	-0.10223614
	0.5386	-0.06772704		0.7986	-0.05100202
	0.2104	0.22011125		0.30989	0.15963988
	0.08216	0.56095926		0.12025	0.44116122
	0.03209	0.36436772		0.04666	0.53500940

**TABLE Ib.**  
**Exponents and Coefficients of Development of  $(n + 1)p$  Orbital in Ground State of Electronic Configuration  $nd^x(n + 1)s^1(n + 1)p^1$  for Second Row Transition Metals ( $n = 4$ ).**

Element	Exponent	Coefficient	Element	Exponent	Coefficient
Y	3.5640	0.029461	Ru	4.944	0.036040
	0.7957	-0.239632		1.306	-0.262122
	0.3022	-0.111670		0.4891	-0.033519
	0.06290	0.769803		0.0830	0.832449
	0.02230	0.333942		0.0250	0.247314
Zr	3.506	0.032636	Rh	5.235	0.036824
	0.9009	-0.253701		1.488	-0.224651
	0.3346	-0.102243		0.5655	-0.056510
	0.0724	0.764223		0.0869	0.794897
	0.0243	0.346052		0.0257	0.298912
Nb	3.986	0.035682	Pd	5.085	0.035127
	1.013	-0.259352		1.560	-0.232909
	0.3801	-0.086506		0.5804	-0.036720
	0.0752	0.788161		0.0899	0.799843
	0.0247	0.310911		0.0262	0.290295
Mo	4.483	0.035385	Ag	5.594	0.032186
	1.095	-0.261476		1.683	-0.208618
	0.4120	-0.063661		0.6177	-0.026568
	0.0780	0.798627		0.0833	0.814438
	0.0247	0.294992		0.0252	0.262809
Tc	4.321	0.034943	Cd ( <sup>3</sup> P)	6.085	0.030297
	1.229	-0.238312		1.854	-0.175207
	0.4700	-0.081588		0.7771	-0.080250
	0.0895	0.757556		0.1287	0.534645
	0.0246	0.368233		0.0405	0.560282
				0.0135	0.028122

were augmented with a diffuse GTO whose exponent is taken from the basis set given for the ECP including the  $ns$  and  $np$  orbitals in the core (two in the case of the platinum atom). The exponents and coefficients of the  $6p$  orbital are reported in Table Ic. The total energies for the lowest spectroscopic states of the  $nd^x(n + 1)s^2$ ,  $nd^{x+1}(n + 1)s^1$ , and  $nd^x(n + 1)s^1(n + 1)p^1$  configurations are reported in Table II. These energies are obtained for spherical atoms by equivalence of the orbitals within the subshells  $p$  and  $d$  and therefore may be used to calculate true dissociation energies when one fragment is reduced to the transition metal.

#### APPLICATION TO RELATIVE STABILITY OF TWO ISOMERS OF $\text{IrBe}_2\text{H}_5$ SYSTEM

A previous study<sup>8</sup> of the relative stability of classical versus nonclassical isomers of the  $\text{IrBe}_2\text{H}_5$  system showed that electron correlation was a key factor: at the Hartree-Fock (HF) level the two isomers are isoenergetic, while the classical iso-

mer is more stable than the nonclassical one by  $-14$  to  $-16$  kcal/mol including electron correlation using both perturbation theory and variational methods. To study the effect of transition metal basis set contractions, the geometries of the two isomers were optimized at the Hartree-Fock level, using an uncontracted basis set for the Ir atom, a minimal (73) basis set for Be,<sup>9</sup> and a triple- $\zeta$  (311) basis set for the hydrogen atom.<sup>10</sup> The ECP and the associated basis set was taken from Ref. 1. An extra  $p$  Gaussian function (exponent = 0.0464) was added to the basis set to represent the  $6p$  orbital of Ir if needed in the molecular calculation leading to an uncontracted ( $5s6p4d$ ) basis set. All calculations were performed using GAMESS-UK<sup>11</sup> with six components of the  $d$  Gaussian orbitals. While the geometry is slightly changed from that reported previously (see Fig. 1) a more important difference is that, even at the HF level, the classical isomer is more stable than the nonclassical isomer by  $-7.0$  kcal/mol (see Table III).

TABLE Ic.

Exponents and Coefficients of Development of the  $(n + 1)p$  Orbital in Ground State of Electronic Configuration  $nd^x(n + 1)s^1(n + 1)p^1$  for Third Row Transition Metals ( $n = 5$ ).

Element	Exponent	Coefficient	Element	Exponent	Coefficient
La	1.5660	0.073936	Os	3.9040	0.071053
	0.5698	-0.295846		1.4683	-0.207748
	0.2199	-0.100628		0.6801	-0.222828
	0.0403	0.919634		0.3074	0.104273
	0.0179	0.136213		0.1063	0.600623
Hf			Ir	0.0407	0.447455
	2.6086	0.104586		2.8117	0.512240
	1.5141	-0.169099		2.4614	-0.574894
	0.6290	-0.237047		0.8901	-0.217906
	0.2784	-0.049974		0.3920	-0.042016
Ta	0.09998	0.550176	Pt	0.1447	0.495575
	0.03701	0.573765		0.0464	0.638929
	2.6352	0.179882		3.3722	0.191558
	1.8751	-0.234346		2.5328	-0.208271
	0.7722	-0.162605		1.2740	-0.182120
W	0.3749	-0.229161	Au	0.6238	-0.126315
	0.1585	0.485376		0.2210	0.163353
	0.0433	0.740610		0.0966	0.657745
				0.0288	0.343058
				3.5306	0.216777
Re	3.0085	0.107347	Hg ( <sup>3</sup> P)	2.6122	-0.281637
	1.7265	-0.158977		0.9813	-0.201024
	0.7364	-0.287295		0.4266	-0.068572
	0.3189	0.064361		0.1475	0.668176
	0.09046	0.555726		0.0318	0.541434
	0.0441	0.480606		3.7197	0.147635
	3.1417	0.173441		2.4806	-0.210679
	1.9360	-0.224107		1.0219	-0.176050
	0.8283	-0.264657		0.4514	-0.028238
	0.3795	-0.099560		0.1558	0.427891
	0.1476	0.638254		0.0512	0.625399
	0.0460	0.544649		0.0171	0.093931

Using this optimized geometry, a HF calculation was performed using the previous ECP and basis set fully uncontracted ( $5s5p3d$ ) from Ref. 2c. The isomerization energy is then equal to  $-9.1$  kcal/mol. The ECP from Ref. 1 is built with six or seven functions, whereas the ECP from Ref. 2c with five or six functions. This factor, and the difference in size of the associated basis sets, is the origin of this 2-kcal/mol difference. Augmenting the basis set from Ref. 2c with an extra  $d$  function (exponent = 0.07) reduces the difference by 1 kcal/mol to  $-8.0$  kcal/mol (see Table III). Thus, the difference between these new results and the previously published ones is due to a difference in the basis set contraction.

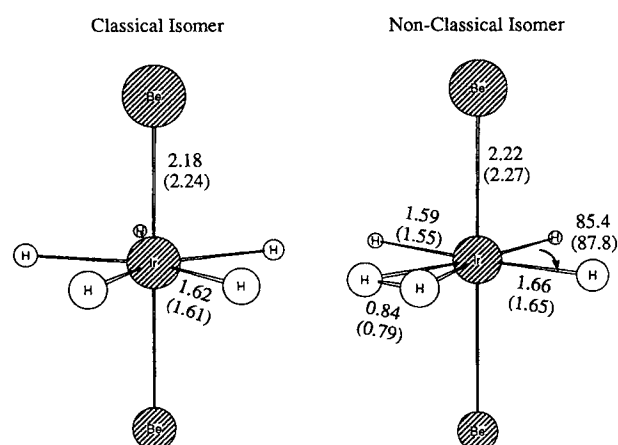
The standard contraction (541/41/211) of the Hay and Wadt basis set was used in the previous

HF calculation. In a similar contraction of the Ermler basis set (541/51/211), the  $5s$  and  $5p$  are fully contracted, the  $6s$  and  $5d$  are split to evolve with the molecular environment, while the  $6p$  character can only be described by the added diffuse GTO. In this calculation, the basis set contraction error is even larger than in the previous publication and results in a nonclassical isomer which is more stable by 5.9 kcal/mol rather than the previous 4.4 kcal/mol (see Table III).

In order to prove that the  $5s$  and  $5p$  orbitals do not have any effect in the relative stability of the two isomers, a HF calculation was performed in the uncontracted basis set while freezing the four occupied " $5s$ " and " $5p$ " molecular orbitals at their atomic expression (calculations performed with a quadratic convergent MCSCF code developed in

**TABLE II.**  
**Total Hartree-Fock Energies (a.u.) for Lowest Spectroscopic States of Different Electronic Configurations**  
**Using ECP and Basis Sets From Ref 1.**

	$nd^x(n+1)s^2$	$nd^{x+1}(n+1)s^1$	$nd^x(n+1)s^1(n+1)p^1$
Sc	$^2D - 46.05502$	$^4F - 46.00967$	$^4F - 46.01877$
Ti	$^3F - 57.49290$	$^5F - 57.46444$	$^5G - 57.45847$
V	$^4F - 70.54456$ $^4P - 70.48033$	$^6D - 70.53504$	$^6G - 70.50890$
Cr	$^5D - 85.93068$	$^7S - 85.97697$ $^5S - 85.93456$	$^7F - 85.89485$
Mn	$^6S - 103.25381$	$^6D - 103.12318$	$^8P - 103.21400$
Fe	$^5D - 122.60350$	$^5F - 122.52609$	$^7D - 122.56150$ $^7F - 122.54736$
Co	$^4F - 144.97370$ $^4P - 144.89054$	$^4F - 144.89928$	$^6F - 144.91540$ $^6D - 144.90941$
Ni	$^3F - 168.59031$	$^3D - 168.52995$	$^5D - 168.51733$ $^5G - 168.51334$
Cu	$^2D - 195.44613$	$^2S - 195.44425$	$^4P - 195.36526$ $^4F - 195.35182$
Zn	$^1S - 225.11851$		$^3P - 225.01468$
Y	$^2D - 37.72720$	$^4F - 37.69788$	$^4F - 37.69882$
Zr	$^3F - 46.31071$	$^5F - 46.30884$	$^5G - 46.28590$
Nb	$^4F - 56.11246$ $^4P - 56.06534$	$^6D - 56.14351$ $^4D - 56.08717$	$^6G - 56.08866$
Mo	$^5D - 67.23137$	$^7S - 67.32209$ $^5S - 67.26068$ $^5G - 67.21685$	$^7F - 67.20762$
Tc	$^6S - 79.77903$	$^6D - 79.74821$ $^4D - 79.69712$	$^8P - 79.75201$
Ru	$^5D - 93.65454$	$^5F - 93.68353$ $^3F - 93.64500$ $^5P - 93.62836$	$^7D - 93.62488$
Rh	$^4F - 109.18030$	$^4F - 109.23176$ $^2F - 109.20382$ $^4P - 109.17284$ $^2D - 109.17145$	$^6F - 109.12680$
Pd	$^3F - 126.29675$ $^3P - 126.23057$	$^3D - 126.37517$ $^1D - 126.35709$	$^5D - 126.23167$
Ag	$^2D - 145.14762$	$^2S - 145.29392$	$^4F - 145.06372$
Cd	$^1S - 165.92757$		$^3P - 165.84223$
La	$^2D - 31.01278$	$^4F - 31.02337$ $^2D - 31.02142$ $^4P - 30.99469$	$^4F - 30.98798$ $^4D - 30.98373$
Hf	$^3F - 48.16392$ $^1D - 48.13152$ $^3P - 48.12578$	$^5F - 48.12705$	$^5G - 48.13114$
Ta	$^4F - 57.04977$ $^4P - 57.00690$ $^2G - 57.00489$	$^6D - 57.03791$	$^6G - 57.01672$
W	$^5D - 66.92753$ $^3H - 66.86548$	$^7S - 66.97677$	$^7F - 66.89537$
Re	$^6S - 78.10339$ $^4G - 78.00318$ $^4P - 77.98680$	$^6D - 78.03360$	$^8P - 78.06756$
Os	$^5D - 90.32324$ $^3H - 90.25361$	$^5F - 90.29943$ $^3F - 90.23548$	$^7F - 90.28259$ $^7D - 90.26035$
Ir	$^4F - 103.87319$ $^4P - 103.81729$ $^2G - 103.81371$	$^4F - 103.86626$ $^2F - 103.81930$ $^4P - 103.81336$	$^6F - 103.79958$
Pt	$^3F - 118.71506$	$^3D - 118.72909$	$^5D - 118.62484$
Au	$^2D - 134.94053$	$^2S - 135.01004$	$^4F - 134.82127$
Hg	$^1S - 152.29880$		$^3P - 152.16413$



**FIGURE 1.** Geometries of HF optimized classical and nonclassical isomers of  $\text{IrBe}_2\text{H}_5$ . The numbers in parentheses are from ref. 8.

the group). The total HF energy is only higher by 1.7 and 1.5 kcal/mol compared to the unconstrained HF energy, for the two isomers. Thus, the relative energy of the classical and nonclassical isomers of  $\text{IrBe}_2\text{H}_5$  at the HF level involves only the valence electrons and their orbital representation.

The  $s$  and  $d$  contraction quality can be estimated by performing a HF calculation contracting the  $s$  and  $d$  functions while totally uncontracting  $p$  functions. Here, the total energy is higher than the fully uncontracted basis set's HF energy for the classical and nonclassical isomers by 2.4 kcal/mol and 2.2 kcal/mol respectively (see Table IV). The relative energy difference between the isomers is then reduced from  $-7.0$  to  $-6.8$  kcal/mol. (0.2 kcal/mol is considered to be an acceptable error

**TABLE III.** Total Hartree-Fock Energies and Relative Energy ( $E_{\text{nonclassical}} - E_{\text{classical}}$ ) for the Classical and Nonclassical Isomers of  $\text{IrBe}_2\text{H}_5$  in Different Basis Sets.<sup>a</sup>

	Total HF energy		Relative difference (kcal/mol)
	classical (a.u.)	nonclassical (a.u.)	
Ref. 1 (5s6p4d) uncontracted	-135.86922	-135.85799	-7.0
Ref. 2c (5s5p3d) uncontracted	-135.79993	-135.78541	-9.1
Ref. 2c (5s5p4d) uncontracted	-135.80319	-135.79036	-8.0
Ref. 1 (5s6p4d) uncontracted with 5s and 5p frozen	-135.86639(1.7)	-135.85566(1.5)	-6.8
Ref. 1 (541, 51, 211)	-135.78687(51.6)	-135.79621(38.8)	+5.9
Ref. 2c (541, 41, 211)	-135.72259(50.6)	-135.72955(38.2)	+4.4
Ref. 2 (541/521/211) <sup>b</sup>	-135.77290(19.0)	-135.76824(13.9)	-2.9

<sup>a</sup> The numbers in parentheses is equal equal to difference of the total HF energies between the fully uncontracted basis set and the current one (kcal/mol).

<sup>b</sup> Calculations performed with quadratic convergent MCSCF code developed in the group.

**TABLE IV.** Total Hartree-Fock Energies and Relative Energy for the Classical and Nonclassical Isomers of  $\text{IrBe}_2\text{H}_5$  for Different Contractions of the Same Basis Set.<sup>a</sup>

	Total HF energy		Relative difference (kcal/mol)
	Classical (a.u.)	Nonclassical (a.u.)	
Ref. 1 (5s6p4d) uncontracted	-135.86922	-135.85799	-7.0
Ref. 1 (541, 111111, 211)	-135.86537 (2.4)	-135.85454 (2.2)	-6.8
Ref. 1 (541, 411, 211)	-135.85744 (7.4)	-135.84797 (6.3)	-6.0
Ref. 1 (541, 66, 211)	-135.85104	-135.84455	-4.0
Ref. 1 (541, 651, 211)	-135.86473 (2.8)	-135.85323 (3.0)	-7.2

<sup>a</sup> The numbers in parentheses is equal to difference of the total HF energies between the fully uncontracted basis set and the current one (kcal/mol).



due to basis set contraction constraints). Thus, the isomerization energy at the HF level is extremely sensitive in the  $p$  basis function contraction that describes valence orbitals with a  $6p$ -like character.

To better describe the  $6p$ -like character, a HF calculation is performed by splitting-off the two most diffuse GTOs of the  $5p$  orbital. In this  $p$  basis set contraction now (411), instead of the previous one (51), the relative energy value ( $-6.0$  kcal/mol) is then in good agreement with the fully uncontracted value ( $-7.0$  kcal/mol) (see Table IV). However, the difference between the total HF energy in this basis set and the total HF energy in the previous calculation (contraction of the  $s$  and  $d$  functions only) is approximately 5 kcal/mol, twice the energy constraint of contracting  $s$  and  $d$  functions.

To focus on the Ir  $6p$  effect in the molecular calculation, two HF calculations were performed: the first one uses the atomic  $6p$  function optimized in an atomic calculation of Ir  $5d^7 6s^1 6p^1$  (Table Ic) fully contracted; in the second one, the  $6p$  function is split to be reoptimized in the molecular calculation. The first calculation gives not only the correct sign for the HF relative energy but 57% of its actual value (see Table IV). The major influence on the relative stability of the isomers at the HF level is then the ability of the basis set to recreate the Ir  $6p$  function. It is expected, following the previous study on orbital transferability, that only the "valence part" of the Ir  $6p$  orbital (development of the orbital on the most contracted GTOs) may be transferable from the atom to the molecule; the most diffuse GTO governing the asymptotic behaviors of the molecular orbitals cannot be transferred from a fragment. Indeed, the double- $\zeta$  representation of the  $6p$  (split-51) allows to reproduce accurately the relative energy ( $-7.2$  kcal/mol) and the total HF energy.

Thus, at the HF level, the basis set constructed using the  $5s$  (fully contracted),  $6s$  (split-41),  $5p$  (fully contracted),  $6p$  (split-51), and  $5d$  (split-211) reproduces accurately the fully uncontracted basis set relative energy difference between the classical and nonclassical isomers of IrBe<sub>2</sub>H<sub>5</sub> and also the total HF energy. With this contraction pattern, the difference in the total HF energies due to contraction constraints is equal to 2.8 and 3.0 kcal/mol for the classical and nonclassical isomers, respectively, and is mostly arising from the  $s$  and  $d$  contractions (2.4 and 2.2 kcal/mol, respectively).

Hay and Wadt<sup>2a</sup> published a set of ECPs and basis sets in which the  $ns$  and  $np$  orbitals are included in the ECP. To generate  $p$  exponents to

be used in molecular calculations, they optimized a  $p$  basis set for the  $nd^{x+1}(n+1)p^1$  electronic configuration of the metals. The electronic states deriving from this configuration have generally more Rydberg character than states from the  $nd^x(n+1)s^1(n+1)p^1$  configuration. Thus,  $(n+1)p$  orbital optimized for the former configuration may be too diffuse compared to the  $(n+1)p$  orbital optimized for the latter valence state. The standard "LANL2DZ" basis set in Gaussian94<sup>12</sup> uses the ECPs with the  $ns$  and  $np$  treated as valence functions<sup>2c</sup> and adds the previously determined  $(n+1)p$  function.<sup>2a</sup> This basis set is then split (541/521/21) to form a double- $\zeta$  representation. Here, we augment this basis set with an additional diffuse  $d$  function ( $\alpha = 0.07$ ) so that it is closer to the basis sets used earlier. A HF calculation is then performed in this basis set and results in an isomerization energy equal to  $-2.9$  kcal/mol (see Table III). Though the  $6p$ -like character of the molecular orbitals can be described with the  $6p$  orbital optimized in a  $5d^8 6p^1$  configuration of the Ir atom, the HF calculation shows the inability of the basis set contraction to recreate the valence  $6p$  orbital. Work by Jonas et al.<sup>13</sup> also showed the necessity to use a highly uncontracted  $p$  space in order to achieve accurate energies in titanium complexes.

The previous work on orbital transferability<sup>6</sup> showed the importance of the calculation of the valence state in which transferable orbitals have to be optimized. This particular example reflects the importance of optimizing the  $6p$  orbital in a valence state (electronic configuration  $5d^7 6s^1 6p^1$ ) of the Ir atom. The valence  $6p$  orbitals optimized in the Hay and Wadt basis sets and ECPs<sup>2c</sup> are listed in Table V. HF calculation using the  $5s$  (fully contracted),  $6s$  (split-41),  $5p$  (fully contracted),  $6p$  (split-41), and  $5d$  (split-211) with the Hay and Wadt ECPs was performed on the two isomers. The isomerization energy is then equal to  $-8.1$  kcal/mol and agrees with the value obtained in the fully uncontracted basis set  $-8.0$  kcal/mol (see Table VI) and also gives a total HF energy very close to the total energy obtained in the fully uncontracted basis set.

To evaluate the influence of electron correlation on the stability of the two isomers, a Moller-Plesset second-order perturbation calculation (MP2) was performed at the HF-optimized geometry in different basis sets. The total MP2 energies and MP2 relative energies are reported in Table VII. These calculations agree qualitatively with the

TABLE V.

Exponents and Coefficients of Development of  $(n + 1)p$  Orbital in Ground State of Electronic Configuration  $nd^x(n + 1)s^1(n + 1)p^1$  for Transition Metals Using Hay and Wadt ECPs and Basis Sets.<sup>2c</sup>

Element	Exponents	Coefficients	Element	Exponents	Coefficients
Sc	10.4000	0.01108427	Zr	4.1920	0.02948950
	1.3110	-0.16590718		0.8764	-0.26300615
	0.4266	-0.05004602		0.3263	-0.09735154
	0.0470	0.96305244		0.0724	0.75115178
	0.0140	0.06500382		0.0243	0.35895744
Ti	12.5200	0.01011601	Nb	4.5190	0.02556282
	1.4910	-0.16798398		0.9406	-0.27762094
	0.4859	-0.03888326		0.3492	-0.06220852
	0.0530	0.95022331		0.0752	0.77414507
	0.0160	0.08003017		0.0247	0.32352188
V	13.7600	0.00993419	Mo	4.8950	0.02754991
	1.7120	-0.15510970		1.0440	-0.27074496
	0.5587	-0.03760528		0.3877	-0.04916928
	0.0590	0.93454572		0.0780	0.78019601
	0.0180	0.10199175		0.0247	0.31411379
Cr	16.4200	0.00946073	Tc	5.2780	0.02857053
	1.9140	-0.15308638		1.1560	-0.25518730
	0.6241	-0.03827185		0.4302	-0.06471027
	0.0630	0.92254673		0.0895	0.74588970
	0.0190	0.11805903		0.0246	0.37969416
Mn	18.2000	0.00825160	Ru	4.8590	0.02740523
	2.1410	-0.14094275		1.2190	-0.27726740
	0.7009	-0.03167127		0.4413	-0.01280913
	0.0690	0.89909425		0.0830	0.81566400
	0.0210	0.14908129		0.0250	0.26388668
Fe	19.4800	0.00895416	Rh	5.4400	0.02587041
	2.3890	-0.14499864		1.3290	-0.24940656
	0.7795	-0.02959800		0.4845	-0.02125155
	0.0740	0.91186913		0.0869	0.77650977
	0.0220	0.13193032		0.0257	0.31568208
Co	21.3900	0.00813053	Pd	5.9990	0.02670153
	2.6500	-0.12748849		1.4430	-0.24578288
	0.8619	-0.03399214		0.5264	-0.01426049
	0.0800	0.87357075		0.0899	0.78981103
	0.0230	0.18846826		0.0262	0.29844438
Ni	23.6600	0.00713147	Ag	6.5530	0.02492651
	2.8930	-0.10899095		1.5650	-0.21763196
	0.9435	-0.04615260		0.5748	-0.00996879
	0.0860	0.80255197		0.0833	0.80663588
	0.0240	0.28564511		0.0252	0.26958179
Cu	25.6300	0.00766286	La	1.5540	0.06520690
	3.1660	-0.11806908		0.5622	-0.29239827
	1.0230	-0.03073332		0.2239	-0.14890219
	0.0860	0.86983532		0.0483	0.80277856
	0.0240	0.19496824		0.0179	0.30442795
Y	3.8840	0.02507810	Hf	1.5540	0.20577326
	0.7660	-0.25481217		0.5622	-0.36650688
	0.2890	-0.10186429		0.2239	-0.17722872
	0.0629	0.75232237		0.0483	0.74080250
	0.0223	0.35147295		0.0179	0.37824300

**TABLE V.**  
(continued)

Element	Exponents	Coefficients	Element	Exponents	Coefficients
Ta	2.5650	0.09520789	Ir	2.7920	0.12041235
	1.2290	-0.28573883		1.5410	-0.32723595
	0.4244	-0.13874624		0.5285	-0.07907718
	0.0840	0.76602828		0.0980	0.76325322
	0.0280	0.34672667		0.0290	0.34770965
W	3.0050	0.07783880	Pt	2.9110	0.17029664
	1.2280	-0.28402129		1.8360	-0.35103695
	0.4415	-0.11614801		0.5982	-0.10107358
	0.0900	0.76459312		0.0996	0.78032917
	0.0280	0.35404565		0.2900	0.32930887
Re	3.3580	0.07220640	Au	3.6840	0.07934225
	1.2710	-0.28110995		1.6660	-0.26630197
	0.4644	-0.08502109		0.5989	-0.06487433
	0.0890	0.76774965		0.0977	0.75373414
	0.0280	0.33800872		0.0279	0.35550537
Os	2.5180	0.12646279			
	1.4600	-0.32981709			
	0.4923	-0.09451131			
	0.0980	0.72382959			
	0.0290	0.39925186			

**TABLE VI.**

**Total Hartree-Fock Energies and Relative Energy for Classical and Nonclassical Isomers of IrBe<sub>2</sub>H<sub>5</sub> for Different Contractions of the Same Basis Set.<sup>a</sup>**

	Total HF energy (a.u.)		Relative difference (kcal/mol)
	Classical (a.u.)	Nonclassical (a.u.)	
Ref. 2c (5s6p4d) uncontracted	-135.80319	-135.79036	-8.0
Ref. 2c (541, 311, 211)	-135.78627 (10.6)	-135.77670 (8.6)	-6.0
Ref. 2c (541, 541, 211)	-135.79801 (3.2)	-135.78516 (3.3)	-8.1

<sup>a</sup> The numbers in parentheses is equal to difference of the total HF energies between the fully uncontracted basis set and the current one (kcal/mol).

**TABLE VII.**

**Total MP2 Energies and Relative Energy for Classical and Nonclassical Isomers of IrBe<sub>2</sub>H<sub>5</sub> for Different Contractions of the Same Basis Set.**

	Total MP2 energy (a.u.)		Relative difference (kcal/mol)
	Classical (a.u.)	Nonclassical (a.u.)	
Ref. 1 (541, 51, 211)	-136.05344	-136.04001	-8.5
Ref. 1 (541, 411, 211)	-136.19363	-136.16008	-21.0
Ref. 1 (541, 651, 211)	-136.20567	-136.16965	-22.6

published results, where the classical isomer is more stable than the nonclassical one. The accurate contraction procedure of the  $p$  Gaussian functions change the value of the relative energy from  $-15.4^8$  to  $-22.6$  kcal/mol at the MP2 level.

In the classical isomer of  $\text{IrBe}_2\text{H}_5$ , the electronic structure can be interpreted as  $5\sigma$  bonds in the plane  $\text{IrH}_5$  between the Ir atom and the five hydrogen atoms that are correctly represented at the HF level by a  $sp^2d^2$  hybridization among the  $5s$ ,  $5d_{xy}$ ,  $5d_{x^2-y^2}$ ,  $6p_x$ , and  $6p_y$  orbitals of the iridium atom. The explicit treatment of the Ir  $6p$  orbital allows the possibility for such hybridization, and thus stabilizes the classical isomer as opposed to the nonclassical one.

## Conclusion

These outer  $p$  orbitals for transition metal ECP basis sets provide a compact way to represent the essential contribution of this orbital to the metal–ligand bond. By using these orbitals one can reduce the number of contracted basis functions needed for a given accuracy. One can also avoid the unexpectedly large error associated with a gross (chemical) deficiency in the 1-electron orbital space of many standard basis sets as illustrated by the isomers of  $\text{IrBe}_2\text{H}_5$ .

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