

Molecular Orbital Theory of the Properties of Inorganic and Organometallic Compounds. 6. Extended Basis Sets for Second-Row Transition Metals

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A series of efficient split-valence basis sets for second-row transition metals, termed 3-21G, has been constructed based on previously formulated minimal expansions of Huzinaga, and in a manner analogous to the previous development of 3-21G basis sets for first-row metals. The Huzinaga three Gaussian expansions for *s*- and *p*-type orbitals of given *n* quantum number have been fit by least squares to new three Gaussian combinations in which the two sets of functions share the same Gaussian exponents. The original three Gaussian expansions for 1*s*, 3*d*, and 4*d* atomic orbitals have been employed as is. The valence description comprises 4*d*- 5*s*- and 5*p*-type functions, each of which has been split into two and one Gaussian parts. 5*p* functions, while not populated in the ground state of the free atom, are believed to be important in the description of the bonding in molecules.

The performance of the 3-21G basis sets is examined with regard to the calculation of equilibrium geometries and normal-mode vibrational frequencies for a variety of simple inorganic and organometallic compounds incorporating second-row transition metals.

INTRODUCTION

Ab initio molecular orbital calculations have now been extensively and successfully employed to examine the properties of molecules incorporating main-group elements.¹ Several Gaussian-type basis sets are currently in widespread use, ranging from minimal basis sets, such as STO-3G,² to more flexible split-valence basis sets, such as the 3-21G representations 3-21G^(*) for second-row and heavier main-group elements),³ to polarization-type basis sets such as the 6-31G* and 6-31G** representations.⁴ STO-3G basis sets are generally satisfactory in reproducing experimental equilibrium geometries, whereas 3-21G 3-21G^(*) representations usually provide even better descriptions of molecular structure and are also reasonably successful in calculating vibrational frequencies, relative energies, and electric dipole moments. The 6-31G* and 6-31G** polarization basis sets generally fare better in all of these tasks, yielding results which appear to be close to those from much larger representations.

In a previous article,^{3e} 3-21G basis sets were introduced for the first-row transition metals, and were critically evaluated with regard to the calculation of molecular geometries and normal-mode vibrational frequencies. The satisfactory performance of these basis sets now has encouraged the generation of analogous representations for the second-row transition elements. The development of efficient split-valence basis sets for the second transition series, as well as a critical evaluation of their effectiveness in obtaining molecular properties, will be discussed following a survey of the efforts in the area in the last 5 years. Previous accounts of the development and application of *ab initio* molecular orbital theory for transition-metal systems through 1980 have been given by Schaefer⁵ and by Pietro and Hehre,⁶ while our recent article^{3e} reviewed the theoretical literature with first-row transition elements since 1981.

Most efforts to formulate simple basis sets for transition metals has focused on first-row metals, although some work has been expended on metals from the second and third transition series. A compilation of system-

atically prepared minimal Gaussian basis sets, which vary in expansion pattern, has been presented by Huzinaga and coworkers⁷ for the atoms Li through Rn, and the limited investigations with molecular systems carried out to date have led Huzinaga to express optimism about the ability of representations of this size to closely reproduce experimental equilibrium geometries.⁸ STO-3G minimal basis sets for first- and second-row transition metals⁶ have also been applied to the calculation of molecular properties, in particular, equilibrium geometries. It is, however, now apparent that these representations for transition metals do not provide as reliable or as uniform an account of molecular equilibrium geometry as the analogous basis sets for main-group elements, although some aspects of bonding, especially in organometallic compounds, do appear to be well described. While more exploratory work with STO-3G is still needed, the evidence in hand suggests that they (and presumably other minimal basis sets) lack the flexibility to properly describe the bonding in transition-metal-containing systems.

Gaussian basis sets of medium size (14 *s*-, 8 *p*-, and 7 *d*-type functions), have been obtained by Hyla-Kryspin *et al.*⁹ for second-row transition metals. Rather than use atomic ground-state configurations of the metal atoms, the authors chose $4d^{n-1} 5s^1$ configurations for the atomic optimization procedure; this was thought to better describe the metal atom in typical molecular environments. Pettersson and Wahlgren¹⁰ have devised a contraction scheme for Mo and Pd, in which the previously mentioned Gaussian basis sets of Hyla-Kryspin and coworkers⁹ have been modified such that the core region is almost minimal (the 1*s* shell has been split), the valence 5*s* and 5*p* orbitals are doubly split, and the 4*d* shell is quadruply split. Gaussian basis sets, which consist of 12 *s*-, 8 *p*-, and 7 *d*-type functions, have been optimized by Friedlander *et al.*¹¹ for the neutral, monopositive, and dipositive atoms of the second transition series. Walch, Bauschlicher, and Nelin¹² have provided optimized values for diffuse 4*d*, 5*p*, and 4*f* functions to be used to supplement Huzinaga's Gaussian basis sets for second-row transition metals.¹³

It is apparent that basis set efficiency must be seriously considered before applications of

nonempirical molecular orbital methods to transition-metal systems become routine. Not only should the number of primitive functions employed be kept as small as possible, but wherever appropriate, *s*-, *p*-, and *d*-type functions of the same *n* quantum number should be constrained to share common exponents. This leads to significant computational savings in the evaluation of the two-electron integrals which arise in atomic and molecular orbital calculations.¹⁴ Thus far, aside from the minimal STO-3G representations, the only basis sets for second-row transition metals, which have been so formulated are the recently published well-tempered Gaussian basis sets of Huzinaga and Klobukowski.^{15a} A successive article by the same authors^{15b} reported calculations on the first three lowest-energy configurations of the atoms of the second transition series, using basis sets that were augmented by an extra valence *d* function.

REVIEW OF APPLICATIONS TO MOLECULAR SYSTEMS

Transition-Metal Dimers and Related Small Systems

The electronic structure and nature of bonding in transition-metal dimers have been intensely investigated both by theorists and experimentalists; these molecules are the simplest models with which to study surface chemisorption and heterogeneous catalysis. Experimental work on the Mo₂ molecule¹⁶ has shown unequivocally that the metal-metal bond is very short. Theoretical treatments of this molecule,¹⁷ which range from single-determinant (Hartree-Fock) level to calculations which involve configuration interaction (CI) techniques, have revealed a double-well potential curve for the ground state. The inner minimum, which is near the experimental bond distance, was indicative of a quintuple bond, comprising one σ , two π , and two δ bonds, whereas the shallower outer minimum is best described in terms of a single σ bond. *Ab initio* Hartree-Fock and CI calculations of Cotton and Shim¹⁸ on Nb₂ show two shallow minima in the potential energy curve for the $^1\Sigma_g^+$ ground state. Anal-

ogous calculations on Ru_2 ¹⁹ predict a $^7\Delta_u$ ground-state configuration and a bond length of 2.71 Å. The metal-metal bond in this dimeric species involves important contributions from both the 5s and 4d orbitals. Shim and Gingerich²⁰ have performed Hartree-Fock and CI calculations on Pd_2 , yielding a bond length of 2.751 Å for the $^1\Sigma_g^+$ state. The PdPd linkage is indicated to be a σ bond involving an overlap of 5s orbitals. A similar bonding picture was reported by Shim and Gingerich^{21a} and by McLean^{21b} in CI calculations on Ag_2 . The former study involved a double-zeta Gaussian basis set (the 4d orbital is represented by a triple-zeta expansion), and led to a bond length of 2.76 Å, while the latter, which involved a Slater basis set of similar quality but augmented by *f* functions, yielded a bond length of 2.72 Å. The experimental distance in diatomic silver, 2.48 Å,²² is significantly shorter. Hartree-Fock calculations were utilized by Shim and Gingerich²³ to examine the $^2\Delta$, $^2\Sigma^+$, and $^2\Pi$ electronic states of the YPd molecule. The bond in this mixed-metal dimer was shown to involve donation from the $d\sigma$ and $d\pi$ orbitals of Pd into the $d\sigma$ and $d\pi$ orbitals of Y, with concomitant back donation from the yttrium 5s orbital into the 5s orbital of palladium.

Binary compounds which incorporate a second-row transition metal bonded to hydrogen or to a main-group element also have been investigated by *ab initio* techniques. Large Slater-type basis sets were employed by Lee and McLean²⁴ to obtain a bond length of 1.774 Å in AgH, to be compared with the experimental value of 1.618 Å.²⁵ When the Ag basis set was augmented by *f* functions and electron correlation was taken into account,^{21b} the calculated bond length shortened to 1.702 Å, still 0.084 Å longer than the experimental value. The $^2\Sigma^+$ ground state of PdH was examined both by Hartree-Fock and CI methods using a very large Slater basis set.²⁶ The most extensive calculation yielded a PdH bond distance of 1.64 Å, still 0.1 Å longer than the experimental value of 1.53 Å.²⁵ Calculations beyond the single-determinant level were performed on MoO, PdO, and AgO by Bauschlicher, Nelin, and Bagus.²⁷ These show that the bonding in the low-lying electronic states is mostly ionic, with the *d* orbitals involved to some extent in

covalent interactions. Shim and Gingerich²⁸ have studied the electronic structures of the metal monocarbides, RuC, RhC, and PdC, at the Hartree-Fock level with the inclusion of CI. RuC and RhC were found to have triple bonds, involving primarily 4d orbitals, i.e., without significant participation from the 5s orbital. On the other hand, the calculations indicate only a single linkage in PdC.

Transition-Metal Inorganic Compounds

Compounds that possess multiple metal-metal bonds continue to attract the attention of inorganic theorists. Atha *et al.*²⁹ have carried out *ab initio* calculations on $\text{Mo}_2(\text{O}_2\text{CH})_4$ to aid in the interpretation of core-electron ionization energies (ESCA spectra). In order to obtain a good estimate of the dissociation energy of the MoMo triple bond, Kok and Hall³⁰ performed generalized molecular orbital (GMO) and CI calculations on Mo_2H_6 . Using assumed geometrical parameters, dissociation of the MoMo triple bond in this compound was predicted to require 68 kcal mol⁻¹. Complete geometry optimizations at the STO-3G level were performed by Dobbs, Francl, and Hehre³¹ to examine the conformation preferences in Mo_2L_6 complexes (L=H, F, OH). Staggered conformations of Mo_2H_6 and Mo_2F_6 were indicated to be favored over the eclipsed arrangements, whereas $\text{Mo}_2(\text{OH})_6$ preferred an eclipsed conformation. The small rotational barriers found for Mo_2F_6 (1.0 kcal mol⁻¹) and $\text{Mo}_2(\text{OH})_6$ (0.5 kcal mol⁻¹) were rationalized in terms of the metal-ligand bonding orbitals in these systems being of much lower energy and more highly localized than those in Mo_2H_6 , where the rotational barrier was calculated to be 7.6 kcal mol⁻¹.

A theoretical analysis of the geometrical distortions in the experimentally determined structure of $[\text{Rh}(\text{PPh}_3)_3]^+$ ³² was carried out by Dedieu and Hyla-Kryspin³³ using $[\text{Rh}(\text{PH}_3)_3]^+$, $[\text{Rh}(\text{PH}_3)_2(\text{H}_2\text{PCH}=\text{CH}_2)]^+$ and $\text{Ru}(\text{PH}_3)_2(\text{H}_2\text{PCH}=\text{CH}_2)$ as model systems. The authors suggested that a stabilizing interaction which exists between the vinyl moiety and the rhodium center may be analogous to interactions between the phenyl ring and rhodium center in $[\text{Rh}(\text{PPh}_3)_3]^+$. Multi-reference configuration interaction calcu-

lations were used by Brandemark *et al.*³⁴ to investigate the addition of H_2 to both Pd and to $Pd(H_2O)_2$. While Pd was found to interact only weakly with H_2 , leaving the HH bond distance essentially unchanged, the water ligands in $Pd(H_2O)_2$ allowed the breaking of the HH bond and the subsequent formation of covalent metal-hydrogen bonds. Sakaki, Morokuma, and Ohkubo³⁵ studied the coordination of H_2 to $RhCl(PH_3)_2$ using energy decomposition analyses. This suggested that end-on coordination of N_2 was favored over side-on coordination, and further that the π back donation contributes more to the total coordination interaction than σ donation from the metal. Toward modeling the interaction of CN on a silver surface, Bauschlicher³⁶ performed CI calculations on AgCN, and found the metal-carbon bond to be essentially ionic with very little d participation.

Organometallic Chemistry

Significant research in theoretical organometallic chemistry has been given to the examination of metal carbenes. Francl *et al.*³⁷ have shown that the planar structure for $H_2Zr=CH_2$ is favored over the corresponding perpendicular conformation at the STO-3G level. The conformational preference of a Schrock-type metal carbene complex, $H_2(CH_3)Nb=CH_2$, was studied using minimal basis sets at the Hartree-Fock level.³⁸ The calculated barrier to rotation, $11.3 \text{ kcal mol}^{-1}$, was noted to be significantly larger than barriers typical of Fischer-type metal carbenes,³⁹ the difference being rationalized by the absence of degenerate $d\pi$ -type lone-pair orbitals. The reactivity of the carbene carbon toward electrophiles and of the Nb atom toward nucleophiles was interpreted as being frontier-orbital controlled rather than charge controlled. More extensive basis sets were used by Nakamura and Dedieu⁴⁰ to compare the rotational barriers of the carbene ligands in $(CO)_4Mo(CH_2)_2$ and $(CO)_4Mo[C(NH_2)_2]_2$. A staggered relationship between the axial CH_2 ligands was indicated to be preferred over an eclipsed geometry by 11 kcal mol^{-1} . The near zero rotational barrier determined for the aminocarbene ligands, was traced to the interaction of the π orbitals

on nitrogen with the π orbital on carbon. Taylor and Hall⁴¹ carried out generalized molecular orbital (GMO) and limited CI calculations on the Fischer-type carbenes, $(CO)_5Mo(CH_2)$, and $(CO)_5Mo(CHOH)$, as well as on the Schrock-type carbenes, $CpNbCl_2(CH_2)$ and $CpNbCl_2(CHOH)$. The calculated methylene rotational barrier in the latter system, $14.6 \text{ kcal mol}^{-1}$, compared favorably with the temperature-dependent NMR data on tantalum-carbene complexes.⁴² Calculated metal-carbon, double-bond dissociation energies, coupled with an analysis of electron density distributions, led the authors to conclude that Fischer-type metal carbenes involve a singlet metal fragment binding datively to a singlet carbene fragment, while Schrock-type metal carbenes bind covalently as triplet fragments.

Theoretical models have also been used to examine reaction mechanisms in which an organotransition-metal complex is believed to play an active role. High-valent complexes of Mo (also Cr and W) were studied using the generalized valence bond (GVB) method by Rappe and Goddard⁴³ in order to provide some mechanistic insight for olefin metathesis. The oxygen ligand in oxoalkylidene-metal complexes, believed to be the stable metathesis catalysts, has been suggested to be intimately involved in the catalytic process. These same authors performed a similar mechanistic study for hydrocarbon oxidation by molybdyl (and chromyl) chloride, MoO_2Cl_2 ,⁴⁴ and suggested that the second oxo group plays a key role in stabilizing critical intermediates. In order to investigate the role of a Lewis acid as a cocatalyst in olefin metathesis, Nakamura and Dedieu⁴⁵ performed *ab initio* calculations on $MoOCl(CH_3)_3$ and $MoOCl(CH_2)(CH_3)$, as well as on the corresponding AlH_3 adducts. Coordination of AlH_3 to the oxygen ligand was greatly preferred over coordination at chlorine or on the carbene. Simultaneous bonding of AlH_3 to the oxygen and carbene ligands was also found to be unfavorable. The calculated reduction in the methylene rotational barrier upon forming the Lewis acid adduct (from 30.6 to $23.1 \text{ kcal mol}^{-1}$) was explained in terms of repulsive interactions between the π component on carbon and the lone-pair electrons on the oxygen. Additional theoretical work on

olefin metathesis was pursued by Dedieu and Eisenstein⁴⁶ by way of SCF calculations on the metal-carbene-olefin complex, $\text{MoCl}_4(\text{C}_2\text{H}_4)(\text{CH}_2)$, and on the corresponding metallacyclobutane, $\text{MoCl}_4(\text{C}_3\text{H}_6)$. The calculations suggested that the metal-carbene-olefin is the more stable complex. By way of Hartree-Fock calculations on $\text{Pd}(\text{C}_2\text{H}_5)(\text{H})(\text{PH}_3)$ and on the corresponding β -elimination product, $\text{Pd}(\text{C}_2\text{H}_4)(\text{H})_2(\text{PH}_3)$, Morokuma and coworkers⁴⁷ examined the role of agostic interactions in β elimination. The authors concluded that a strong agostic interaction exists for the Pd-ethyl complex, facilitating β elimination to form the Pd-ethylene complex. The method of paired interacting orbitals was utilized by Fujimoto and Yamasaki⁴⁸ in a theoretical analysis of Pd(II)-catalyzed nucleophilic additions to carbon-carbon double bonds. Both *trans* and *cis* additions of hydroxide and hydride anions to ethylene were studied using both PdCl_3^- or $\text{PdCl}_2(\text{H}_2\text{O})$ as catalysts.

CONSTRUCTION OF 3-21G SPLIT-VALENCE BASIS SETS FOR SECOND-ROW TRANSITION METALS

Development of 3-21G basis sets for second-row transition metals closely parallels previous efforts for first-row metals. Inner-shell orbitals are each represented by a single basis function, while valence atomic orbitals each comprise inner and outer parts, i.e.,

1s
2s, 2p_x, 2p_y, 2p_z
3s, 3p_x, 3p_y, 3p_z, 3d_{xx}, 3d_{yy}, 3d_{zz}, 3d_{xy}, 3d_{xz}, 3d_{yz}
4s, 4p_x, 4p_y, 4p_z
4d'_{xx}, 4d'_{yy}, 4d'_{zz}, 4d'_{xy}, 4d'_{xz}, 4d'_{yz}
4d''_{xx}, 4d''_{yy}, 4d''_{zz}, 4d''_{xy}, 4d''_{xz}, 4d''_{yz}
5s', 5p'_x, 5p'_y, 5p'_z
5s'', 5p''_x, 5p''_y, 5p''_z

Each of the inner-shell atomic basis functions is represented by three Gaussian functions (termed primitives); inner and outer parts of valence basis functions are in terms of two and one Gaussians, respectively, i.e.,

$$\phi_{1s}(r) = \sum_{k=1}^3 d_{1s,k} g_s(\alpha_{1s,k}, r)$$

$$\phi_{2s}(r) = \sum_{k=1}^3 d_{2s,k} g_s(\alpha_{2sp,k}, r)$$

$$\phi_{2p}(r) = \sum_{k=1}^3 d_{2p,k} g_p(\alpha_{2sp,k}, r)$$

$$\phi_{3s}(r) = \sum_{k=1}^3 d_{3s,k} g_s(\alpha_{3sp,k}, r)$$

$$\phi_{3p}(r) = \sum_{k=1}^3 d_{3p,k} g_p(\alpha_{3sp,k}, r)$$

$$\phi_{3d}(r) = \sum_{k=1}^3 d_{3d,k} g_d(\alpha_{3d,k}, r)$$

$$\phi_{4s}(r) = \sum_{k=1}^3 d_{4s,k} g_s(\alpha_{4sp,k}, r)$$

$$\phi_{4p}(r) = \sum_{k=1}^3 d_{4p,k} g_p(\alpha_{4sp,k}, r)$$

$$\phi'_{4d}(r) = \sum_{k=1}^2 d_{4d',k} g_d(\alpha_{4d',k}, r)$$

$$\phi'_{5s}(r) = \sum_{k=1}^2 d_{5s',k} g_s(\alpha_{5sp',k}, r)$$

$$\phi'_{5p}(r) = \sum_{k=1}^2 d_{5p',k} g_p(\alpha_{5sp',k}, r)$$

$$\phi''_{4d}(r) = g_d(\alpha''_{4d}, r)$$

$$\phi''_{5s}(r) = g_s(\alpha''_{5sp}, r)$$

$$\phi''_{5p}(r) = g_p(\alpha''_{5sp}, r)$$

The parameters α and d are Gaussian exponents and linear expansion coefficients, respectively. g_s , g_p , and g_d are normalized Gaussian functions, e.g.,

$$g_s(\alpha, r) = (2\alpha/\pi)^{3/4} \exp(-\alpha r^2)$$

$$g_x(\alpha, r) = (128\alpha^5/\pi^3)^{1/4} x \exp(-\alpha r^2)$$

$$g_{xx}(\alpha, r) = (2048\alpha^7/9\pi^3)^{1/4} x^2 \exp(-\alpha r^2)$$

with similar expressions for the remaining p - and d -type functions. For computational efficiency,¹⁴ the Gaussians that comprise s - and p -type atomic orbitals of given n quantum number are constrained to have the same exponents. This is the same constraint as previously applied to the construction of 3-21G 3-21G(*) basis sets for main-group elements^{3a-d} and first-row transition metals.^{3e} Different sets of Gaussians are used to construct $3d$ and $4d$ orbitals than are employed for $3s$ and $3p$ and $4s$ and $4p$ functions, respectively.

Paralleling previous efforts for third- and fourth-row main-group elements^{3d} and for first-row transition metals,^{3e} 3-21G representations for second-row transition metals have been formulated around the uniform series of minimal basis sets recently published by

Huzinaga for the first 86 elements of the Periodic Table.⁷ In these representations, each atomic orbital is described by a sum of three Gaussians, the individual Gaussian exponents and linear expansion coefficients being first determined as least-squares fits to atomic Hartree-Fock functions, and then further refined by total (atomic) energy minimization. Full details of the numerical procedures involved have already been provided by Huzinaga.⁷ The entire transition series has been fitted to a uniform series of atomic wavefunctions in which the 5s orbital is doubly occupied. This parallels the previous development of 3-21G representations for first-row transition metals,^{3e} although it should be noted that except for Y, Zr, and Cd, these assignments correspond to excited-state configurations for the free atoms. The original Huzinaga expansions for 1s and 3d orbitals are taken as is. Those describing 4d orbitals are split into two-Gaussian (the two largest Gaussian exponents) and one-Gaussian parts, and then renormalized. This is the same procedure recommended by Huzinaga for development of split basis sets from minimal representations.⁷

Expansions describing 2s, 2p, 3s, 3p, 4s, and 4p orbitals are modified somewhat from those provided by Huzinaga. Specifically, functions of given n quantum number, e.g., 2s, 2p_x, 2p_y, 2p_z, are constrained to be made up of Gaussian primitives sharing a common set of exponents. This involves simultaneous least-square fitting of the Huzinaga s - and p -type functions (of given n quantum number) to expansions in which the Gaussian exponents are held in common. This procedure was also employed in the construction of 3-21G and 3-21G^(*) for third- and fourth-row main-group elements and for first-row transition metals from the original Huzinaga representations.^{3d,e}

5s and 5p atomic orbitals are handled in a similar manner. Specifically, the Huzinaga three-Gaussian expansions for 5s,⁷ as well as the single-Gaussian 5p orbital recommended for use as polarization functions⁷ are simultaneously fit to three-Gaussian expansions in which the exponents of the individual s and p functions are held in common. These are later split into two-Gaussian and one-Gaussian parts, and renormalized.

Final constrained basis functions for first-row transition metals are provided in Table I.

For convenience 1s and 3d functions [already provided by Huzinaga (ref. 7)] also have been included in the tabulation.

PERFORMANCE OF 3-21G BASIS SETS

Evaluation of 3-21G basis sets for second-row transition metals follows in a similar manner to that for first-row transition metals.^{3e} Experimental structure and frequency data for simple molecules incorporating second-row transition metals are more scarce than for compounds with first-row metals or with main-group elements. In addition, molecular calculations are more difficult than for molecules incorporating first-row metals, limiting comparisons with experimental data mainly to small inorganic molecules. Still, sufficient comparisons exist to enable some evaluation of performance of the basis sets developed in this article. Experimental relative energy and dipole moment data on transition-metal inorganic and organometallic systems are even more scarce, and comparisons with calculated quantities will not be undertaken at this time.

3-21G equilibrium structures for a number of inorganic compounds and two organometallic species incorporating a single second-row transition metal are compared with experimental geometries in Table II. Following our practice in dealing with first-row metals,^{3e} the 3-21G basis has been used throughout. The structure of silver chloride has also been optimized with the 3-21G^(*) basis set for chlorine used in place of 3-21G.

Metal fluorine bond lengths calculated at the 3-21G level for YF, ZrF₄, MoF₆, and F₄MoO are shorter than experimental values, but only by 0.02 Å or less. The calculated bond length in silver fluoride is longer, although again the error (0.036 Å) is relatively small. Overall, the performance of the theory here is somewhat better than that for the corresponding first-row compounds, e.g., the error in the ZrF bond length in ZrF₄ is 0.010 Å, compared with an error of 0.026 Å for the TiF bond length in TiF₄. Calculated bond distances between chlorine and second-row transition metals are consistently longer than experimental values, sometimes significantly so, e.g., by 0.204 Å in AgCl. The situation does not improve significantly by replacement of the 3-21G basis set for chlorine by

Table I. Gaussian basis functions for second-row transition metals.

Atom	Shell	α	d_s	d_p	d_d
Y	1s	7.646421(+03)	6.189050(-02)		
		1.156863(+03)	3.702068(-01)		
		2.537152(+02)	6.877560(-01)		
	2sp	3.418540(+02)	-1.119001(-01)	1.485717(-01)	
		7.420986(+01)	8.680524(-02)	5.943067(-01)	
		2.351352(+01)	9.667847(-01)	4.196040(-01)	
	3sp	1.886260(+01)	-1.477873	-7.041407(-01)	
		1.645405(+01)	1.347259	1.057862	
		3.484500	1.006231	7.393821(-01)	
	3d	5.035375(+01)			1.367956(-01)
		1.353078(+01)			5.019062(-01)
		3.944996			5.788598(-01)
	4sp	3.221733	-3.699580(-01)	2.494435(-03)	
		1.050705	4.308639(-01)	4.537623(-01)	
		3.925923(-01)	8.020874(-01)	6.130679(-01)	
	4d'	1.530137			3.384033(-01)
		6.300673(-01)			7.293289(-01)
	4d''	2.165884(-01)			1.0
	5sp'	4.327637(-01)	-3.464582(-01)	-1.336559(-03)	
		5.701219(-02)	1.132777	1.000440	
	5sp''	2.375370(-02)	1.0	1.0	
Zr	1s	8.084592(+03)	6.157760(-02)		
		1.221668(+03)	3.693989(-01)		
		2.676917(+02)	6.887280(-01)		
	2sp	3.610212(+02)	-1.119067(-01)	1.487616(-01)	
		7.830495(+01)	8.583993(-02)	5.965690(-01)	
		2.484523(+01)	9.675130(-01)	4.167849(-01)	
	3sp	2.000628(+01)	-1.544349	-7.568480(-01)	
		1.757415(+01)	1.409596	1.112090	
		3.742985	1.009349	7.368024(-01)	
	3d	5.472323(+01)			1.348240(-01)
		1.477416(+01)			5.005544(-01)
		4.358961			5.787823(-01)
	4sp	3.554788	-3.793873(-01)	2.599455(-03)	
		1.178992	4.232847(-01)	4.599758(-01)	
		4.446966(-01)	8.140676(-01)	6.058485(-01)	
	4d'	1.862842			2.850320(-01)
		6.433135(-01)			7.972074(-01)
	4d''	1.993954(-01)			1.0
	5sp'	5.050488(-01)	-3.295118(-01)	-1.248930(-03)	
		6.211612(-02)	1.120709	1.000384	
	5sp''	2.557955(-02)	1.0	1.0	
Nb	1s	8.466517(+03)	6.180380(-02)		
		1.281261(+03)	3.698049(-01)		
		2.812311(+02)	6.880795(-01)		
	2sp	3.794729(+02)	-1.121063(-01)	1.496674(-01)	
		8.233589(+01)	8.650279(-02)	5.987182(-01)	
		2.622248(+01)	9.670574(-01)	4.132382(-01)	
	3sp	2.116294(+01)	-1.555131	-7.554622(-01)	
		1.858978(+01)	1.417939	1.113966	
		4.009981	1.010620	7.327672(-01)	
	3d	5.901219(+01)			1.337104(-01)
		1.601279(+01)			5.000390(-01)
		4.777185			5.775384(-01)
	4sp	3.836375	-3.891037(-01)	3.290347(-03)	
		1.303325	4.349696(-01)	4.716451(-01)	
		4.934306(-01)	8.115899(-01)	5.936990(-01)	
	4d'	1.970443			3.106809(-01)
		6.619347(-01)			7.800691(-01)
	4d''	2.059972(-01)			1.0

Table I. (continued)

Atom	Shell	α	d_s	d_p	d_d
Mo	5sp'	5.723734(−01)	−3.156094(−01)	−1.133018(−03)	
		6.820320(−02)	1.114047	1.000338	
	5sp''	2.715715(−02)	1.0	1.0	
	1s	8.899491(+03)	6.170640(−02)		
		1.346764(+03)	3.694536(−01)		
		2.956352(+02)	6.884343(−01)		
	2sp	3.993139(+02)	−1.121440(−01)	1.500665(−01)	
		8.659356(+01)	8.601148(−02)	6.007695(−01)	
		2.763904(+01)	9.674335(−01)	4.103865(−01)	
	3sp	2.250292(+01)	−1.422306	−6.680661(−01)	
		1.949171(+01)	1.284185	1.030346	
		4.278180	1.010866	7.283480(−01)	
	3d	6.378045(+01)			1.317388(−01)
		1.737358(+01)			4.985316(−01)
		5.230784			5.781775(−01)
	4sp	4.163021	−3.964233(−01)	2.962629(−03)	
		1.435305	4.370792(−01)	4.791471(−01)	
		5.437821(−01)	8.148462(−01)	5.864869(−01)	
	4d'	2.270937			3.112644(−01)
		7.546530(−01)			7.810342(−01)
	4d''	2.351422(−01)			1.0
Tc	5sp'	6.318014(−01)	−3.033617(−01)	−1.079133(−03)	
		7.325791(−02)	1.108413	1.000313	
	5sp''	2.802515(−02)	1.0	1.0	
	1s	9.329482(+03)	6.171190(−02)		
		1.412506(+03)	3.693370(−01)		
		3.102643(+02)	6.884724(−01)		
	2sp	4.188175(+02)	−1.124025(−01)	1.500719(−01)	
		9.125078(+01)	8.531816(−02)	6.000567(−01)	
		2.911212(+01)	9.681774(−01)	4.109856(−01)	
	3sp	2.591064(+01)	−1.380446	−1.655271	
		2.326770(+01)	1.197900	1.986020	
		4.707083	1.052649	7.290339(−01)	
	3d	6.878375(+01)			1.296930(−01)
		1.880389(+01)			4.966191(−01)
		5.705228			5.795466(−01)
	4sp	4.441138	−4.041144(−01)	1.229062(−02)	
		1.595639	4.398379(−01)	4.632067(−01)	
		5.955598(−01)	8.219360(−01)	5.983826(−01)	
	4d'	2.599164			3.092195(−01)
		8.622757(−01)			7.829056(−01)
	4d''	2.706073(−01)			1.0
Ru	5sp'	6.738812(−01)	−2.700028(−01)	−9.197676(−04)	
		7.724070(−02)	1.099150	1.000264	
	5sp''	2.869556(−02)	1.0	1.0	
	1s	9.786161(+03)	6.160520(−02)		
		1.481477(+03)	3.689816(−01)		
		3.254122(+02)	6.888451(−01)		
	2sp	4.398665(+02)	−1.123912(−01)	1.503791(−01)	
		9.576273(+01)	8.469449(−02)	6.019294(−01)	
		3.060566(+01)	9.686379(−01)	4.084639(−01)	
	3sp	2.727737(+01)	−1.395553	−1.668618	
		2.451082(+01)	1.210852	2.002799	
		5.008946	1.054045	7.251435(−01)	
	3d	7.398330(+01)			1.277598(−01)
		2.028149(+01)			4.951474(−01)
		6.194298			5.806552(−01)
	4sp	4.765812	−4.103627(−01)	1.127417(−02)	
		1.734531	4.480025(−01)	4.727032(−01)	
		6.466355(−01)	8.198083(−01)	5.898430(−01)	
	4d'	2.889108			3.159938(−01)

Table I. (continued)

Atom	Shell	α	d_s	d_p	d_d
Rh		9.539610(−01)			7.780656(−01)
	4d''	2.958807(−01)			1.0
	5sp'	7.406620(−01)	−2.639655(−01)	−7.620441(−04)	
		8.217096(−02)	1.094857	1.000212	
	5sp''	3.009659(−02)	1.0	1.0	
	1s	1.021771(+04)	6.173240(−02)		
		1.548412(+03)	3.691533(−01)		
		3.404990(+02)	6.885138(−01)		
	2sp	4.607593(+02)	−1.124461(−01)	1.508582(−01)	
		1.003289(+02)	8.438113(−02)	6.035139(−01)	
		3.213971(+01)	9.689016(−01)	4.060249(−01)	
	3sp	2.879329(+01)	−1.404091	−1.712218	
		2.591768(+01)	1.216169	2.047603	
		5.320640	1.056555	7.229831(−01)	
	3d	7.925597(+01)			1.261896(−01)
		2.178945(+01)			4.939541(−01)
		6.697518			5.813296(−01)
	4sp	5.109748	−4.126469(−01)	9.374064(−03)	
		1.875414	4.518853(−01)	4.815544(−01)	
		6.995578(−01)	8.188989(−01)	5.822312(−01)	
	4d'	3.190908			3.210399(−01)
		1.054575			7.738518(−01)
	4d''	3.260791(−01)			1.0
	5sp'	8.005711(−01)	−2.553480(−01)	−7.759711(−04)	
		8.732134(−02)	1.091308	1.000212	
	5sp''	3.140693(−02)	1.0	1.0	
Pd	1s	1.072874(+04)	6.142950(−02)		
		1.624074(+03)	3.683282(−01)		
		3.567937(+02)	6.895025(−01)		
	2sp	4.824783(+02)	−1.126789(−01)	1.510793(−01)	
		1.050590(+02)	8.461197(−02)	6.050916(−01)	
		3.368145(+01)	9.687868(−01)	4.039804(−01)	
	3sp	3.018654(+01)	−1.418547	−1.709817	
		2.716642(+01)	1.229444	2.049308	
		5.635934	1.057083	7.186296(−01)	
	3d	8.423691(+01)			1.256429(−01)
		2.324919(+01)			4.937201(−01)
		7.196760			5.803431(−01)
	4sp	5.475374	−4.172610(−01)	1.158391(−02)	
		1.997604	4.705878(−01)	4.974548(−01)	
		7.439302(−01)	8.046363(−01)	5.655272(−01)	
	4d'	3.473077			3.281543(−01)
		1.148050			7.680267(−01)
	4d''	3.548106(−01)			1.0
	5sp'	8.901632(−01)	−2.784324(−01)	−1.271580(−03)	
		9.282090(−02)	1.093028	1.000332	
	5sp''	3.377394(−02)	1.0	1.0	
Ag	1s	1.119078(+04)	6.149480(−02)		
		1.695077(+03)	3.684053(−01)		
		3.726752(+02)	6.893247(−01)		
	2sp	5.046162(+02)	−1.126577(−01)	1.514798(−01)	
		1.098718(+02)	8.402784(−02)	6.065142(−01)	
		3.529513(+01)	9.692344(−01)	4.018302(−01)	
	3sp	3.156877(+01)	−1.422028	−1.673366	
		2.834397(+01)	1.234098	2.018976	
		5.945127	1.055683	7.126889(−01)	
	3d	8.993335(+01)			1.240159(−01)
		2.487496(+01)			4.923831(−01)
		7.738191			5.814968(−01)
	4sp	5.800256	−4.196171(−01)	1.430410(−02)	
		2.127256	4.843501(−01)	5.071943(−01)	
		7.935512(−01)	7.952035(−01)	5.539736(−01)	

Table I. (continued)

Atom	Shell	α	d_s	d_p	d_d
Cd	4d'	3.796557 1.256644			3.314259(-01) 7.651634(-01)
	4d''	3.881333(-01)			1.0 ^a
	5sp'	9.285445(-01) 9.725467(-02)	-2.523005(-01) 1.087392	-1.480711(-03) 1.000388	
	5sp''	3.493292(-02)	1.0	1.0	
	1s	1.168609(+04) 1.770111(+03) 3.892090(+02)	6.142650(-02) 3.681567(-01) 6.895722(-01)		
	2sp	5.276004(+02) 1.148329(+02) 3.695829(+01)	-1.125925(-01) 8.326963(-02) 9.697978(-01)	1.518051(-01) 6.077598(-01) 3.999632(-01)	
	3sp	3.301548(+01) 2.954543(+01) 6.278508	-1.406471 1.218156 1.055520	-1.609024 1.959568 7.080271(-01)	
	3d	9.547274(+01) 2.648196(+01) 8.282886			1.230828(-01) 4.916768(-01) 5.815408(-01)
	4sp	6.150596 2.259746 8.414261(-01)	-4.229209(-01) 4.987714(-01) 7.850755(-01)	1.448229(-02) 5.186611(-01) 5.426658(-01)	
	4d'	4.082141 1.357279			3.379410(-01) 7.591679(-01)
	4d''	4.208308(-01)			1.0
	5sp'	9.490686(-01) 1.014878(-01)	-2.215547(-01) 1.080944	-1.540266(-03) 1.000412	
	5sp''	3.598726(-02)	1.0	1.0	

3-21G^(*); the resultant bond length is still 0.175 Å longer than the experimental distance. The calculations reproduce the observation that the axial metal chlorine bond lengths in NbCl₅ are longer than the equatorial distances, although the magnitude of the difference calculated (0.024 Å) is much smaller than that measured (0.097 Å). Metal-oxygen double-bond lengths are underestimated at the 3-21G level; a result which was also observed for compounds incorporating first-row transition metals.^{3e} However, the errors are small, ranging from a minimum of 0.005 Å (in OMoF₄) to a maximum of 0.020 Å (in OMoCl₄).

Comparisons involving organometallic systems have been limited to tetramethylzirconium and dimethylcadmium. While the theory performs moderately well in its description of metal-carbon bond lengths (the calculated ZrC bond lengths in ZrMe₄ closely reproduce the average value found in tetrabenzylzirconium, while the calculated CdC bond length in Cd(Me)₂ is 0.11 Å shorter than the experimental distance), further data are needed to properly assess the performance of

the 3-21G basis sets for the structures of organometallic compounds.

Overall, the mean absolute deviation of 3-21G from experimental bond distances (connecting heavy atoms) is 0.058 Å, and is similar to the average deviation found for inorganic and organometallic systems of the first transition series.^{3e}

3-21G bond angles are in good accord with experimental values, consistent with previous results for first-row transition metals at the same level of theory.

A number of STO-3G equilibrium geometries, also included in Table II, are available for comparison with the 3-21G results and with experiment.^{2d} Although the minimal basis set does well in reproducing bond lengths for a few compounds, e.g., in ZrCl₄, the method is generally inferior to 3-21G in reproducing experimental equilibrium structures. The mean absolute deviation of STO-3G from experimental bond lengths (connecting heavy atoms) is 0.091 Å, considerably larger than the corresponding average error found in comparisons involving the 3-21G basis set.

Table II. Calculated and experimental equilibrium geometries for transition-metal inorganic and organometallic compounds (bond lengths in Angstroms, bond angles in degrees).

Molecule	Point Group	Geometrical Parameter	STO-3G	3-21G	Expt.
YF	$C_{\infty v}$	$r(\text{YF})$	1.975	1.909	1.926 ^a
YCl	$C_{\infty v}$	$r(\text{YCl})$	2.486	2.495	2.406 ^a
ZrF ₄	T_d	$r(\text{ZrF})$	1.870	1.876	1.886 ^b
ZrCl ₄	T_d	$r(\text{ZrCl})$	2.316	2.387	2.32 ^c
NbCl ₅	D_{3h}	$r(\text{NbCl}_{ax})$		2.362	2.338 ^d
		$r(\text{NbCl}_{eq})$		2.338	2.241
MoF ₆	O_h	$r(\text{MoF})$		1.814	1.820 ^e
OMoF ₄	C_{4v}	$r(\text{MoF})$	1.776	1.830	1.836 ^f
		$r(\text{MoO})$	1.611	1.645	1.650
		$\angle(\text{OMoF})$	107.3	105.9	103.8
OMoCl ₄	C_{4v}	$r(\text{MoCl})$		2.359	2.279 ^g
		$r(\text{MoO})$		1.638	1.658
		$\angle(\text{OMoCl})$		103.5	102.8
RuO ₄	T_d	$r(\text{RuO})$		1.691	1.706 ^c
AgH	$C_{\infty v}$	$r(\text{AgH})$		1.782	1.618 ^a
AgF	$C_{\infty v}$	$r(\text{AgF})$	1.633	2.019	1.983 ^a
AgCl	$C_{\infty v}$	$r(\text{AgCl})$	2.083	2.485 ^h	2.281 ^a
Zr(CH ₃) ₄	T_d	$r(\text{ZrC})$	2.257	2.221	2.26 ⁱ
		$r(\text{CH})$	1.086	1.092	—
		$\angle(\text{HCH})$	107.3	107.2	—
Cd(CH ₃) ₂	D_{3h}	$r(\text{CdC})$	2.003	2.220	2.112 ^j
		$r(\text{CH})$	1.084	1.087	1.09 ^k
		$\angle(\text{HCH})$	106.2	108.2	108.4

^aSee ref. 25.^b*Spectroscopic Properties of Inorganic and Organometallic Compounds*, Vol. 16, The Royal Society of Chemistry, The Garden City Press Limited, London, 1984, p. 362.^cJ. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, *Structure Data on Free Polyatomic Molecules*, Landolt-Börnstein, New Series, Group II, Vol. 7, Springer-Verlag, Berlin, 1976.^dA. A. Ischenko, T. G. Strand, A. V. Demidov, and V. P. Spiridonov, *J. Mol. Struct.*, **43**, 227 (1978).^eH. M. Seip and R. Seip, *Acta Chem. Scand.*, **20**, 2698 (1966).^fK. Iijima, *Bull. Chem. Soc. Jpn.*, **50**, 373 (1977).^gK. Iijima and S. Shibata, *Bull. Chem. Soc. Jpn.*, **48**, 666 (1975).^hBond length for 3-21G(*) basis set on chlorine = 2.456 Å.ⁱAverage of four ZrC bond distances in tetrabenzylzirconium; G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, and A. J. P. Pioli, *J. Chem. Soc., Chem. Commun.*, 677 (1971).^jK. S. Rao, B. P. Stoicheff, and R. Turner, *Can. J. Phys.*, **38**, 1516 (1960).^kAssumed.

Normal-mode vibrational frequencies for several transition-metal inorganic and organometallic compounds obtained at the 3-21G level are compared with experimental values in Table III. Calculated frequencies are generally larger than experimental values, although there are significant exceptions. For example, the calculated frequencies in YCl and AgCl are significantly smaller than their respective experimental values (by 8% and 28%, respectively), consistent with the overestimation of bond lengths in these systems at the 3-21G level. While the calculations are remarkably successful in reproducing experimental vibrational frequencies for some polyatomic systems, e.g., ZrCl₄ and NbCl₅, they are much less satis-

factory for others, e.g., OMoCl₄. Overall the large range of errors in calculated frequencies does not encourage frequency assignments with this level of theory.

CONCLUSIONS

A series of computationally-efficient 3-21G split-valence basis sets has been formulated for second-row transition metals, based on previously defined minimal representations of Huzinaga.⁷ Each inner-shell atomic orbital has been represented by a single basis function (written in terms of three Gaussians), while each of the 4*d*, 5*s*, and 5*p* valence orbitals has been split into two parts, and writ-

Table III. Calculated and experimental normal-mode vibrational frequencies for transition-metal inorganic and organometallic compounds (cm^{-1}).

Molecule	Symmetry of Mode	Description of Mode	Frequency	
			3-21G	Expt. ^a
YF			739	631
YCl			349	381
ZrCl ₄	a_1	sym. stretch	348	377
	e	deg. deform.	99	98
	t_2	deg. stretch	417	418
	t_2	deg. deform.	105	113
NbCl ₅	a'_1	NbCl ₃ sym. stretch	393	394 ^b
	a'_1	NbCl ₂ sym. stretch	302	317
	a''_2	NbCl ₂ asym. stretch	431	409
	a''_2	NbCl ₃ deform.	177	148
	e'	NbCl ₃ deg. stretch	418	430
	e'	NbCl ₃ deg. deform.	187	180
	e'	NbCl bend	42	54
	e''	NbCl bend	144	148
OMoCl ₄	a_1		1198	1015 ^c
	a_1		369	450
	a_1		163	143
	b_1		271	400
	b_1		51	148
	b_2		213	220
	e		397	396
	e		263	256
	e		127	172
RuO ₄	a_1	sym. stretch	1005	885
	e	deg. deform.	339	322
	t_2	deg. stretch	958	921
	t_2	deg. deform.	328	336
Cd(CH ₃) ₂	a'_1	CH ₃ sym. stretch	3162	2903
	a'_1	CH ₃ sym. deform.	1354	1127
	a'_1	CCd sym. stretch	457	459
	a''_1	torsion	42	0
	a''_2	CH ₃ sym. stretch	3162	2923
	a''_2	CH ₃ sym. deform.	1353	1136
	a''_2	CCd asym. stretch	520	535
	e'	CH ₃ deg. stretch	3235	2980
	e'	CH ₃ deg. deform.	1656	1315
	e'	CH ₃ rock	757	700
	e'	CCdC deform.	113	124
	e''	CH ₃ deg. stretch	3233	2859
	e''	CH ₃ deg. deform.	1634	1427
	e''	CH ₃ rock	705	634
AgH			1422	1251
AgF			535	513
AgCl			248	343

^aExcept for where otherwise noted, experimental data for diatomic molecules from ref. 25, and for polyatomic molecules from: T. Shimanouchi, *J. Phys. Chem. Ref. Data*, **6**, 993 (1977).

^bSee footnote d of Table II for reference to experimental data.

^cSee footnote g of Table II for reference to experimental data.

ten in terms of two and one Gaussian functions, respectively.

The performance of the 3-21G basis sets has been examined with regard to the calculation of equilibrium geometries and normal-mode vibrational frequencies for a small set of inorganic and organometallic compounds incorporating second-row transition metals. The

simple model fares reasonably well in reproducing experimental geometries for transition-metal inorganic systems. Since the number of organometallic systems in the study is very limited, no general conclusion may be made about the application of 3-21G to the calculation of metal-carbon bond lengths. 3-21G normal-mode vibrational fre-

quencies for transition-metal molecules are not as uniform as those for main group molecules at the same level of theory. More research is required for a more thorough assessment of 3-21G before its general application to molecular systems incorporating second-row transition metals can be recommended.

APPENDIX

Total Energies

Total energies for all molecules dealt with in this article are provided in *Table IV*.

Table IV. Total energies (hartrees) for transition-metal inorganic and organometallic compounds.

Molecule	Energy
YF	-3414.82831
YCl	-3773.22687
ZrF ₄	-3918.16822
ZrCl ₄	-5351.70927
NbCl ₅	-6022.48347
MoF ₆	-4550.17440
OMoF ₄	-4426.84256
OMoCl ₄	-5860.40178
RuO ₄	-4718.13064
AgH	-5174.34249
AgF	-5272.70446
AgCl	-5631.17942
Zr(CH ₃) ₄	-3679.76899
Cd(CH ₃) ₂	-5518.93910

References

- For a recent review, see: W.J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
- (a) W.J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) W.J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *ibid.*, **52**, 2769 (1979); (c) W. J. Pietro, B. A. Levi, W. J. Hehre, and R. F. Stewart, *Inorg. Chem.*, **19**, 2225 (1980); (d) W. J. Pietro, E. S. Blurock, R. F. Hout, Jr., W. J. Hehre, D. J. DeFrees, and R. F. Stewart, *ibid.*, **20**, 3650 (1981).
- (a) J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980); (b) M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, *ibid.*, **104**, 2797 (1982); (c) W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople, and J. S. Binkley, *J. Am. Chem. Soc.*, **104**, 5039 (1982); (d) K. D. Dobbs and W. J. Hehre, *J. Comput. Chem.*, **7**, 359 (1986); (e) K. D. Dobbs and W. J. Hehre, *J. Comput. Chem.*, **8**, 861 (1987).
- (a) P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, **66**, 217 (1972); (b) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973); (c) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, *J. Chem. Phys.*, **77**, 3654 (1982).
- H. F. Schaefer, III, *J. Mol. Struct. (THEOCHEM)*, **76**, 117 (1981).
- W. J. Pietro and W. J. Hehre, *J. Comput. Chem.*, **4**, 241 (1983).
- S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radio-Andzelm, Y. Sakai and H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations*, Elsevier, New York, 1984.
- L. Seijo, Z. Barandiaran, M. Klobukowski, and S. Huzinaga, *Chem. Phys. Lett.*, **117**, 151 (1985).
- I. Hyla-Kryspin, J. Demuynck, A. Strich, and M. Benard, *J. Chem. Phys.*, **75**, 3954 (1981).
- L. Pettersson and U. Wahlgren, *Chem. Phys. Lett.*, **89**, 26 (1982).
- M. E. Friedlander, J. M. Howell, and G. Snyder, *J. Chem. Phys.*, **77**, 1921 (1982).
- S. P. Walch, C. W. Bauschlicher, Jr., and C. J. Nelin, *J. Chem. Phys.*, **79**, 3600 (1983).
- S. Huzinaga, *J. Chem. Phys.*, **66**, 4245 (1977).
- J. A. Pople and W. J. Hehre, *J. Comput. Phys.*, **27**, 161 (1978).
- (a) S. Huzinaga and M. Klobukowski, *Chem. Phys. Lett.*, **120**, 509 (1985); (b) M. Klobukowski and S. Huzinaga, *J. Chem. Phys.*, **84**, 323 (1986).
- J. B. Hopkins, P. R. R. Langridge-Smith, M. D. Morse, and R. E. Smalley, *J. Chem. Phys.*, **78**, 1627 (1983).
- (a) P. M. Atha and I. H. Hillier, *Mol. Phys.*, **45**, 285 (1982); (b) M. M. Goodgame and W. A. Goddard, III, *Phys. Rev. Lett.*, **48**, 135 (1982); (c) A. D. McLean and B. Liu, *Chem. Phys. Lett.*, **101**, 144 (1983).
- F. A. Cotton and I. Shim, *J. Phys. Chem.*, **89**, 952 (1985).
- F. A. Cotton and I. Shim, *J. Am. Chem. Soc.*, **104**, 7025 (1982).
- I. Shim and K. A. Gingerich, *J. Chem. Phys.*, **80**, 5107 (1984).
- (a) I. Shim and K. A. Gingerich, *J. Chem. Phys.*, **79**, 2903 (1983); (b) A. D. McLean, *ibid.*, **79**, 3392 (1983).
- See ref. 12 in ref. 21b.
- I. Shim and K. A. Gingerich, *Chem. Phys. Lett.*, **101**, 528 (1983).
- Y. S. Lee and A. D. McLean, *J. Chem. Phys.*, **76**, 735 (1982).
- K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structures. IV. Constants of Diatomic Molecules*, Van Nostrand-Reinhold, New York, 1979.
- P. S. Bagus and C. Björkman, *Phys. Rev. A*, **23**, 461 (1981).
- C. W. Bauschlicher, Jr., C. J. Nelin, and P. S. Bagus, *J. Chem. Phys.*, **82**, 3265 (1985).
- (a) I. Shim and K. A. Gingerich, *J. Chem. Phys.*, **76**, 3833 (1982); (b) I. Shim and K. A. Gingerich, *J. Chem. Phys.*, **81**, 5937 (1984); (c) I. Shim and K. A. Gingerich, *Surf. Sci.*, **156**, 623 (1985).
- P. M. Atha, I. H. Hillier, A. A. MacDowell, and M. F. Guest, *J. Chem. Phys.*, **77**, 195 (1982).
- R. A. Kok and M. B. Hall, *Inorg. Chem.*, **22**, 728 (1983).
- K. D. Dobbs, M. M. Francl, and W. J. Hehre, *Inorg. Chem.*, **23**, 24 (1984).
- Y. W. Yared, S. L. Miles, R. Bau, and C. A. Reed, *J. Am. Chem. Soc.*, **99**, 7076 (1977).
- A. Dedieu and I. Hyla-Kryspin, *J. Organomet. Chem.*, **220**, 115 (1981).
- U. B. Brandemark, M. R. A. Blomberg, L. G. M. Pettersson, and P. E. M. Siegbahn, *J. Phys. Chem.*, **88**, 4617 (1984).

35. S. Sakaki, K. Morokuma, and K. Ohkubo, *J. Am. Chem. Soc.*, **107**, 2686 (1985).
36. C. W. Bauschlicher, Jr., *Surf. Sci.*, **154**, 70 (1985).
37. M. M. Francl, W. J. Pietro, R. F. Hout, Jr., and W. J. Hehre, *Organometallics*, **2**, 815 (1983).
38. J. Ushio, H. Nakatsuji, and T. Yonezawa, *J. Am. Chem. Soc.*, **106**, 5892 (1984).
39. See ref. 3e for a discussion of theoretically derived rotational barriers for Fischer-type metal carbenes.
40. S. Nakamura and A. Dedieu, *Theoret. Chim. Acta*, **64**, 461 (1984).
41. T. E. Taylor and M. B. Hall, *J. Am. Chem. Soc.*, **106**, 1576 (1984).
42. J. D. Fellmann, G. A. Rupprecht, C. D. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, **100**, 5964 (1978).
43. A. K. Rappe and W. A. Goddard, III, *J. Am. Chem. Soc.*, **104**, 448 (1982).
44. A. K. Rappe and W. A. Goddard, III, *J. Am. Chem. Soc.*, **104**, 3287 (1982).
45. S. Nakaura and A. Dedieu, *Nouv. J. Chim.*, **6**, 23 (1982).
46. A. Dedieu and O. Eisenstein, *Nouv. J. Chim.*, **6**, 337 (1982).
47. N. Koga, S. Obara, K. Kitaura, and K. Morokuma, *J. Am. Chem. Soc.*, **107**, 7109 (1985).
48. H. Fujimoto and T. Yamasaki, *J. Am. Chem. Soc.*, **108**, 578 (1986).