

Molecular Orbital Theory of the Properties of Inorganic and Organometallic Compounds 5. Extended Basis Sets for First-Row Transition Metals

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A series of efficient split-valence basis sets for first-row transition metals, termed 3-21G, has been constructed based on previously-formulated minimal expansions of Huzinaga, in which each atomic orbital has been represented by a sum of three gaussians. The original Huzinaga expansions for s- and p-type orbitals (except those for ls) have been fit by least squares to new three-gaussian combinations in which the two sets of orbitals (of the same n quantum number) share gaussian exponents. The Huzinaga three-gaussian expansions for ls and 3d atomic orbitals have been employed without alteration. The valence description of the 3-21G basis sets comprises 3d-, 4s- and 4p-type functions, each of which has been split into two- and one-gaussian parts. 4p functions, while not populated in the ground state of the free atoms, are believed to be important to 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 inorganic and organometallic compounds containing first-row transition metals. Calculated equilibrium structures, while generally superior to those obtained at STO-3G, are not as good as those for compounds containing main-group elements only. The calculations generally underestimate the lengths of double bonds between transition metals and main-group elements, and overestimate the lengths of single linkages. Calculated normal-mode vibrational frequencies for metal-containing systems are less uniform than in those for main-group compounds.

INTRODUCTION

Hartree–Fock molecular orbital theory has now been widely and successfully applied to the calculation of the properties of molecules incorporating main-group elements.¹ Even simple minimal basis sets, such as STO-3G² have proven to be capable of reproducing a wide variety of experimental equilibrium structures to a reasonable degree of accuracy. More flexible split-valence basis sets, such as the 3-21G representation³, 3-21G^(*) for second- and higher-row elements^{3c,d}, fare even better in the task of structure determination. In addition, theoretical treatments at this level are moderately successful in describing molecular vibrational frequencies, as well as relative isomer energies and electric dipole moments. Larger representations, such as 6-31G* basis sets (presently available only for first- and second-row elements⁴ generally lead to further improvements in calculated properties for both normal- and hyper-valent molecules. In addition, they

appear to be among the simplest representations suitable for calculations beyond the single-determinant (Hartree–Fock) level.^{5,6}

There is much less experience with regard to the performance of simple non-empirical molecular orbital methods in describing the properties of molecules incorporating transition metals. Efforts in the development and application of *ab initio* molecular orbital theory to transition-metal systems have been reviewed through 1980 both by Schaefer⁷ and by Pietro and Hehre.⁸ Here, we update these reviews to include developments in this area which have occurred since 1981 for first-row transition metals.

The formulation of simple basis sets for the transition elements has proven to be a difficult process. It has, however, been possible to gain some degree of insight into the size and characteristics of a basis set needed to obtain a given level of accuracy by performing calculations on a variety of atomic and molecular systems. Such an approach is well illustrated

in the work of Huzinaga and coworkers⁹, who have systematically prepared a series of minimal and split-valence basis sets for transition-metal atoms, and have applied these representations to the calculation of atomic orbital energies. The minimal basis sets developed by Huzinaga (termed MINI-1, MINI-2, MINI-3 and MINI-4) differ in the number of expansion functions used to represent s-, p-, and d-type orbitals. The corresponding split-valence basis sets (termed MIDI-1, MIDI-2, MIDI-3 and MIDI-4) are formed from the minimal representations by splitting the outermost functions of each angular type into two parts. Unfortunately, relatively few applications of the Huzinaga basis sets to molecular systems have as yet appeared in the literature. The applications of the MINI basis sets to molecular systems incorporating transition metals which have been considered have, however, led Huzinaga to express optimism about the ability of representations of this size to closely reproduce experimental equilibrium geometries^{9d,e}.

STO-3G minimal basis sets for first- and second-row transition metals⁸ have been widely applied to the calculation of molecular properties, in particular, equilibrium geometries. These basis sets, like the analogous main-group representations², are formed as fits to Slater-type (exponential) functions, scaled to be suitable for use in molecular systems. It is now apparent that STO-3G 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 these representations lack the flexibility to properly describe the bonding in transition-metal-containing systems.

Gaussian basis sets of medium size (13s-, 7p-, and 5d-type functions,) have been obtained by Hyla-Kryspin, et al.¹⁰ for the elements of the first transition series. Rather than use the atomic ground state configuration of the metal atom, the authors chose a $3d^{n-1} 4s^1$ configuration for the atomic optimization procedure, since this was thought to better describe the metal atom in typical mo-

lecular environments. Rappé, Smedley, and Goddard¹¹ have used the large gaussian basis sets of Wachters¹² in creating flexible basis sets for the elements Sc through Cu, in which the d functions were optimized for the $3d^n$ state rather than for the $3d^{n-2} 4s^2$ state. The authors have concluded that five d primitive gaussians contracted to four- and one-gaussian parts (5/41) are ideally suited for routine molecular calculations. A contraction scheme for Fe and Ni has been devised by Pettersson and Wahlgren¹³, in which the large primitive gaussian basis sets of Roos and coworkers¹⁴ have been modified such that the core region is almost minimal (the 1s shell has been split,) the valence 4s and 4p orbitals are doubly split, and the 3d shell is triply split.

Aside from the minimal STO-3G representations, none of the basis sets developed thus far for transition metals have been constructed to take maximum advantage of advances in numerical algorithms for molecular orbital calculations. In particular, imposition of exponent constraints among gaussian functions of different angular type, i.e., s, p, d, but of the same n quantum number has been shown to lead to significant computational savings in the evaluation of the two-electron integrals which arise in atomic and molecular calculations.¹⁵ Clearly, basis set efficiency is an issue that needs to be seriously addressed before applications of non-empirical molecular orbital methods to transition-metal systems become routine.

APPLICATIONS TO MOLECULAR SYSTEMS

A. Transition-Metal Dimers and Related Small Systems

The driving force behind the study of transition-metal dimers has been the desire to understand the metal-metal bond, thereby helping to elucidate the role of transition metals in surface chemisorption and heterogeneous catalysis. Experimental work on the Cr_2 molecule¹⁶ has shown that the metal-metal bond is very short, 1.68 Å vs. 2.49 Å in the bulk metal, and hence presumably of considerable strength. Theoretical treatments of this molecule¹⁷ which range from the single-determinant (Hartree-Fock) level to calcu-

lations which involve CAS SCF/CI (complete active space SCF/configuration interaction) techniques, have, however, had difficulty in uncovering a bound state for the molecule. The most extensive calculations performed to date^{17e,f} suggest a shallow potential well centered near the experimental equilibrium distance, and suggest that both π - and δ -type molecular orbitals are involved to some degree in the overall bonding. The calculations have also suggested that it is important to include f-type functions in the basis set in order to achieve a proper description of the bonding. These same conclusions have also been reached in investigations of the electronic structure of the V_2 molecule^{17f,g}, although here there is less difficulty in reproducing the experimental bond distance, 1.757 Å.¹⁸ The best calculations yield values of 1.77 Å^{17f} and 1.79 Å.^{17g}

Ab initio calculations have also been performed on other dimers involving first-row transition metals. Extensive CAS SCF/CI calculations on Sc_2 by Walch and Bauschlicher¹⁹ have predicted a bond length of 2.79 Å for the $^5\Sigma_u^-$ state. A split-valence basis set was utilized by Tatewaki, Miyoshi, and Nakamura²⁰ to obtain an optimized CuCu bond length of 2.41 Å in copper dimer. This is to be compared with the experimental value of 2.22 Å.²¹ Correlated methods reduced this bond length to 2.32 Å²², still 0.1 Å longer than the experimental value. All of the theoretical studies carried out on this molecule have concluded that the single bond, which binds the two copper atoms, involves overlap of the 4s orbitals. Shim and Gingerich²³ utilized both Hartree-Fock and configuration interaction techniques to investigate the electronic structures of Fe_2 and Co_2 . The best of their calculations yielded bond distances of 2.40 Å and 2.43 Å for Fe_2 and Co_2 , respectively. The electronic states of NiFe were examined by Shim²⁴ with a limited configuration interaction method; this resulted in a predicted molecular ground state of $^5\Pi$ with a bond length of 2.46 Å. Minimal gaussian basis sets were recently used by Goldstein, Flores, and Hsia²⁵ to investigate the electronic structures of Fe_2 , FeMn, FeCo, FeCu, and FeNi. A correlation between the Mössbauer isomer shifts and calculated bond strengths was uncovered.

Binary compounds involving a first-row transition metal bonded to hydrogen or to a

main-group element have also been investigated at the *ab initio* level. The $^2\Delta$ ground state of NiH was examined both by Hartree-Fock and CI methods.²⁶ The most extensive calculations yielded NiH bond distances in the range of 1.47-1.50 Å, in reasonable agreement with the experimental value of 1.475 Å.²⁷ Using large gaussian basis sets which included 4p functions as well as f functions on the metals, Walch and Bauschlicher²⁸ performed CAS SCF/CI calculations on a series of transition metal hydrides, MH ($M = Ti, V, Cr, Mn, Fe, \text{ and } Ni$). The resulting equilibrium structures were in good accord with available experimental data. Schilling, *et al.*²⁹ analyzed the bonding in transition-metal hydride cations, MH^+ ($M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu \text{ and } Zn$) using the GVB (generalized valence bond) method. Calculated dissociation energies were in excellent agreement with experimental values. Bauschlicher and Walch³⁰ have obtained a bond length of 1.78 Å for the ScH molecule using both Hartree-Fock and CI levels. Harrison³¹ utilized GVB and MCSCF (multiconfiguration SCF) methods, coupled with CI techniques to study the electronic structures of ScH, ScF, and ScLi. A bond distance of 1.78 Å was calculated for ScH; the ScF molecule was indicated to be highly ionic with a bond length of 1.811 Å, in reasonable agreement with the experimental value of 1.787 Å.²⁷ However, a meaningful assignment of the ground-state configuration could not be made for ScLi. Calculations beyond the single-determinant level were performed on diatomic TiO³² and TiC.³³ The TiC molecule was best described as incorporating a polarized double bond, and TiO a triple bond. The best CI calculations on the $^1\Sigma^+$ state of NiS by Bauschlicher³⁴ yielded a bond distance of 2.11 Å and a description of the bond as a covalent interaction between the Ni 3d and the S 3p orbitals. Extensive gaussian basis sets plus the incorporation of correlation through the coupled-pair-formalism method have been used in examining the $^2\Pi$ state of both CuO and CuS molecules.³⁵ The bonding in both molecules was found to be essentially covalent at this level of theory. The calculations reproduced the experimental bond distances to reasonable accuracy.

MCSCF and CI techniques, using a basis set including f functions in the basis set for the metal, were used by Larsson, Roos,

and Siegbahn³⁶ to predict values for the d-d transition energies for the CuF₂ molecule. Shashkin and Goddard³⁷ have obtained a bond length of 1.781 Å for this same molecule (constrained to a linear geometry) using a CI method. CI calculations on the first few doublet states of CuO₂³⁸ have suggested a ground state of ²Π_g symmetry. Blomberg and Siegbahn³⁹ have obtained an optimized structure for NiH₂ with the aid of the multi-reference direct configuration interaction (MRDCI) method. NiH₂ is predicted to have a highly-bent geometry (NiH = 1.44 Å, ∠HNiH = 57°) in which the bonding involves significant d participation.

B. Coordination Compounds

The investigation of the bonding in transition metal coordination compounds continues to attract widespread attention from experimentalists and theorists alike. Of particular importance is understanding the role which metal ions have on the activity of biological systems.

In 1981, Miyoshi, *et al.*⁴⁰ carried out Hartree-Fock and CI calculations on CoF₆⁴⁻, CoF₆³⁻ and CoF₆²⁻, the purpose for which was to interpret both the d-d and charge-transfer transitions previously observed for these systems. Hexacyano complexes [M(CN)₆]³⁻ (*M* = Cr, Mn, Fe and Co) and [Fe(CN)₆]⁴⁻ have also been studied using large gaussian basis sets, but only at the single-determinant level.⁴¹ Calculated core-orbital energies and valence-shell ionization potentials were found to be in good agreement with experimental XPS (X-ray photoelectron spectroscopy) results. Kowalewski and coworkers⁴² have applied single-determinant Hartree-Fock methods to the investigation of paramagnetic hexaquo complexes, [M(H₂O)₆]²⁺ (*M* = Mn, Fe, Co, Ni, and Cu). The authors have discussed their results in terms of interactions between the nuclear spin of the ligand and the unpaired electron spin localized on the metal center. Minimal basis sets have been used in an *ab initio* study of tetragonally-distorted octahedral complexes of metal cations.⁴³ Potential energy surfaces for *trans*-MCl₂(NH₃)₄ (*M* = Co³⁺, Fe²⁺, Ni²⁺ and Zn²⁺) were obtained to investigate the electronic factors or metal-ion characteristics which bring about the experimentally-observed correlation of out-of-plane bond

lengths with in-plane distances in these systems.

C. Organometallic Chemistry

The rich chemistry of organometallic compounds offers the opportunity for theory to provide fundamental insights into the nature of the metal-carbon bond, as well as to the way in which metal complexation alters the structures and reactivities of the organic ligands. Both the experimental and theoretical subdisciplines are in their infancy and both stand to benefit from interaction.

Metal-carbonyl compounds provide a bridge between traditional coordination chemistry and the emerging organometallic area. Among the simplest systems is nickel tetracarbonyl; a number of Hartree-Fock level studies of which have recently appeared.⁴⁴⁻⁴⁶ The calculations by Spangler, *et al.*⁴⁴, using basis sets of double-zeta quality for all atoms, yields NiC bond lengths of 1.884 Å, to be compared to the experimental value of 1.836 Å.⁴⁷ A simpler calculation⁴⁵, which employs a minimal-basis description for nickel but split-valence representations for carbon and oxygen, does not fare as well, yielding NiC bond lengths of 1.920 Å (for fixed CO distances of 1.15 Å). Basis sets of varying size were employed by Faegri and Almlöf⁴⁶ to optimize the geometry of Ni(CO)₄. A double-zeta basis yielded a NiC bond length of 1.819 Å, only 0.017 Å shorter than the experimental value of 1.836 Å⁴⁷ and consistent with earlier work at a comparable level.⁴⁴ However, higher-level calculations utilizing a basis set of better than triple-zeta quality which included polarization *f* functions for Ni and polarization *d* functions for C and O, yielded a NiC bond distance of 1.921 Å.

In order to better understand the metal-carbonyl bond in Ni(CO)₄ as well as in Fe(CO)₅, Bauschlicher and Bagus⁴⁸ performed Hartree-Fock calculations coupled with the constrained-space-orbital-variation (CSOV) method on these molecules at their respective experimental geometries. They concluded that the metal-to-CO π* donation is energetically much more important than the CO-to-metal σ donation, and that the metal 4s and 4p orbitals make only a very small contribution to the interaction energy with the CO ligands. Bauschlicher⁴⁹ has also recently studied the bonding in Fe₂(CO)₉,

at the single-determinant level and with geometrical parameters fixed at the experimental values. Instead of a direct metal-metal bond, he concluded that the Fe atoms are held together by three-center Fe-(CO)-Fe bonds which include $d\pi^*$ donation into bridging CO π^* orbitals, as well as bridging CO σ donation into empty Fe d_π orbitals.

An *ab initio* calculation on tris (η^3 -allyl) chromium⁵⁰, including consideration of electron correlation, yielded orbital energies which were reasonably consistent with the interpretation of the photoelectron spectrum of this π complex.⁵⁰ Gaussian-lobe functions, based on either a minimal or a split-valence basis set, were used to calculate the angles of deviation of the hydrogen atoms out of the allyl plane of *trans*-bis (η^3 -allyl)-nickel.⁵¹ The theoretical results agreed well with a low-temperature neutron-diffraction study of the compound.⁵¹ Large, flexibly-contracted gaussian basis sets were used to obtain a structure for the eclipsed conformation of bis(cyclobutadiene) nickel.^{52a} These theoretical results must await comparison with a forthcoming crystal structure of the cyclobutadiene sandwich compound, $(\eta^4-C_4Ph_4)_2Ni$.^{52b} Experimental structures were employed for generalized molecular orbital (GMO) calculations on the diene complexes $(\eta^4-C_4H_4)Fe(CO)_3$, $(\eta^4-C_4H_4)CoCp$, $(\eta^4-C_4H_4)(CO)Fe(CO)_3$ and $(\eta^4-C_4H_4)(CO)CoCp$.⁵³ The diene—Co bond was reported to be more covalent than the diene—Fe bond, and deformation density plots showed a shift of electron density toward the diene in the more ionic diene—Fe $(CO)_3$ complexes.

Bond-dissociation energies for simple transition-metal methylene cations, MCH_2^+ , have been determined in recent gas-phase experiments.⁵⁴ Two theoretical studies quickly followed in order to examine the structure and bonding characteristics of the metal-carbon bond in these simple organometallic species. Vincent, Yoshloka, and Schaefer⁵⁵ have performed a Hartree-Fock study on the high-spin electronic states of $MnCH_2^+$ and $CrCH_2^+$, in which near triple-zeta basis sets were used for the metal atoms, while the CH_2 fragment was represented by a triple-zeta-plus-polarization basis set. Full structure optimizations on the 7B_1 state of $MnCH_2^+$ and the 6B_1 state of $CrCH_2^+$ yielded metal-carbon single bond distances of 2.076 Å and 2.064 Å for MnC and CrC, respectively. Additional CI

calculations were performed on these structures, leading to bond-dissociation energies of 36.0 kcal mol⁻¹ ($MnCH_2^+$; experimental value = 53 ± 5 kcal mol⁻¹⁵⁴ and 18.3 kcal mol⁻¹ ($CrCH_2^+$; experimental value = 65 ± 7 kcal mol⁻¹.⁵⁴ A more recent calculation on $CrCH_2^+$ has been carried out with the GVB method by Carter and Goddard.⁵⁶ The structure was optimized with a split-valence basis set, resulting in a 4B_1 ground state and a calculated CrC bond length of 1.91 Å. A covalent CrC double bond was predicted, with a calculated bond-dissociation energy of 44 kcal mol⁻¹, in better agreement with the experimental value than that previously determined.⁵⁵

Work by Kitaura, Sakaki and Morokuma⁵⁷, has resulted in partially optimized structures for $Ni(PH_3)_2(C_2H_4)$ and $Ni(PH_3)_2-(C_2H_2)$ (geometry of phosphine ligands based on the experimental structure of $Ni(PPh_3)_2(C_2H_4)$).⁵⁸ Analysis of the binding energies and electron distributions in these molecules revealed that π back donation was the major contributor to the total metal-olefin binding interaction. In their analysis (via the GVB method) of $Cl_2Ti(C_2H_4)$, Steigerwald and Goddard⁵⁹ concluded that a metallocyclopropane structure was preferred over the π -complex form, and that the reactivity of the TiC bonds resulted from relieving the strain of the three-membered ring. Other metallocyclic complexes that have received attention from theorists are $Cl_2TiCH_2CH_2CH_2$ ⁶⁰ and $H_2TiCH_2AlH_2Cl$.⁶¹ GVB calculations on the former complex have indicated that the metallocyclobutane incorporates a planar skeleton, but one which is easily deformable. Metal-alkyl bonds in these systems were indicated to be essentially covalent, composed primarily of d orbitals on the metal. The calculated (STO-3G) structure for H_2Ti-CH_2/AlH_2Cl (a model for the Tebbe reagent) supports description in terms of a strong intramolecular complex rather than as implied above, an intermolecular metal-carbene/Lewis acid adduct; this, in turn, has led to the suggestion that reactions with this reagent do not involve a free alkylidene, i.e., dissociated from the Lewis acid, but rather a displacement mechanism.

Morokuma and coworkers have performed energy-decomposition analyses on two carbon dioxide complexes, $Ni(PH_3)_2(CO_2)$ and $[Cu$

$(\text{PH}_3)_2(\text{CO}_2)]^+$ ⁶², as well as on the related systems, $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$ and $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$.⁶³ In the first study, the side-on mode of coordination for CO_2 was determined to be the most stable for the Ni complex, whereas the CO_2 ligand in the Cu complex coordinated in an end-on fashion. The former coordination mode was explained as the result of the Lewis basicity of the $\text{Ni}(\text{PH}_3)_2$ fragment enhancing the back-bonding interaction, while the positive charge on $\text{Cu}(\text{PH}_3)_2^+$ was found to enhance the electrostatic interaction. The analysis for $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$ determined that a pseudotetrahedral structure was more stable than a planar arrangement, while for $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$, the most stable structure was found to be planar, in which the H_2CO ligand coordinated in a side-on fashion.

The first *ab initio* molecular orbital calculation of a transition-metal carbene complex was performed by Spangler, *et al.*⁴⁴ on $(\text{CO})_3\text{Ni}=\text{CH}_2$; here, the only optimized parameters were the NiC bond and the HCH angle. Subsequent systematic theoretical studies of a variety of metal-carbenes by Franci, *et al.*⁶⁴ have shown that planar carbene structures are favored over the corresponding perpendicular conformations, and that distorted structures of metal carbenes are the result of electron donation of the alkylidene CH bonding pair into a vacant orbital on the metal. In addition, the theoretical investigations have suggested that π bonds between carbon and transition metals may be stronger than those found in analogous main-group compounds. More recent Hartree Fock investigations of molecules incorporating metal-carbon multiple bonds have been reported by Nakatsuji and coworkers.⁶⁵ One study^{65a} examined the structures and reactivities of the Fischer-type carbenes, $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$ and $(\text{CO})_4\text{Fe}=\text{CH}(\text{OH})$, using minimal basis sets for all atoms. Low rotational barriers of $0.4 \text{ kcal mol}^{-1}$ and $2.9 \text{ kcal mol}^{-1}$ were found for $\text{Cr}=\text{C}$ and $\text{Fe}=\text{C}$, and explained to result from the degeneracy of the $d\pi$ -type lone pair orbitals of the metal fragment. The reactivity of the carbene carbon toward nucleophiles was interpreted as being frontier-orbital controlled rather than charge controlled. The Fischer-type carbyne complexes, $\text{Cl}(\text{CO})_4\text{Cr}\equiv\text{CH}$ and $[(\text{CO})_5\text{Cr}\equiv\text{CH}]^+$ ^{65b} were also studied using a minimal basis sets the Hartree-Fock

level. Frontier-orbital arguments were invoked to interpret the reactivities of these metal-carbyne complexes.

In their study of $\text{Ti}(\text{C}_2\text{H}_5)(\text{PH}_3)_2(\text{Cl})_2(\text{H})$, Morokuma and coworkers⁶⁶ provided the first theoretical evidence of intramolecular CH activation by a transition metal. This system was chosen to simulate the structurally-characterized complex, $\text{Ti}(\text{C}_2\text{H}_5)(\text{dmpe})(\text{Cl})_3$ (dmpe = dimethylphosphinoethane).⁶⁷ A subsequent study by these same investigators⁶⁸ on a similar complex, in which the ethyl group was replaced by a methyl group, again revealed significant intramolecular $\text{CH}\cdots\text{M}$ interaction. The most recent work in this area by Morokuma and coworkers⁶⁹, examined the role of agostic interaction in β -elimination by way of Hartree-Fock calculations on $\text{Ni}(\text{C}_2\text{H}_5)(\text{H})-(\text{PH}_3)_3$, and on the corresponding β -elimination product, $\text{Ni}(\text{C}_2\text{H}_4)-(\text{H})_2(\text{PH}_3)_3$. The authors concluded that a small agostic interaction exists for the Ni-ethyl complex, and furthermore, that the Ni-ethylene complex would more likely undergo an insertion reaction in contrast to the preference of the Ni-ethyl complex to undergo β -elimination.

Theoretical models have also been used to examine proposed reaction mechanisms in which an organotransition metal complex may play an active role. High-valent complexes of Cr (also, Mo and W) were studied using the GVB method by Rappé and Goddard⁷⁰ in order to provide some mechanistic insight for olefin metathesis. Oxoalkylidene-metal complexes were suggested to be the stable metathesis catalysts, and the oxygen ligand of these complexes were determined to be intimately involved in the catalytic process. These same authors performed a similar mechanistic study for hydrocarbon oxidation by chromyl chloride, CrO_2Cl_2 ⁷¹, and suggested that the second oxo group plays a key role in stabilizing critical intermediates. The mechanism of formation of CH_3CuH , from the photochemical reaction of metallic copper trapped in a low-temperature methane matrix⁷², has been discussed by Poirier, *et al.*⁷³ Steigerwald and Goddard⁷⁴ utilized the GVB method to analyze the activation energies and transition-state geometries for reactions of D_2 with Cl_2TiH^+ , Cl_2TiH , and Cl_2SCH . These theoretical models for organometallic exchange and insertion pro-

cesses suggested that a four-center concerted mechanism is likely, and that an increase in the metal d character of the MH bond should lead to a decrease in the activation barrier. The reactivities of metal-carbon and metal-hydrogen bonds were investigated by Fujimoto and coworkers⁷⁵ in their analysis of a cyclic reaction model for insertion of C_2H_4 into the TiC and TiH bonds of $CH_3TiCl_2^+$ and $HTiCl_2^+$, respectively. By considering the orbitals of the olefin and of the metal system as fragments of a four-center transition state for insertion, they concluded that insertion is facilitated by the presence of low-lying unoccupied orbitals which have significant metal d character.

D. Assessment of the Performance of Hartree-Fock Models in Describing the Properties of Transition-Metal Inorganic and Organometallic Systems

Discussion of the application of quantum mechanical methods to the study of transition-metal inorganic and organometallic systems is not complete without mention of the criticism that the single-determinant Hartree-Fock method has received in the literature. For example, Lüthi, Ammeter, Almlöf, and Faegri⁷⁶ have performed Hartree-Fock calculations on both ferrocene and decamethylferrocene with a series of basis sets ranging from single-zeta to better than triple-zeta quality. The best value calculated for the metal-ring distance, 1.88 Å (for both molecules), was 0.23 Å longer than the experimental distance of 1.65 Å⁷⁷ in ferrocene. Almlöf, Faegri, Schilling, and Lüthi⁷⁸ used double-zeta basis sets to optimize the metal-ring distances for the dicyclopentadienyl complexes, Cp_2M ($M=V, Mn, Co$, and Ni) and Cp_2^{M+} ($M=Fe$ and Co), as well as for $CpNi(NO)$. Their results did not agree well with the corresponding experimental values (the smallest error was still 0.1 Å,) and the authors suggested that charge-transfer effects need to be considered in applying correlation methods to these molecules. As previously mentioned, basis sets of varying size were employed by Faegri and Almlöf to optimize the geometry of $Ni(CO)_4$.⁴⁶ The authors concluded that very extensive basis sets were required to achieve stable results for geometrical parameters, and the final (Hartree-Fock) geometries may not com-

pare favorably with experimental values. Lüthi, Siegbahn, Almlöf, Faegri, and Heiberg⁷⁹ have shown that large-scale MCSCF and CI calculations on ferrocene yield a metal ring distance of 1.73 Å, overestimating the experimental value of 1.65 Å. In their concluding remarks, the authors pointed out that the poor agreement between theory and experiment is not a basis set effect, but rather a manifestation of the inadequacies of the Hartree-Fock model itself to properly account for the covalent character of the metal-ligand bond. Essentially the same conclusion was recently echoed by Taylor and Hall⁸⁰, who performed GMO and CI calculations on ferrocene and obtained a similar metal-ring distance (1.720 Å).

One cannot contest the fact that these calculations on cyclopentadienyl systems as well as on nickel tetracarbonyl represent impressive computational efforts. We are, however, not ready to accept the general conclusion about the poor performance of Hartree-Fock methods for the description of equilibrium geometry of organometallic systems, especially since this conclusion is based on a very limited selection of molecules. Further systematic studies are needed before final judgement is made about the applicability of the Hartree-Fock method to organometallic systems.

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

Development of 3-21G split-valence basis set for first-row transition metals proceeds along similar lines to the previous development of the corresponding basis sets for main-group elements.³ In particular, functions which comprise the valence shell are split into two (inner and outer) parts, while inner-shell atomic orbitals are each represented by a single basis function. 3-21G basis sets for first-row transition metals comprise $3d$, $4s$ and $4p$ valence functions, 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}
 3d''_{xx}, 3d''_{yy}, 3d''_{zz}, 3d''_{xy}, 3d''_{xz}, 3d''_{yz}
 4s', 4p'_x, 4p'_y, 4p'_z
 4s'', 4p''_x, 4p''_y, 4p''_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.,

$$\begin{aligned}\phi_{1s}(r) &= \sum_{k=1}^3 d_{1s,k} g_s(\alpha_{1,k}, r) \\ \phi_{2s}(r) &= \sum_{k=1}^3 d_{2s,k} g_s(\alpha_{2sp,k}, r) \\ \phi_{2p}(r) &= \sum_{k=1}^3 d_{2p,k} g_p(\alpha_{2sp,k}, r) \\ \phi_{3s}(r) &= \sum_{k=1}^3 d_{3s,k} g_s(\alpha_{3sp,k}, r) \\ \phi_{3p}(r) &= \sum_{k=1}^3 d_{3p,k} g_p(\alpha_{3sp,k}, r) \\ \phi'_{3d}(r) &= \sum_{k=1}^2 d'_{3d,k} g_d(\alpha'_{3d,k}, r) \\ \phi'_{4s}(r) &= \sum_{k=1}^2 d'_{4s,k} g_s(\alpha'_{4sp,k}, r) \\ \phi'_{4p}(r) &= \sum_{k=1}^2 d'_{4p,k} g_p(\alpha'_{4sp,k}, r) \\ \phi''_{3d}(r) &= g_d(\alpha''_{3d}, r) \\ \phi''_{4s}(r) &= g_s(\alpha''_{4sp}, r) \\ \phi''_{4p}(r) &= g_p(\alpha''_{4sp}, r)\end{aligned}$$

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.,

$$\begin{aligned}g_s(\alpha, r) &= (2\alpha/\pi)^{3/4} \exp(-\alpha r^2) \\ g_x(\alpha, r) &= (128\alpha^5/\pi)^{1/4} x \exp(-\alpha r^2) \\ g_{xx}(\alpha, r) &= (2048\alpha^7/9\pi^3)^{1/4} x^2 \exp(-\alpha r^2)\end{aligned}$$

with similar expressions for the remaining p - and d -type functions. For computational efficiency,¹⁵ 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.³ A different set of gaussians has, however, been used to construct the $3d$ atomic orbitals than are employed for $3s$ and $3p$ functions. The radial distributions of these two sets ($3s$ and $3p$ making up the inner shell of a transition metal and $3d$ the valence shell)

are too different to be adequately fit by a single constrained expansion.

Paralleling our previous efforts for third- and fourth-row main-group elements^{3d}, 3-21G representations for first-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.^{9d} 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.^{9d} Atomic-ground-state functions have been used for all elements except chromium and copper. Here excited state configurations, $3d^4 4s^2$ and $3d^9 4s^2$, respectively, have been employed. Thus, the entire transition series is fitted to a uniform series of atomic wavefunctions in which the $4s$ orbital is doubly occupied. Expansions representing $1s$ orbitals are taken as is. Those describing $3d$ orbitals are split into two-gaussian (the two largest gaussian exponents) and one-gaussian parts, and then renormalized. This is the procedure recommended by Huzinaga for development of split-valence basis sets from the minimal representations.^{9d}

Expansions describing $2s$, $2p$, $3s$ and $3p$ atomic orbitals are modified somewhat from those provided by Huzinaga. Specifically, all 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-squares 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 from the original Huzinaga representations.^{3d}

$4s$ and $4p$ atomic orbitals are handled in a similar manner. In particular, the Huzinaga three-gaussian expansions for $4s$ ^{9d}, as well as the single-gaussian $4p$ orbital recommended by Huzinaga for use as polarization functions^{9d} 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, 1*s* functions (already provided by Huzinaga^{9d}) have also been included in the tabulation.

PERFORMANCE OF 3-21G BASIS SETS

3-21G basis sets for main-group elements have found widespread use for the calculation of equilibrium structures, relative energies, normal-mode vibrational frequencies and electric dipole moments. The model is computationally simple and broadly applicable to molecules incorporating five to ten heavy (non-hydrogen) atoms. Calculations for molecules incorporating first-row transition metals are more difficult, and the scope of applications is necessarily more limited. Even so, enough comparisons with experimental structures and vibrational frequencies exist to enable thorough assessment of its performance. Experimental relative energy and dipole moment data on transition-metal inorganic and organometallic systems are more scarce, and comparisons with calculated quantities will not be undertaken at this time.

A. Transition-Metal Inorganic Compounds

3-21G equilibrium structures for a number of inorganic compounds incorporating a first-row transition metal are compared to experimental geometries in Table II. The 3-21G basis set has been employed, in lieu of 3-21G^(*), for second-row elements. Limited calculations have been performed using 3-21G^(*) basis sets for second-row atoms, the results of which are also provided in the table.

Calculated bond lengths between fluorine and a transition-metal center are consistently shorter than experimental values, sometimes significantly so, e.g., by 0.140 Å in CuF. Trends in metal-fluorine bond lengths are, however, more favorably handled. For example, the calculations show that the axial VF bond distances in VF₅ are 0.022 Å longer than the equatorial lengths, in reasonable agreement with the experimental difference of 0.031 Å. Calculated bond distances to chlo-

rine are, on the other hand, consistently longer than experimental values, although the errors here are generally modest relative to those for metal-fluorine lengths. The bond length in CuCl obtained from use of the 3-21G^(*) basis set on chlorine is, on the other hand, significantly shorter than the experimental distance. Metal-oxygen double bond lengths are consistently underestimated at the 3-21G level, errors ranging from a minimum of 0.049 Å (in VOF₃) to a maximum of 0.079 Å (in CrO₂Cl₂). The length of the vanadium-nitrogen linkage in ClNVC1₃ is underestimated by 0.1 Å. Overall, the mean absolute deviation of 3-21G from experimental bond lengths (connecting heavy atoms) is 0.055 Å.

Bond angles calculated using 3-21G basis set are in good accord with experimental values. Thus, the theory at this level is capable of reproducing experimental skeletal geometry.

STO-3G equilibrium geometries, also included in Table II, are generally (but not always) inferior to 3-21G structures. Differences are particularly large for multiple-bond lengths, where the minimal basis set method underestimates the experimental distances by 0.1 Å or more. The mean absolute deviation of STO-3G from experimental bond lengths (connecting heavy atoms) is 0.088 Å, considerably larger than the corresponding average error found in comparisons involving the 3-21G basis set.

Normal-mode vibrational frequencies for the transition-metal inorganic compounds obtained at the 3-21G level are compared to experimental values in Table III. With few exceptions, the calculated frequencies are larger than experimental values. The range of errors, from 7% below the experimental value to 33% above, is too large to encourage the use of theory at this level for frequency assignments. While part of the problem no doubt lies in the restriction to single determinant wavefunctions, we suspect that the extreme electron deficiency of some of the systems leads to potential surfaces which deviate significantly from quadratic.⁸¹

B. Metal Carbonyl Complexes

Calculated 3-21G level equilibrium geometries for a small selection of transition-metal carbonyls, carbonyl nitrosyl and carbonyl hy-

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

Atom	Shell	α	d_s	d_p	d_d
Sc	1s	2.119887 (+03)	6.442080 (-02)		
		3.204299 (+02)	3.791603 (-01)		
		6.989893 (+01)	6.789629 (-01)		
	2sp	8.976450 (+01)	-1.093837 (-01)	1.363278 (-01)	
		1.938510 (+01)	1.050699 (-01)	5.418598 (-01)	
		5.731423	9.522045 (-01)	4.950551 (-01)	
	3sp	5.491938	-2.852107 (-01)	1.761356 (-02)	
		1.743742	3.241555 (-01)	4.336448 (-01)	
		5.662273 (-01)	8.565921 (-01)	6.425507 (-01)	
	3d'	5.722215			2.652364 (-01)
		1.360849			8.558605 (-01)
	3d''	3.226516 (-01)			1.0
		5.168015 (-01)	-2.626780 (-01)	3.270567 (-04)	
	4sp'	6.721404 (-02)	1.108079	9.998935 (-01)	
Ti	4sp''	2.598452 (-02)	1.0	1.0	
	1s	2.335020 (+03)	6.421660 (-02)		
		3.530441 (+02)	3.784120 (-01)		
		7.705845 (+01)	6.796813 (-01)		
	2sp	9.957387 (+01)	-1.094719 (-01)	1.372966 (-01)	
		2.154671 (+01)	1.019427 (-01)	5.458753 (-01)	
		6.413965	9.546224 (-01)	4.890681 (-01)	
	3sp	6.238279	-2.861372 (-01)	1.923665 (-02)	
		1.996108	3.218278 (-01)	4.404422 (-01)	
		6.464899 (-01)	8.595511 (-01)	6.356195 (-01)	
	3d'	7.083666			2.629210 (-01)
		1.709634			8.557721 (-01)
	3d''	4.141225 (-01)			1.0
		5.732849 (-01)	-2.424500 (-01)	2.920158 (-04)	
V	4sp'	7.311942 (-02)	1.100075	9.999067 (-01)	
	4sp''	2.653794 (-02)	1.0	1.0	
	1s	2.563877 (+03)	6.394750 (-02)		
		3.875340 (+02)	3.775940 (-01)		
		8.459823 (+01)	6.805421 (-01)		
	2sp	1.097938 (+02)	-1.098355 (-01)	1.384210 (-01)	
		2.376921 (+01)	1.007070 (-01)	5.504894 (-01)	
		7.122961	9.556327 (-01)	4.824165 (-01)	
	3sp	6.981204	-2.884588 (-01)	2.182075 (-02)	
		2.219839	3.364357 (-01)	4.567616 (-01)	
		7.198030 (-01)	8.481903 (-01)	6.186750 (-01)	
	3d'	8.342917			2.640620 (-01)
		2.032944			8.539665 (-01)
	3d''	4.957115 (-01)			1.0
		6.312620 (-01)	-2.364899 (-01)	1.899536 (-04)	
Cr	4sp'	8.006166 (-02)	1.097721	9.999396 (-01)	
	4sp''	2.886489 (-02)	1.0	1.0	
	1s	2.798294 (+03)	6.382380 (-02)		
		4.231370 (+02)	3.770840 (-01)		
		9.243886 (+01)	6.809889 (-01)		
	2sp	1.202806 (+02)	-1.177790 (-01)	1.398782 (-01)	
		2.603727 (+01)	1.014311 (-01)	5.559834 (-01)	
		7.844172	9.571981 (-01)	4.748183 (-01)	
	3sp	7.793276	-2.888567 (-01)	2.218471 (-02)	
		2.497196	3.351147 (-01)	4.616250 (-01)	
		8.051419 (-01)	8.502481 (-01)	6.145386 (-01)	
	3d'	9.625339			2.655959 (-01)
		2.362264			8.521557 (-01)
	3d''	5.770944 (-01)			1.0
		7.039206 (-01)	-2.322508 (-01)	1.799645 (-04)	
	4sp'	8.616195 (-02)	1.093671	9.999448 (-01)	
	4sp''	3.219882 (-02)	1.0	1.0	

Table I. (Continued)

Atom	Shell	α	d_s	d_p	d_d
Mn	1s	3.041686 (+03)	6.374490 (-02)		
		4.600901 (+02)	3.767490 (-01)		
		1.005958 (+02)	6.812474 (-01)		
	2sp	1.317673 (+02)	-1.102964 (-01)	1.404540 (-01)	
		2.856915 (+01)	9.818963 (-02)	5.578022 (-01)	
		8.660501	9.576595 (-01)	4.715006 (-01)	
	3sp	8.569081	-2.917135 (-01)	2.422379 (-02)	
		2.768178	3.439630 (-01)	4.686598 (-01)	
		8.872882 (-01)	8.451975 (-01)	6.074211 (-01)	
	3d'	1.106884 (+01)			2.652718 (-01)
		2.730707			8.517945 (-01)
	3d''	6.685095 (-01)			1.0
	4sp'	7.674426 (-01)	-2.300039 (-01)	3.078886 (-04)	
		9.202527 (-02)	1.091450	9.999074 (-01)	
	4sp''	3.326490 (-02)	1.0	1.0	
Fe	1s	3.299184 (+03)	6.358590 (-02)		
		4.990886 (+02)	3.762016 (-01)		
		1.091614 (+02)	6.817845 (-01)		
	2sp	1.434652 (+02)	-1.105517 (-01)	1.411006 (-01)	
		3.116858 (+01)	9.684681 (-02)	5.603874 (-01)	
		9.483612	9.587974 (-01)	4.676444 (-01)	
	3sp	9.464565	-2.920555 (-01)	2.376201 (-02)	
		3.100373	3.375236 (-01)	4.689113 (-01)	
		9.864930 (-01)	8.519416 (-01)	6.083113 (-01)	
	3d'	1.235449 (+01)			2.686110 (-01)
		3.055605			8.492717 (-01)
	3d''	7.385909 (-01)			1.0
	4sp'	8.534123 (-01)	-2.279441 (-01)	-4.262652 (-04)	
		9.881222 (-02)	1.088287	1.000124	
	4sp''	3.644214 (-02)	1.0	1.0	
Co	1s	3.564762 (+03)	6.348660 (-02)		
		5.393908 (+02)	3.758181 (-01)		
		1.180449 (+02)	6.821217 (-01)		
	2sp	1.554382 (+02)	-1.109867 (-01)	1.420642 (-01)	
		3.381561 (+01)	9.676742 (-02)	5.634439 (-01)	
		1.033323 (+01)	9.589921 (-01)	4.630244 (-01)	
	3sp	1.038152 (+01)	-2.922622 (-01)	2.631326 (-02)	
		3.382714	3.432507 (-01)	4.769170 (-01)	
		1.076954	8.469634 (-01)	5.991543 (-01)	
	3d'	1.374070 (+01)			2.709550 (-01)
		3.408983			8.473421 (-01)
	3d''	8.186409 (-01)			1.0
	4sp'	9.090155 (-01)	-2.174599 (-01)	2.284428 (-04)	
		1.050406 (-01)	1.084998	9.999337 (-01)	
	4sp''	3.725658 (-02)	1.0	1.0	
Ni	1s	3.848005 (+03)	6.326610 (-02)		
		5.820307 (+02)	3.751710 (-01)		
		1.273674 (+02)	1.828238 (-01)		
	2sp	1.682896 (+02)	-1.111151 (-01)	1.424905 (-01)	
		3.665633 (+01)	9.532380 (-02)	5.655470 (-01)	
		1.123212 (+01)	9.601613 (-01)	4.599926 (-01)	
	3sp	1.135877 (+01)	-2.920604 (-01)	1.613762 (-02)	
		3.738846	3.375407 (-01)	4.765980 (-01)	
		1.182463	8.525330 (-01)	6.003798 (-01)	
	3d'	1.522069 (+01)			2.726060 (-01)
		3.786020			8.459279 (-01)
	3d''	9.045574 (-01)			1.0
	4sp'	9.889038 (-01)	-2.136872 (-01)	2.943514 (-04)	
		1.110250 (-01)	1.081933	9.999170 (-01)	
	4sp''	3.925822 (-02)	1.0	1.0	

Table I. (Continued)

Atom	Shell	α	d_s	d_p	d_d
Cu	1s	4.134302 (+03)	6.318780 (-02)		
		6.254912 (+02)	3.748448 (-01)		
		1.369556 (+02)	6.831002 (-01)		
	2sp	1.814960 (+02)	-1.113198 (-01)	1.430844 (-01)	
		3.957431 (+01)	9.448679 (-02)	5.677561 (-01)	
		1.216246 (+01)	9.608790 (-01)	4.567141 (-01)	
	3sp	1.235111 (+01)	-2.922231 (-01)	2.772714 (-02)	
		4.049651	3.429909 (-01)	4.835244 (-01)	
		1.279225	8.479463 (-01)	5.929779 (-01)	
	3d'	1.675938 (+01)			2.741125 (-01)
		4.178977			8.446245 (-01)
	3d''	9.943270 (-01)			1.0
	4sp'	1.049804	-2.065079 (-01)	1.385032 (-04)	
		1.169329 (-01)	1.079273	9.999613 (-01)	
Zn	4sp''	7.506963 (-04)	1.0	1.0	
	1s	4.432288 (+03)	6.309280 (-02)		
		6.706601 (+02)	3.745038 (-01)		
		1.469024 (+02)	6.834160 (-01)		
	2sp	1.950042 (+02)	-1.116283 (-01)	1.438055 (-01)	
		4.256889 (+01)	9.433553 (-02)	5.700019 (-01)	
		1.312143 (+01)	9.611002 (-01)	4.533119 (-01)	
	3sp	1.340231 (+01)	-2.917811 (-01)	2.870528 (-02)	
		4.399906	3.426145 (-01)	4.862515 (-01)	
		1.385148	8.482840 (-01)	5.902353 (-01)	
	3d'	1.836820 (+01)			2.753856 (-01)
		4.591304			8.434773 (-01)
	3d''	1.090203			1.0
	4sp'	1.121558	-2.023706 (-01)	3.440941 (-04)	
		1.229436 (-01)	1.077035	9.999053 (-01)	
	4sp''	4.219327 (-02)	1.0	1.0	

drude complexes are compared to experimental structures in Table IV. The method does remarkably well in reproducing the metal-carbon distances in nickel tetracarbonyl, especially when compared to the performance of the minimal basis set STO-3G model. As indicated earlier, this result is fortuitous; more complete Hartree-Fock treatments yield coordinate bond distances a tenth of an Angström greater than the experimental value.³⁴ The performance of the simple model for iron pentacarbonyl is more typical and much less impressive. Experimentally, both axial and equatorial metal-carbon bond lengths are essentially the same; the calculations closely reproduce the equatorial distances but overestimate the axial lengths by nearly 0.2 Å. Metal-hydrogen bond lengths are also poorly reproduced at the 3-21G level, overestimating experimental values by more than 0.1 Å. The mean absolute deviation of 3-21G from experimental bond lengths for these compounds is 0.105 Å which is about twice the error associated with

calculations at the 3-21G level (0.055 Å) for the transition-metal inorganic molecules.

Normal-mode vibrational frequencies calculated for nickel tetracarbonyl are compared to experimental values in Table V. As with previous comparisons (Table III) the data here are less uniform than frequencies obtained at the corresponding levels for main-group compounds. Again we suspect that the anharmonicity of the potential surface plays a role.

C. Transition-Metal Organometallics

Table VI compares calculated and experimental equilibrium structures for a few simple organometallics. Only mononuclear systems have been considered, and only those described in terms of singlet electronic ground states.

The 3-21G model fares well in describing lengths to metal-bonded methyl groups. Examples involving titanium, copper and zinc are available and all show comparable re-

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

Molecule	Point Group	Geometrical Parameter	STO-3G	3-21G	Expt.
ScF	C _{∞v}	r(ScF)	1.845	1.775	1.787 ^a
ScF ₃	D _{3h}	r(ScF)	1.852	1.812	1.91 ^b
TiF ₄	T _d	r(TiF)	1.701	1.719	1.745 ^c
TiCl ₄	T _d	r(TiCl)	2.167	2.186	2.170 ^b
VOF ₃	C _{3v}	r(VO)	1.494	1.520	1.569 ^d
		r(VF)	1.619	1.687	1.729
		∠(FVF)	108.7	110.4	111.2
VOCl ₃	C _{3v}	r(VO)	1.465	1.511	1.570 ^e
		r(VCl)	2.108	2.157	2.142
		∠(ClVCl)	110.1	110.7	111.3
VF ₅	D _{3h}	r(VF _{ax})	1.648	1.695	1.734 ^f
		r(VF _{eq})	1.616	1.673	1.703
ClNVCl ₃	C _s	r(VN)	1.526	1.553	1.651 ^g
		r(VCl)	2.111	2.186	2.138
		r(NCl)	1.715	1.705	1.597
		∠(ClNV)	179.9	178.9	169.7
		∠(NVCl)	109.9	106.6	106.0
		∠(ClVCl)	109.0	112.2	113.4
CrO ₂ F ₂	C _{2v}	r(CrO)	1.442	1.506	1.575 ^h
		r(CrF)	1.584	1.670	1.720
		∠(OCrO)	109.6	108.6	107.8
		∠(FCrF)	106.8	109.8	111.9
CrO ₂ Cl ₂	C _{2v}	r(CrO)	1.425	1.502	1.581 ⁱ
		r(CrCl)	2.091	2.160	2.126
		∠(OCrO)	106.6	107.3	108.5
		∠(ClCrCl)	110.2	112.7	113.3
CrO ₄ ²⁻	T _d	r(CrO)	1.520	1.604	1.66 ^b
MnO ₄ ⁻	T _d	r(MnO)	1.455	1.552	1.629 ^j
CuH	C _{∞v}	r(CuH)		1.382	1.462 ^a
CuF	C _{∞v}	r(CuF)	1.595	1.605	1.745 ^a
CuCl	C _{∞v}	r(CuCl)	2.071	2.093	2.051 ^a
				(1.957) ^k	

^a Ref. 27.^b J. 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.^c *Spectroscopic Properties of Inorganic and Organometallic Compounds*, Vol. 16, The Royal Society of Chemistry, The Garden City Press Limited, London, 1984, p. 362.^d A. Almennigen, S. Samdal and D. Christen, *J. Mol. Struct.*, **48**, 69 (1978).^e K.-I. Karakida and K. Kuchitsu, *Inorg. Chim. Acta*, **13**, 113 (1975).^f K. Hagen, M. M. Gilbert, L. Hedberg and K. Hedberg, *Inorg. Chem.*, **21**, 2690 (1982).^g *Molecular Structure by Diffraction Methods*, Vol. 4, The Chemical Society, Adlard & Son, Ltd., Bartholomew Press, Dorking, 1976, p. 15.^h R. J. French, L. Hedberg, K. Hedberg, G. L. Gard and B. M. Johnson, *Inorg. Chem.*, **22**, 892 (1983).ⁱ C. J. Marsden, L. Hedberg and K. Hedberg, *Inorg. Chem.*, **21**, 1115 (1982).^j G. J. Palenik, *Inorg. Chem.*, **6**, 503 (1967).^k Value in parentheses corresponds to use of the 3-21G^(**) basis set on chlorine.

sults. In contrast, the performance of the STO-3G model is poor (except in the titanium system). The nickel-carbon distance in CpNi(NO) calculated at the 3-21G level also agrees well with the experimental value; however, the nickel-nitrogen bond length is almost 0.1 Å longer than the experimental value. Overall, the mean absolute deviation of 3-21G from experimental bond distances for this small group of organometallic compounds is 0.052 Å.

Calculated normal-mode vibrational frequencies of dimethyl zinc are compared to the experimental values in Table VII. The experimental vibrational data has been interpreted for a molecule with a linear carbon-metal-carbon structure. The calculations constrained to a linear skeletal geometry reveal imaginary frequencies corresponding to CZnC bending. Removal of the D_{3h} symmetry constraint resulted in a C_{2v} symmetry structure incorporating a CZnC angle of 171.0°. It

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

Molecule	Symmetry of Mode	Description of Mode	Frequency	
			3-21G	Expt. ^a
ScF			860	736
TiCl ₄	a ₁	sym. stretch	364	389
	e	deg. deform.	130	114
	t ₂	deg. stretch	500	498
	t ₂	deg. deform.	143	136
VOF ₃	a ₁	VO stretch	1346	1055 ^b
	a ₁	VF ₃ sym. stretch	871	720
	a ₁	VF ₃ sym. bend	285	256
	e	VF ₃ asym. stretch	978	801
	e	F ₃ VO rock	351	304
	e	VF ₃ asym. bend	223	204
VOCl ₃	a ₁	VO stretch	1350	1042
	a ₁	VCl ₃ sym. stretch	412	408
	a ₁	VCl ₃ sym. deform.	175	163
	e	VCl ₃ deg. stretch	496	502
	e	VCl ₃ deg. deform.	279	246
	e	VCl ₃ rock	135	125
VF ₅	a ₁ '	VF ₃ sym. stretch	886	718
	a ₁ '	VF ₂ sym. stretch	769	608
	a ₂ "	VF ₂ asym. stretch	991	784
	a ₂ "	VF ₃ deform.	370	331
	e'	VF ₃ deg. stretch	994	810
	e'	VF ₃ deg. deform.	302	282
	e'	VF bend	126	110
	e''	VF bend	387	336
CrO ₂ Cl ₂	a ₁	CrO sym. stretch	1274	991
	a ₁	CrCl sym. stretch	471	470
	a ₁	CrO ₂ scissors	377	356
	a ₁	CrCl ₂ scissors	141	139
	a ₂	CrO ₂ twist	261	224
	b ₁	CrO asym. stretch	1320	1002
	b ₁	CrO ₂ rock	228	212
	b ₂	CrCl asym. stretch	523	503
	b ₂	CrO ₂ wag	285	257
CuH			2020	1941
CuF			928	623
CuCl			402	415

^aExcept where otherwise noted, references to experimental data for diatomic molecules are given in footnote ^a of Table II. Experimental data 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 ⁱ of Table II for reference to experimental data.

is not clear to us at the present time whether dimethyl zinc actually adopts a non-linear skeletal structure, or whether the present result is an artifact of the theory.

COMPARISON OF 3-21G AND OTHER GAUSSIAN BASIS SETS

In a recent paper, Huzinaga and co-workers⁸² compared the performance of a number of small and medium size Gaussian basis sets for the calculation of equilibrium

geometries, normal-mode vibrational frequencies, atomization energies as well as a number of one-electron properties in compounds incorporating transition metals. The objectives of their study were to analyze the effects of "(a) the size of the inner-core part of the basis sets, (b) the splitting of the valence part, (c) the p-type polarization functions on the transition-metal atom, (d) the triple splitting of the *d* shell³, (e) the d-type polarization functions on the ligand atom, (f) the f-type polarization functions on the metal atom". While the authors provided no firm recom-

Table IV. Calculated and experimental equilibrium geometries (bond lengths in Å, bond angles in degrees) for transition-metal carbonyls and carbonyl hydrides.

Molecule	Point Group	Geometrical Parameter	STO-3G	3-21G	Expt.
$\text{H}_2\text{Fe}(\text{CO})_4$	C_{2v}	$r(\text{FeC}_{\text{ax}})$		1.965	1.832 ^a
		$r(\text{FeC}_{\text{eq}})$		1.986	1.802
		$r(\text{FeH})$		1.707	1.556
		$r(\text{C}_{\text{ax}}\text{O}_{\text{ax}})$		1.125	1.145
		$r(\text{C}_{\text{eq}}\text{O}_{\text{eq}})$		1.124	1.145
		$\angle(\text{HFeH})$		100.4	100.4
		$\angle(\text{C}_{\text{ax}}\text{FeC}_{\text{ax}})$		151.6	148.5
		$\angle(\text{C}_{\text{eq}}\text{FeC}_{\text{eq}})$		105.4	96.0
$\text{HCo}(\text{CO})_4$	C_{3v}	$r(\text{CoC}_{\text{ax}})$		1.955	1.764 ^a
		$r(\text{CoC}_{\text{eq}})$		1.894	1.818
		$r(\text{CoH})$		1.668	1.556
		$r(\text{C}_{\text{ax}}\text{O}_{\text{ax}})$		1.122	1.141
		$r(\text{C}_{\text{eq}}\text{O}_{\text{eq}})$		1.130	1.141
		$\angle(\text{C}_{\text{eq}}\text{CoC}_{\text{ax}})$		97.2	99.7
$\text{Fe}(\text{CO})_5$	D_{3h}	$r(\text{FeC}_{\text{ax}})$	2.016	2.008	2.807 ^b
		$r(\text{FeC}_{\text{eq}})$	1.643	1.844	1.827
		$r(\text{C}_{\text{ax}}\text{O}_{\text{ax}})$	1.147	1.124	1.152
		$r(\text{C}_{\text{eq}}\text{O}_{\text{eq}})$	1.171	1.139	1.152
$\text{Ni}(\text{CO})_4$	T_d	$r(\text{NiC})$	1.583	1.831	1.838 ^c
		$r(\text{CO})$	1.162	1.131	2.141
$(\text{CO})_4\text{Mn}(\text{NO})$	C_{2v}	$r(\text{MnC}_{\text{ax}})$		2.003	1.886 ^d
		$r(\text{MnC}_{\text{eq}})$		1.926	1.851
		$r(\text{MnN})$		1.798	1.797
		$r(\text{C}_{\text{ax}}\text{O}_{\text{ax}})$		1.124	1.127
		$r(\text{C}_{\text{eq}}\text{O}_{\text{eq}})$		1.131	1.161
		$r(\text{NO})$		1.205	1.152
		$\angle(\text{C}_{\text{ax}}\text{MnC}_{\text{ax}})$		168.1	
		$\angle(\text{C}_{\text{eq}}\text{MnC}_{\text{eq}})$		104.4	118.9

^a E. A. McNeill and F. R. Scholer, *J. Am. Chem. Soc.*, **99**, 6243 (1976).^b B. Beagley and D. G. Schmidling, *J. Mol. Struct.*, **22**, 466 (1974).^c L. Hedberg, T. Iijima and K. Hedberg, *J. Chem. Phys.*, **70**, 3224 (1979).^d B. A. Frenz, J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **8**, 1288 (1969).**Table V.** Calculated and measured normal-mode vibrational frequencies (cm^{-1}) for nickel tetracarbonyl.

Symmetry of Mode	Description of Mode	Frequency	
		3-21G	Expt. ^a
a_1	CO stretch	2355	2154
a_1	NiC stretch	445	371
e	NiCO bend	491	380
e	CNiC bend	62	62
t_2	CO stretch	2270	2092
t_2	NiCO bend	527	459
t_2	NiC stretch	421	423
t_2	CNiC bend	122	79
t_1	NiCO bend	342	300

^a See footnote^c of Table IV for reference to experimental data.

mendation insofar as a choice of basis set for general use in calculations on molecules incorporating transition metals, the strong suggestion was that the basis set labelled VII, in which 3p, 3d and 4s orbitals are represented by (21), (41) and (21) splits, respectively, and

two single-gaussian p-type "polarization" functions are added to the valence shell, was as suitable as any of the larger representations. Comparison of equilibrium geometries (Table VIII), and normal-mode vibrational frequencies (Table IX) obtained using this basis set with those obtained from the present work, suggests that 3-21G provides as good an overall description of these important molecular properties as the larger Huzinaga representations. In particular, the data suggest that while a 41 gaussian representation for metal *d* orbitals might well be crucial for proper description of the state of transition metal atoms, the smaller 21 split utilized here is entirely appropriate for molecular properties.

CONCLUSION

A series of computationally-efficient 3-21G split-valence basis sets has been formulated

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

Molecule	Point Group	Geometrical Parameter	STO-3G	3-21G	Expt. ^a
Ti(CH ₃) ₄	T _d	r(TiC)	2.096	2.082	2.14 ^b
		r(CH)	1.085	1.090	—
		∠(HCH)	107.2	107.8	—
(C ₅ H ₅)Ni(NO)	C _{5v}	r(NiC)	2.081	2.132	2.11
		r(NiN)	1.424	1.530	1.626
		r(CC)	1.420	1.419	1.43
		r(NO)	1.268	1.168	1.165
		r(CH)	1.078	1.066	1.09 ^c
Cu(CH ₃) ₂ ⁻	D _{3d}	r(CuC)		1.901	1.935 ^d
		r(CH)		1.098	
		∠(HCH)		105.3	
Zn(CH ₃) ₂	D _{3h}	r(ZnC)	1.682	1.944 ^e	1.929
		r(CH)	1.083	1.088	1.090 ^f
		∠(HCH)	105.6	106.9	107.7
Zn(CH ₃) ₄ ²⁻	T _d	r(ZnC)	1.774	2.154	2.07 ^g
		r(CH)	1.111	1.104	—
		∠(HCH)	100.2	105.6	—

^a Except where otherwise noted, references to experimental data are given in footnote^b of Table II.

^b Average of four TiC bond distances in tetrabenzyltitanium; I. W. Bassi, G. Allegra, R. Scordamaglia and G. Chioccola, *J. Am. Chem. Soc.*, **93**, 3787 (1971).

^c Assumed.

^d H. Hope, M. M. Olmstead, P. P. Power, J. Sandell and X. Xu *J. Am. Chem. Soc.*, **107**, 4337 (1985).

^e Not a minimum on the 3-21G potential surface. See text.

^f Assumed; error in HCH angle following depends on validity of assumption.

^g E. Weiss and R. Wolfram, *Chem. Ber.*, **101**, 35 (1968).

Table VII. Calculated and measured normal-mode vibrational frequencies (cm⁻¹) for dimethylzinc.

Symmetry of Mode	Description of Mode	Frequency	
		3-21G	Expt. ^a
a ₁ '	CH ₃ sym. stretch	3167	2900
a ₁ '	CH ₃ sym. deform.	1416	1157
a ₁ '	CZn sym. stretch	530	503
a ₁ "	torsion	31	0 ^b
a ₂ "	CH ₃ sym. stretch	3158	2915
a ₂ "	CH ₃ sym. deform.	1408	1183
a ₂ "	CZn asym. stretch	595	613
e'	CH ₃ deg. stretch	3215	2966
e'	CH ₃ deg. deform.	1629	1301
e'	CH ₃ rock	779	704
e'	CZnC deform	(c)	134
e"	CH ₃ deg. stretch	3218	2843
e"	CH ₃ deg. deform.	1598	1434
e"	CH ₃ rock	677	620

^a See footnote ^a of Table III for reference to experimental data.

^b Assumed.

^c See text.

for first-row transition metals, based on previously-defined minimal representations of Huzinaga.^{9d} Each inner-shell atomic orbital has been represented by a single basis function (written in terms of three gaussians), while each of the 3d, 4s and 4p valence orbitals are split into two parts, and written

in terms of two and one gaussian functions, respectively.

The performance of 3-21G basis sets has been assessed by comparison of calculated and measured equilibrium geometries and normal-mode vibrational frequencies. The simple model fares reasonably well in reproducing experimental equilibrium geometries for both transition-metal inorganic and organometallic systems, although the performance is not as good as that previously noted for compounds incorporating main-group elements. Calculated normal-mode vibrational frequencies for transition-metal-containing molecules are also generally not as uniform as those for main-group molecules at the same level of theory. Further research, directed both at improving existing basis sets and at exploring the limitations of the single-determinant approximation, is necessary in order to obtain theoretical models suitable for general application to transition-metal systems.

APPENDIX. TOTAL ENERGIES.

Total energies for all molecules dealt with in this paper are presented in Table X.

Table VIII. Comparison of equilibrium bond lengths obtained by Huzinaga^a with those from 3-21G calculations^b and from experiment (Å).

Molecule	Bond length	Huzinaga ^a	3-21G ^b	Expt. ^c
ScF ₃	r(ScF)	1.86	1.812	1.91
TiCl ₄	r(TiCl)	2.18	2.186	2.170
Ni(CO) ₄	r(NiC)	1.86	1.831	1.838
	r(CO)	1.15	1.131	1.141
CuF	r(CuF)	1.81	1.605	1.745
CuCl	r(CuCl)	2.18	2.093	2.051
Zn(CH ₃) ₂	r(ZnC)	1.97	1.944	1.929

^a from ref. 82.^b this work.^c see footnotes to Table II and IV for references to experimental work.**Table IX.** Comparison of totally symmetric normal-mode vibrational frequencies obtained by Huzinaga^a with those from 3-21G calculations^b and from experiment (cm⁻¹).

Molecule	Description of mode	Huzinaga ^a	3-21G ^b	Expt. ^c
TiCl ₄	sym. stretch	380	364	389
Ni(CO) ₄	CO sym. stretch	2120	2355	2154
	NiC sym. stretch	440	445	371
CuF		600	928	623
CuCl		375	402	415
Zn(CH ₃) ₂	ZnC sym. stretch	600	530	503

^a from ref. 82.^b this work.^c see footnotes to Tables III, V, and VII for references to experimental work.**Table X.** Total energies (hartrees) for transition-metal inorganic and organometallic compounds.

Molecule	Energy
ScF	- 855.01850
ScF ₃	-1053.06648
TiF ₄	-1240.23530
TiCl ₄	-2673.74436
VOF ₃	-1309.60052
VOCl ₃	-2384.73892
VF ₅	-1432.95050
ClNVCl ₃	-2821.67090
CrO ₂ F ₂	-1384.81634
CrO ₂ Cl ₂	-2101.58975
CrO ₄ ²⁻	-1335.75135
MnO ₄ ⁻	-1441.67879
CuH	-1631.34310
CuF	-1729.76863
CuCl	-2088.17440
H ₂ Fe(CO) ₄	-1705.73392
HCo(CO) ₄	-1823.55698
Fe(CO) ₅	-1816.69534
Ni(CO) ₄	-1947.86509
(CO) ₄ Mn(NO)	-1721.00904
Ti(CH ₃) ₄	-1001.86444
(C ₅ H ₅)Ni(NO)	-1819.05284
Cu(CH ₃) ₂	-1709.61994
Zn(CH ₃) ₂	-1847.94314
Zn(CH ₃) ₄ ²⁻	-1926.50273

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