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By

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ABSTRACT

THE ELECTRONIC STRUCTURE OF FIRST-ROW NEGATIVE IONS AND TRANSITION METAL ATOMS

By

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Negative Ions

The electron affinities of carbon, oxygen and fluorine have been calculated using a compact MCSCF wavefunction with a [4s,4p,3d] Gaussian basis set. This wavefunction describes radial correlation of the 2p electrons which is found to have a large differential effect between atom and anion, and also includes the $(2s^2 \rightarrow 2p^2)$ near-degeneracy effect. Radial correlation of the 2p electrons increases the calculated electron affinity by as much as 1.2eV over the Hartree-Fock value. An orbital model is discussed which ascribes this effect to the diffuse nature of the orbital occupied by the (Z+1)st electron of the anion. Configuration interaction calculations based upon the MCSCF wavefunction, result in electron affinities comparable in magnitude to the large basis set calculations of Yoshimine and Sasaki.[2] The importance of higher-order angular functions and higher-order excitations is also examined.

Transition Metal Atoms

The major differential valence correlation effects of the lowest lying states arising from the s^2d^n, sd^{n+1}, and d^{n+2} configurations of the first-row transition metal atoms have been characterized using MCSCF and CI procedures. The important correlation effects are found to be first, angular correlation of the $4s^2$ pair arising because of the near degeneracy of the 4s and 4p orbitals, and second, radial correlation of the 3d electron pairs. This large differential radial correlation of the 3d electrons can be interpreted as being due to nonequivalent d-orbitals in the sd^{n+1} and d^{n+2} excited states. Both of these effects can be incorporated into a simple MCSCF wavefunction which reduces the error in the excited state atomic dissociation limits (∿0.2eV in Sc-Cr, and ∿0.5eV in Mn-Cu for the sd^{n+1}-s^2d^n excitation energy), yet still is of a form which lends itself easily to molecular calculations.

This dissertation is dedicated to my whole family
Mom and Dad,
Laurie, Paul,
Dennis and Barbara,
Ruth and George,
and Steve and Carol.
I thank each of you for your patience and love which
have helped me to see my very slow steps as progress.

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And finally, I wish to thank my teacher, my mentor and my friend, Pat Faber, who set the hook back in freshman chemistry and has kept me from drowning ever since; may I have the chance to do the same someday.

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INTRODUCTION

There are many seemingly simple problems of chemical interest which have presented theoreticians with difficulties, both computationally and conceptually, for many years. This work is concerned with two such problems: the determination of accurate atomic electron affinities; and the calculation of the electronic excitation energies of transition metal atoms. Each is of theoretical interest because the procedures developed for accurately describing atomic anions and metal excited states provide the framework in which concepts about the structure and reactivity of molecular species are developed. Experimentally, while the atomic systems are in general well-characterized, molecular species have been difficult to generate and spectra, once obtained, must lean heavily on theory for interpretation. Thus, accurate experimental values aid theory in calibrating the methods which are employed, while reliable theoretical values aid experiment in interpretating data from the more complex molecular systems.

A general development of the methods used in calculation of these quantities is in Part A of this thesis. Part B is concerned specifically with the calculation of the electron affinities of carbon, oxygen and fluorine;

while Part C is concerned with the calculation of the s^2d^n to sd^{n+1} or d^{n+2} electronic excitation energies of scandium to copper.

In both of the atomic systems above the Hartree-Fock wavefunction inadequately represents the states with the 'extra' electron, i.e., the $2s^22p^{n+1}$ anion, or the $4s3d^{n+1}$ and $3d^{n+2}$ states of the metal atoms. Previously, the electron affinities and the excitation energies have only been recovered with high-order configuration interaction (CI) calculations. These types of calculations are inappropriate for molecular systems and can, in fact, obscure important physical information regarding the differential correlation effects. We have found that these states are more properly represented when the 'extra' electron is allowed to be in a radially inequivalent orbital (s^2p^np' for the anions, sd^nd' or $d^nd'd''$ for the metal atoms), which is more diffuse in nature than the other 2p or 3d orbitals. A more balanced zero-order description of the ground/excited state, or atom/anion systems can be obtained from a simple multi-configuration (MCSCF) wavefunction which includes two valence correlation effects:

1. The differential radial correlation effect due to the loosely-bound electron in the excited states and anions,

2. The (s^2,p^2) near degeneracy effect due to the near degeneracy of the ns and unoccupied np orbitals.

This MCSCF wavefunction removes many of the inconsistencies found at the Hartree level resulting in more accurate energy differences. CI calculations based upon the MCSCF wavefunction give electron affinities and excitation energies which are now in good agreement with experiment and provide a simple and consistent method for treating correlation effects in molecular systems containing negative ions or transition metal atoms.

Part A: METHODS

I. INTRODUCTION

The wavefunctions and energies which are used to characterize the electronic properties of atoms and molecules result from solution of the time-independent Schrodinger equation within the Born-Oppenheimer approximation. The nonrelativistic electronic Hamiltonian, in atomic units[1], has the form

$$\hat{H} = \sum_{i}^{n} h_i + \sum_{i<j}^{n} \frac{1}{r_{ij}} + \sum_{A<B}^{N} \frac{Z_A Z_B}{R_{AB}} \tag{1a}$$

$$h_i = -\tfrac{1}{2}\nabla_i^2 - \sum_{A}^{N} \frac{Z_A}{r_{Ai}} \tag{1b}$$

where n corresponds to the number of electrons and N to the number of nuclei in the system.

If there were no interactions between electrons, $1/r_{ij}=0$, each electron would move independently of the others subject only to the attractive field of the nuclei. This problem is exactly separable into n one-electron equations which result in the one-electron orbitals, $\{\phi_i\}$, and the one-electron energies, $\{\varepsilon_i\}$

$$h\phi_i = \varepsilon_i \, \phi_i \tag{2}$$

The total wavefunction is simply a product of these orbitals and the total energy the sum of the one-electron energies

$$\psi\ (1,\ldots,n) = \mathcal{A}\phi_1(1)\ldots\phi_n(n) \tag{3a}$$

$$E = \sum_i^n \varepsilon_i \tag{3b}$$

This product wavefunction can be interpreted as describing n independent particles (electrons) moving in the attractive field of the nuclei.

Because of the Coulombic repulsions between electrons, $1/r_{ij} \neq 0$, the electrons do not move independently of one another, rather their motions are correlated. The Schrodinger equation is no longer exactly separable and approximations must be made to obtain the electronic wavefunctions and energies. There are many methods which have been developed for this purpose. This work has employed three *ab initio* procedures based upon the variation principle: the Hartree-Fock self-consistent field method, the multi-configuration self-consistent field method, and the configuration interaction method. They differ in the functional form of the wavefunction chosen to represent the system, and it is in this way that the approximations necessary to solve the Schrodinger equation are introduced.

The validity of using an assumed form for the wavefunction is founded on two fundamental principles. The first is the variation principle[2] which guarantees that for some approximate normalized wavefunction obeying the boundary conditions of the system ψ_o, the corresponding energy E_o, will always be greater than or equal to the lowest eigenvalue of the Hamiltonian[3]

$$E \leq E_o = \langle \psi_o | \hat{H} | \psi_o \rangle \tag{4}$$

While the choice of ψ_o is arbitrary, it is best chosen to approximate, as closely as possible, the exact wavefunction. For a given functional form, the 'best' wavefunction is one for which the energy is a minimum, i.e., for which the first order change in the energy with respect to any variation in the wavefunction is zero $\delta E(\psi_o)=0$.

Variations in the wavefunction can be introduced by means of the second fundamental principle, the expansion theorem. This theorem states that any normalizable function may be represented as an expansion in terms of a complete set of functions[4]. Thus, the single particle orbitals above may be represented as an expansion in a known basis

$$\phi_i = \sum_\mu a_{i\mu} \chi_\mu \tag{5}$$

and the n-particle wavefunction may in turn be expanded in terms of the orbital basis[5]

$$\psi(1,\ldots,n) = \sum_j C_j \Phi_j \tag{6}$$

where each configuration, Φ_j, is a symmetry-adapted linear combination of Slater determinants possessing the spatial and spin symmetry of the electronic state of interest. Variations in the wavefunction translate into variations in the expansion coefficients $\{a_{i\mu}\}$, $\{C_j\}$, which are determined to minimize the energy, the variational method. A wavefunction is, thus, defined by the configurations included in the n-particle expansion and the expansion bases from which the configurations and orbitals are constructed.

II. HARTREE-FOCK

In the Hartree-Fock (HF) procedure, the simplest form of wavefunction is assumed by truncating the configuration expansion at a single term

$$\psi_{HF}(1,\ldots,n) = \Phi_{HF} \tag{7}$$

thus, as in Equation (3a), the HF wavefunction is a simple antisymmetrized product of orbitals. Minimization of the total energy with respect to variations in the orbitals results in the HF equations for each orbital. For a closed-shell HF wavefunction with n/2 doubly-occupied orbitals these equations are of the form

$$\psi = \mathcal{A}\phi_1\alpha(1)\ \phi_1\beta(2)\ldots\ \phi_{\frac{n}{2}}\beta(n) \tag{8a}$$

$$h^{HF}\ \phi_i = \varepsilon_i\ \phi_i \tag{8b}$$

$$h^{HF} = h + \sum_j (2J_j - K_j) \tag{8c}$$

The J_j and K_j are the familiar Coulomb and exchange operators

$$J_j = \langle\phi_j|\frac{1}{r_{12}}|\phi_j\rangle \tag{8d}$$

$$K_j\ \phi_i = \langle\phi_j|\frac{1}{r_{12}}|\phi_i\rangle\phi_j \tag{8e}$$

Since these operators depend upon all of the occupied orbitals, the equations must be solved self-consistently. Expanding each orbital in terms of a known-set of basis functions[7,8] results in the matrix eigenvalue equation

$$\sum_{\nu} < \chi_{\mu} | h^{HF} | \chi_{\nu} > a_{i\nu} = \varepsilon_{i} \sum_{\nu} < \chi_{\mu} | \chi_{\nu} > a_{i\nu} \tag{9a}$$

$$\mathbb{h}^{HF} \mathbf{a}_{i} = \varepsilon_{i} \mathbb{S} \mathbf{a}_{i} \tag{9b}$$

where the energy is determined from the secular equation

$$| \mathbb{h}^{HF} - \varepsilon_{i} \mathbb{S} | = 0 \tag{10}$$

If $\{\chi_{\mu}\}$ is complete, this is the exact HF solution. Since it is not possible to use a complete basis, only an approximate solution is usually obtained, referred to as the SCF solution.

Since most of the electron density of a chemical system is concentrated around the nuclei, it is reasonable that the expansion basis, or basis set, be comprised of functions which are centered on each atom and which decrease exponentially from their centers, linear combination of atomic orbitals (LCAO). The two types of functions most commonly used are Gaussian and Slater functions which are of the form

$$X^{\ell} Y^{m} Z^{n} e^{-\xi r^{2}} \tag{11a}$$

$$r^{n-1} e^{-\xi r} Y_{\ell m}(\Theta, \phi) \tag{11b}$$

The range of radial and angular functions required to represent different chemical processes has been thoroughly investigated and is summarized in Reference 9. For the two systems of concern here, negative ions and transition metal atoms, it was necessary to augment the atomic bases with diffuse functions to describe ionic and excited-state behavior. This is discussed in more detail in later chapters.

The physical significance of the HF wavefunction is best understood by examining the potential terms in Equation 8b. Note that an electron in orbital i is not exposed to the full $1/r_{ij}$ potential due to the other electrons, rather it sees a potential of

$$\sum_j (2J_j - K_j),$$

averaged over all of the electrons in the system. The nature of the HF potential has been discussed by Sinanoglu[10] where he compared the full Coulomb potential to that of the HF. He showed that the HF potential accounts for the long-range effects of the Coulomb repulsions between electrons. The difference between the two potentials, the interactions neglected in the HF picture, are short range in nature falling off rapidly as the distance between the electrons increases. This implies that there are two effects which determine the nature of the interactions between electrons in atoms and molecules

- The average interactions of each electron with the (n-1) others and,
- The instantaneous interactions as pairs of electrons closely approach one another.

The HF wavefunction, by describing the average interactions among the electrons, accounts for mainly the long-range part of the Coulomb repulsions. Thus, the single-particle picture where each electron moves in an individual orbital, is maintained by the HF method, in the sense that the orbitals are now determined in the average field of the (n-1) other electrons as well as the attractive field of the nuclei. While this neglects the short-range instantaneous interactions, those which are dependent upon the individual motions of the different particles, it still provides a well-defined reference point for more sophisticated approaches. The term 'correlation energy' is defined in terms of the HF model as the difference between the exact nonrelativistic energy of a system and the HF energy[11]

$$E_{corr} = E_{exact} - E_{HF} \tag{12}$$

referring to the interactions neglected in the HF model. This is an appropriate term provided that the HF wavefunction describes the major physical features of the system. For closed-shell species at equilibrium this is the case but, in general, a single configuration description is too restrictive. For example, orbital degeneracy effects or molecular dissociation cannot be represented by a single-configuration[11,12] and consequently, other configurations are needed to give a proper 'zero order' description. Since this deficiency is, not strictly, a correlation effect in the dynamic sense of short-range instantaneous interactions, there are two types of corrections that need to be considered beyond the HF model: those which arise from improper representation because of the single-configuration nature of the HF wavefunction; and the 'true' instantaneous correlation effects arising from short-range Coulomb repulsions between electrons in the same spatial region. Both types of interactions can be represented by wavefunctions that do not truncate the expansion in the orbital basis at a single configuration.

III. CONFIGURATION INTERACTION

In the configuration interaction (CI) procedure the wavefunction is written as a linear combination of many orbital configurations[13], that are, in general, taken to be orthonormal, Equation (6). Variation of the configuration coefficients to minimize the energy leads to the matrix eigenvalue equation

$$(\mathbb{H} - E\mathbb{1})\mathbb{C} = 0 \tag{13}$$

where the elements of H are defined between configurations

$$(\mathbb{H})_{ij} = \langle \Phi_i | \hat{H} | \Phi_j \rangle \tag{14}$$

and the eigenvalues are determined from the secular equation

$$|\mathbb{H} - E\mathbb{1}| = 0 \tag{15}$$

If the expansion basis is complete this results, in principle, in the exact nonrelativistic energy of the system. This energy is independent of the orbital basis, although the convergence of the expansion, the number and types of configurations necessary to achieve a particular level of accuracy can be accelerated significantly if the orbitals reflect the general characteristics of the wavefunction.

In practice, it is not possible to expand the wavefunction in terms of a complete set of functions and both the expansion basis and the configuration set must be truncated. The energy of this approximate wavefunction is no longer independent of the orbital basis. The SCF procedures are used to define a physically relevant set of occupied orbitals. In addition, an appropriate set of correlating orbitals are needed. There are two major requirements which these 'virtual' orbitals should fulfill in order to adequately represent the correlation effects among the occupied orbitals. They should be concentrated in the same region of space as the occupied SCF orbitals; and they should have additional nodal surfaces which can allow for effects such as in/out, left/right, or up/down correlation. Thus, the virtual basis is principally comprised of higher angular functions with radial extents similar to those of the occupied orbitals. These requirements are well understood and are discussed in more detail in Reference 13.

The extent of the configuration expansion is limited by the finite size of the orbital basis. A full CI is one in which all of the possible configurations constructed from a finite basis are used in the expansion. The energy of this wavefunction is dependent only upon the space spanned by the orbital basis not upon the individual orbitals, and is the best energy which can be obtained within the given basis. In general, full CI's are not possible for all but the smallest orbital sets and the configuration list must be further reduced. Configurations can be classified according to the number of replacements, or excitations, which occur relative to a given set of reference configurations, single, double, triple, quadruple, etc. Within each level the resulting energy is independent of the individual virtual orbitals, again dependent only upon the space which they span. If the zero-order wavefunction is a good representation of the system, the dominant correlation effects enter the CI expansion in terms of double excitation configurations[10,13-15]. Thus, most CI calculations consist of single and double excitation configurations relative to the HF configuration or a more general zero-order wavefunction. The importance of the higher order triple and quadruple excitations is a topic of current interest[16,17] and is specifically addressed in this thesis for the two systems noted previously.

IV. MULTI-CONFIGURATION SCF

In the multi-configuration self-consistent field (MCSCF) procedure, as in the CI procedure, the n-particle wavefunction is constructed from a linear combination of configurations (Equation 6), but now both the orbitals, $\{\phi_i\}$, and the CI coefficients, $\{C_i\}$, are optimized simultaneously[18,19]. Thus, the matrix eigenvalue equations for the orbitals (Equation 9b), and for the CI coefficients (Equation 13), must be solved, though the form of the orbital equations are not as simple as the closed-shell HF equations, requiring solution of more than one pseudo-eigenvalue equation.

In this way, the correlating orbitals of the CI expansion discussed previously are well-defined, increasing the occupied SCF space to include a set of active orbitals having variable occupancy to describe correlation effects among the valence orbitals, in addition to the core orbitals which remain doubly-occupied throughout the calculation. The generalized valence-bond (GVB) wavefunction is an example of such a wavefunction which accounts essentially for proper molecular dissociation and orbital degeneracy effects[20]. While this procedure could, in principle, be used to define the entire correlating space, in practice this has not been found to be beneficial[17]. Large MCSCF wavefunctions suffer from problems with convergence and interpretability, but perhaps more importantly, not all of the correlating orbitals need be defined self-consistently. The orbital set can be divided into two groups, the primary and secondary orbital sets[21]. The energy of the chemical system is critically-dependent upon the orbitals of the primary set since it is this set that represents the major physical features of the system. The energy is only weakly-dependent upon the orbitals of the secondary set, that are necessary for providing minor corrections to the wavefunction.

V. GENERAL PROCEDURE

The general procedure used in the following calculations has been to determine a set of occupied orbitals self-consistently, that define the zero-order wavefunction. For many systems, the single-configuration HF wavefunction is appropriate, for other systems, more than one configuration is needed. These orbitals along with a proper set of correlating virtual orbitals are then used in CI calculations to account for other correlation effects.

We have investigated alternative forms of zero-order wavefunctions for negative ions and transition metal excited states since it is found that HF inadequately represents these systems. Consequently, the correlation effects in these systems have been particularly confusing when cast in the HF framework. When cast instead in terms of an MCSCF framework these effects become very consistent and lend insight into the physical nature of these systems.

VI. MOLECULAR CODES

The integrals were calculated using the BIGGMOLI integral program of R. C. Raffenetti[22] as well as his integral transformation programs. The MCSCF calculations were done using the ALIS MCSCF program from Ames Laboratory, Iowa State, by K. Ruedenberg, S. T. Elbert and coworkers[18]. The CI calculations were carried out using the CITWO program from the California Institute of Technology by F. W. Bobrowicz[23].

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[1] The atomic unit of length is the Bohr ($1a_0=0.52918\text{Å}$). The atomic unit of energy is the hartree ($1h=27.121eV=627.51Kcal/m$).

[2] See, for example: L. Pauling and E. B. Wilson, *"Introduction to Quantum Mechanics"*(McGraw-Hill, New York, 1935), chapter 7.

[3] An upper bound to a higher eigenvalue can be obtained when it is possible to insure that the approximate wavefunction is orthogonal to all of the exact eigenfunctions of $\hat{H}$ corresponding to lower eigenvalues.

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Part B: NEGATIVE IONS

Theoretical characterization of negative ions. Calculation of the electron affinities of carbon, oxygen, and fluorine.

I. INTRODUCTION

The electron affinities of atoms have been notoriously difficult to calculate from first principles. While experimentally most atoms are found to have a bound negative ion, Hartree-Fock (HF) theory is unable to predict the stability of all but a few of these.[1] For $Z < 10$, HF finds only C^- (^4S) and F^-(^1S) to be bound, the errors in the calculated electron affinities being 0.7eV for carbon and over 2eV for fluorine (Table I). By including electron correlation beyond HF, in particular through the configuration interaction (CI) method, the stability of anions can be correctly predicted, but it has not been clear what level is necessary to obtain this result. Extensive CI calculations have been reported by Yoshimine and Sasaki[2] (Y&S) of the correlation energies of the first-row atoms and their anions. Despite the use of large basis sets and the inclusion of up to quadruple excitations relative to the HF wavefunction the calculated EA's are still in error by as much as 0.3-0.4eV. Since the error in the HF electron affinity, the neglected differential correlation energy, varies considerably from atom to atom, HF does not provide an appropriate zero-order description of negative ions. Yoshimine and Sasaki's results indicate that CI's based upon the HF configuration are poorly convergent, requiring many configurations for very little improvement in the overall EA. Their approach would be impractical for molecular anions in

TABLE I. Electron affinities and ionization energies of the first-row atoms. All quantities are in eV.

	Electron Affinity		Ionization Energy
	[a]Experimental	[b]Numerical Hartree-Fock	[c]Experimental
Hydrogen	0.754	-0.33	13.60
Helium	<0	-	24.58
Lithium	0.620(7)	-0.122	5.39
Beryllium	<0	-	9.32
Boron	0.278(±.010)[d]	-0.268	8.30
Carbon	1.268(5)	0.549	11.26
Nitrogen	-0.07(8)	-2.150	14.54
Oxygen	1.462(3)	-0.541	13.61
Fluorine	3.399(3)	1.363	17.42

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[a] These are the 'recommended' values taken from reference 1.

[b] From reference 17.

[c] R. B. Leighton, "Principles of Modern Physics", (McGraw Hill, 1959), pp. 727-729.

[d] From reference 10.

which much less extensive treatments are unavoidable, yet electron correlation must be included before accurate results can be obtained from the calculations.

Clearly, a more general *ab initio* procedure needs to be developed which results in a more consistent description of negative ions, though not necessarily giving the exact electron affinity. We have approached this problem by redefining the zero-order wavefunction using a multiconfiguration self-consistent field (MCSCF) function, which provides a more balanced description of both the neutral and the anion and can be used conveniently in singles and doubles CI calculations (MCSCF+1+2). This approach yields consistent errors at the MCSCF level, provides a convenient method for introducing triple and quadruple excitations (relative to the HF function) into the CI wavefunction, and EA's comparable to Y&S using a much smaller basis set and CI expansion.

A. Experimental Background

There are many excellent reviews of the empirical, semi-empirical and theoretical procedures which have been used to determine the electron affinities.[1,3-7] Work relevant to ours is presented below, the reader being referred to the above reviews for more thorough discussions.

Experimental determination of electron affinities is a difficult task so that until recently the EA's of many elements could only be determined by extrapolation procedures based upon trends in isoelectronic series (horizontal analysis[8]). For those systems which could be studied experimentally, there are two standard techniques which have been employed for the direct determination of electron affinities.[1,3] The first is photodetachment threshold spectroscopy where the long wavelength threshold for detachment of the electron is measured, giving the EA of the anion. The second is negative ion photoelectron spectroscopy where a fixed frequency of light, larger than the EA of the neutral, is used to detach the electron, whose kinetic energy is then measured. The EA is determined with respect to a known reference based upon the conservation of energy. While each technique has its own inherent limitations (which are very thoroughly discussed in reference 3) they share two technological problems, the availability of a suitable photon source and a suitable ion source. Advances in laser technology have helped to reduce some of the limitations of the photon source, but lack of ion sources has slowed progress in the measurement of EA's. Recently, sputter-type ion sources have been used to generate beams of atomic anions for many transition metal atoms,[9] and some main group elements,[10] whose EA's were then determined using photoelectron spectroscopy. While the range of elements able to be studied experimentally has broadened, molecular EA's are still largely undetermined.[4] Yet accurate EA's can be critical for determining the properties of many neutral species; for example, the controversy over the singlet-triplet separation of methylene, as measured from the photoelectron spectra, hinges on a knowledge of the electron affinity of the $^3B_1$ state.[11-14]

B. Theoretical Background

Theoretical determination of electron affinities is also a difficult task because a balance must be struck between the description of a neutral species and its negative ion, a system having one more electron. The electron affinity is found by subtracting the calculated ground state energy of the anion from the neutral, a positive value indicating that the anion is stable. Because of the extra correlation energy associated with the (Z+1)st electron in the negative ion, calculations will favor the neutral, resulting in EA's which are in general too low relative to experiment[15] or even negative as is found from most HF calculations.

If the total nonrelativistic energy is expressed as the sum of the HF energy plus the correlation energy,[16] the EA is simply the difference between these quantities:

$$EA = \Delta E_{HF} + \Delta E_{corr} \tag{1}$$

For atoms the HF differences can be calculated very accurately using the near HF-limit energies[17] obtained from numerical procedures[18] and therefore, the problem of calculating electron affinities has been seen as one of obtaining the differential correlation energy between the atom and anion.

One approach to the calculation of electron affinities has been the pair-correlation schemes of Nesbet[19,20] or Weiss.[21,22] In these, the total energy is written as:

$$E = E_{HF} + \sum_{i} \varepsilon_i + \sum_{ij} \varepsilon_{ij} \tag{2}$$

E_{HF} being the total HF energy, ε_i the single-particle correlations, and ε_{ij}, the correlation energy of the ij-pair. It is assumed that the ε's can be calculated independently by separate CI calculations for each ij-pair and summed to obtain the total correlation energy. These methods were compared by Y&S[2] to the more complete CI+1+2 calculations (Table II), where they were able to show that although the EA's obtained are often in excellent agreement with experiment, this is due to cancellations between truncation of the basis set and neglect of higher-order terms, and at the limit of a complete basis set, the pair methods overestimate electron affinities, being 0.2eV too high for both oxygen and fluorine.

Schaefer, *et al.*[23] (1969) approximated the EA's of the first-row atoms based upon a first-order CI wavefunction (FOCI) which includes the internal (near-degeneracy), and the semi-internal (near-degeneracy and

TABLE II. A comparison of calculated electron affinities of hydrogen, lithium and boron through fluorine. All quantities are in eV.

		H	Li	B	C	N	O	F
HF :	[a]Numerical	-0.33	-0.12	-0.27	0.55	-2.15	-0.54	1.36
GVB :	[b]Goddard	0.38	0.28					
FOCI :	[c]Schaefer			-0.61	0.11	-2.45	-1.12	0.53
CI (pairs):	[d]Moser							
	1 and 2 particle terms			0.39	1.46	0.19	2.06	4.18
	+ 3 particle terms			0.22	1.29	-0.12	1.43	3.37
	[e]Weiss						1.47	3.47
	[f]Yoshimine and Sasaki						1.71	3.62
CI :	[g]Yoshimine and Sasaki							
	HF+1+2			0.15	1.11	-0.57	1.04	3.00
	HF+1+2+3+4			0.17	1.13	-0.46	1.17	3.15
	[h]Experiment	0.75	0.62	0.28	1.27	-0.07	1.46	3.40

[a] From Reference 17.

[b] From reference 24.

[c] From reference 23.

[d] From references 19 and 20.

[e] From references 21 and 22.

[f] From reference 2.

[g] Energies obtained from the frozen K-shell values, reference 2.

[h] 'Recommended' values taken from reference 1.

polarization) effects. The effects represented by the FOCI wavefunction were found to favor the neutral atom, and rather than improving the calculated electron affinity, resulted in poorer agreement with experiment.

As mentioned previously, Yoshimine and Sasaki[2] (1974), have published the most extensive CI calculations to date on the first-row atoms and their negative ions. Their intention was to eliminate any basis set error and obtain the exact correlation energy of each by using a very large Slater basis which, upon reduction by an approximate natural orbital analysis, consisted of an (8s,7p,6d,5f,4g,3h,2i) orbital set. Singles and doubles CI calculations were carried out based on the HF reference configuration (HF+1+2), and then the importance of higher-order terms was examined by including selected triple and quadruple excitations (HF+1+2+3+4). Their results are also summarized in Table II where only the L-shell correlation energies have been used since it was shown by their calculations that K-shell and KL-intershell correlations contribute less than 10^{-2}eV to the EA, and, these are the energies most comparable to our 1s(HF) frozen core CI calculations. Note that the singles and doubles CI wavefunction does correctly predict B^- and O^- to be bound whereas the FOCI[23] does not. Although they were able to calculate approximately 95% of the estimated correlation energy of the atom and anion, only approximately 85% of the EA's were obtained. The HF+1+2 EA's are in error by 0.1-0.4eV. Triple and quadruple excitations improve the energies by only ∿0.02eV for boron and carbon, and ∿0.15eV for nitrogen, oxygen and fluorine which reduces the error in the calculated EA's to 0.1-0.3eV.

While all of the previously mentioned calculations have examined the overall correlation energies in the atom and anion, none have addressed some key questions which can lend insight into the description of negative ions:

--What are the minimum correlation effects required to account for the stability of the anion?

--How is the electronic structure of the ion different from that of its isoelectronic neutral?

--What other types of correlation effects are differential between atom and anion and what is the minimum level required to describe each (particularly with respect to the higher angular momentum functions used in all of the previous calculations)?

The first and second of these questions were addressed by Goddard[24] (1968) in his paper on the stability of the negative ions of hydrogen and lithium and will be discussed in detail below. We have attempted to address the last question through MCSCF and CI calculations which isolate various differential contributions to the EA's of carbon, oxygen and fluorine.

II. ORBITAL MODELS FOR NEGATIVE IONS

A negative ion is characterized by a very diffuse charge distribution relative to the neutral atom. If the energy to remove the 'last' electron in an atom, which is on the order of 10eV, is compared to that of the anion, which is on the order of 1eV, it is clear that the (Z+1)st electron is much more loosely bound than the other Z electrons (Table I). The failure of the HF wavefunction to predict the stability of negative ions can be related to its inability to allow for this diffuse nature of the orbital for the (Z+1)st electron. Using Goddard's example,[24] this point is illustrated by contrasting three different zero-order representations of the $^1S(1s^2)$ state of H^-: the restricted Hartree-Fock (RHF) wavefunction; the unrestricted HF (UHF) wavefunction; and the generalized valence bond (GVB) wavefunction;[25] in terms of the physical model represented by each, and their ability to predict the stability of the anion. The RHF wavefunction is of the form:

$$\psi_{RHF} = \mathcal{A} 1s_{HF}^2 \alpha\beta \qquad (3)$$

Physically, this wavefunction represents two electrons singlet-coupled in the same spatial $1s_{HF}$ orbital. The UHF wavefunction is given by:

$$\psi_{UHF} = \mathcal{A} 1s_{\alpha} 1s_{\beta} \alpha\beta \qquad (4)$$

This wavefunction relaxes the restriction that the electrons be in the same spatial orbital, but at the expense of the spin symmetry, ψ_{UHF}, being a mixture of the singlet and triplet couplings of the electrons.

An alternate way to relax the spatial restrictions on the 1s electrons is to use the GVB wavefunction for H^- which allows the two electrons to be in nonequivalent 1s orbitals while maintaining the proper spin symmetry:

$$\psi_{GVB} = \mathcal{A}(1s1s' + 1s'1s)\alpha\beta \tag{5}$$

The overlap between 1s and 1s' is nonzero. Equation 5 can be expressed as an equivalent two configuration MCSCF wavefunction in terms of an orthogonal basis[26] which, computationally, is more convenient to use:

$$\psi_{MC} = \mathcal{A}(c_1 1s_{MC}^2 - c_2 2s_{MC}^2)\alpha\beta \tag{6}$$

$$\langle 1s|2s\rangle = 0$$

$$c_1^2 + c_2^2 = 1$$

The relationship between the nonorthogonal GVB orbitals and the orthogonal MCSCF orbitals is given by:

$$1s = (2)^{-\frac{1}{2}} \left[(1+S)^{\frac{1}{2}}\, 1s_{MC} + (1-S)^{\frac{1}{2}}\, 2s_{MC}\right] \tag{7a}$$

$$1s' = (2)^{-\frac{1}{2}} \left[(1+S)^{\frac{1}{2}}\, 1s_{MC} - (1-S)^{\frac{1}{2}}\, 2s_{MC}\right] \tag{7b}$$

$$S = \langle 1s | 1s' \rangle = \left(\frac{c_1 - c_2}{c_1 + c_2}\right)$$

All of these wavefunctions maintain the single-particle interpretation of an electron moving in an average potential due to the other electron and the nucleus.

The energies and EA's calculated with each of these wavefunctions (Equations 3,4,6) are summarized in Table III. The (5s/3s) hydrogen basis of Huzinaga[27] was used for these calculations but, in order to obtain a negative orbital energy for H^-, it was necessary to augment this set with two diffuse functions (determined by an even-tempered expansion), to give a (7s/5s) basis set.

The RHF wavefunction, which places two electrons in equivalent $1s_{HF}$ orbitals, results in the energy of the anion being 0.33eV *above* the energy of the hydrogen atom, predicting the anion to be unstable relative to the atom. The UHF wavefunction, not being restricted to keeping the electrons in the same spatial orbital, places the extra electron at infinity, also predicting an unbound negative

TABLE III. A comparison of the RHF, UHF and GVB energies for H, H^-, and He. Units are as indicated.

	$^aH(^2S)$ hartree	$^aH^-(^1S)$ hartree	ΔHF eV	EA eV	$^bHe(^1S)$ hartree	ΔHF eV
RHF	-.4998	-0.4877	0.0	-0.33	-2.8612	0.0
UHF		-0.4998[c]	-	0.0	-	
GVB		-0.5250	1.01	0.37	-2.8774	0.44
Experimental				0.75		

[a] Calculated using an augmented (5s/3s) → (7s/5s) basis. See text.

[b] Calculated using the (6s/4s) basis set from reference 29.

[c] Set to atomic value. See reference 24.

ion. The GVB wavefunction, on the other hand, correctly predicts the electron to be bound with an EA of 0.37eV. Thus, by simply allowing the electrons to be in radially nonequivalent 1s orbitals while maintaining the singlet spin symmetry, a proper zero-order physical description of H^- is obtained. Goddard showed this to be true for the $^1S(2s^2)$ state of Li^- as well.[24]

Radial plots of the $1s_{HF}$, and the 1s and 1s' GVB orbitals help to illustrate the difference between the RHF and GVB models. The RHF orbitals for H and H^- are presented in Figure 1a. Since the 1s electrons partially shield one another from the nuclear charge, forcing both electrons to be in the same orbital results in a decrease in the attraction felt by each, and the anion orbital (dashed line) expands relative to the atom (solid). Alternatively, the 2nd electron could be placed in a more diffuse orbital which does not shield the other electron as effectively (GVB), and thus does not decrease the net attraction as significantly.[28] These 1s and 1s' orbitals (dashed lines) are presented in Figure 1b along with the atomic 1s orbital (solid). The diffuse nature of the 1s' orbital is very apparent, the overlap with the tight 1s, being only 0.57. Note that the tight 1s orbital has essentially the same radial form as the atomic orbital.

For comparison Figure 1c shows the $1s_{HF}$, and the 1s and 1s' GVB orbitals for the $^1S(1s^2)$ state of helium using the same two configuration wavefunction as for H^-

Figure 1. A comparison of the RHF and GVB radial amplitudes for the 1s orbitals of H, H^- and He. Distance is in bohr; plots are all on the same scale.

Figure 1a. H (solid) and H^- (dashed) RHF orbitals. $\langle R\rangle = 1.50$ and $2.51a_o$ for H and H^-, respectively.

Figure 1b. H RHF (solid) and H^- GVB (dashed) orbitals. $\langle R\rangle = 1.50$, 1.44 and $5.07a_o$ for $1s_{RHF}$, $1s_{GVB}$ $1s'_{GVB}$, respectively.

Figure 1c. He RHF (solid) and GVB (dashed) orbitals. $\langle R\rangle = 0.93$, 0.69 and $1.22a_o$ for $1s_{RHF}$, $1s_{GVB}$ $1s'_{GVB}$, respectively.

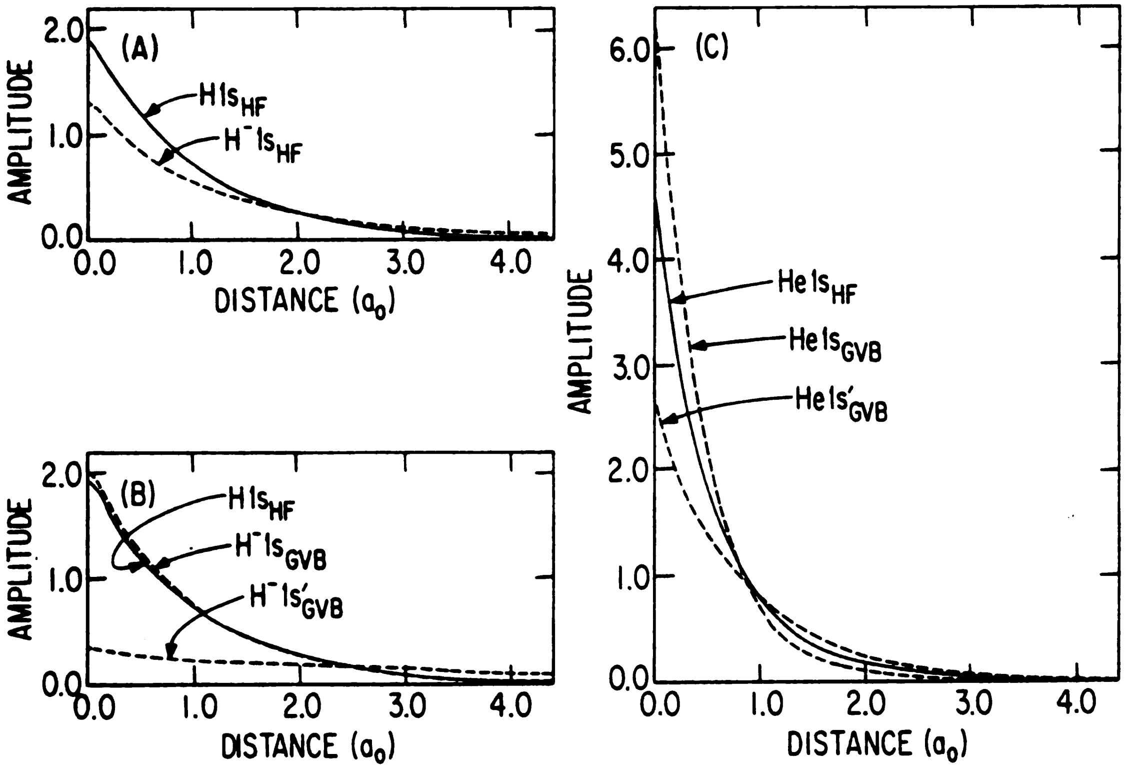
(A)
2.0
1.0
0.0
AMPLITUDE
$H\ 1s_{HF}$
$H^- 1s_{HF}$
0.0
1.0
2.0
3.0
4.0
DISTANCE (a_0)
(B)
2.0
1.0
0.0
AMPLITUDE
$H\ 1s_{HF}$
$H^- 1s_{GVB}$
$H^- 1s'_{GVB}$
0.0
1.0
2.0
3.0
4.0
DISTANCE (a_0)
(C)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
AMPLITUDE
$He\ 1s_{HF}$
$He\ 1s_{GVB}$
$He\ 1s'_{GVB}$
0.0
1.0
2.0
3.0
4.0
DISTANCE (a_0)

Figure 1.

(Equation 6). Note now, the higher overlap between 1s and 1s', S=0.88, and the small deviation from the HF orbital. Further note that the ($1s^2 \rightarrow 2s^2$) radial correlation energy is much smaller for He, 0.44eV, than for H^-, 1.01eV (Table III).

The helium orbitals, with their high overlap, are typical of radial correlation within a singlet-coupled electron pair, indicating that the electrons are bound nearly equivalently. The H^- orbitals, on the other hand, vary much more from one another and the HF orbital, indicating that the electrons are not bound equivalently. Rather, one electron is bound as in the atom while the second is only loosely bound, occupying a much more diffuse orbital.

This suggests a general physical model for negative ions where an anion can be thought of as having Z electrons bound as in the neutral atom with the (Z+1)st electron occupying a more diffuse orbital. A negative ion differs from its isoelectronic neutral because in the neutral all (Z+1) electrons are bound nearly equivalently. Thus F^- is physically very different than Ne, C^- very different than N.

We have applied this model of a loosely-bound electron in the negative ion to developing a balanced zero-order MCSCF wavefunction for the atom and anion of carbon, oxygen, and fluorine. When viewed in terms of this model, many of the apparent inconsistencies in the HF representation are clarified, revealing a very consistent, physically reasonable description of the negative ion.

III. CALCULATIONAL DETAILS

The basis set used in the MCSCF calculations was the (11s,6p) Gaussian basis of Duijneveldt[29] augmented with an additional p function determined by an even-tempered expansion of the last two functions. This was contracted to [4s,4p] using the general contraction scheme of Raffenetti[30], based upon the HF orbitals of the ground state of the atom. This contraction resulted in HF EA's which are about 0.01eV less than the numerical results.[17]

The configurations used in the MCSCF calculations were chosen to describe the differential p^2 pair energies between the atom and anion due to the diffuse nature of the (Z+1)st electron in the anion. This requires configurations similar to those used in H^- and Li^-; double excitations from $2p^2$ into $3p^2$. This type of radial correlation describes not only the tight/diffuse nature of the (Z+1) electrons in an anion, as demonstrated previously for H^-, but also simple in/out type correlation arising from pair repulsions, as seen in He. It must, therefore, be included in the zero-order wavefunction of both the atom and the anion, although as will be seen, the effect is much more dramatic in the anion. Thus the wavefunctions used in the following MCSCF calculations are:

$$\text{Atom:} \quad \mathcal{A}\left[c_1 2s^2 2p^n - c_2 2s^2 2p^{n-2} 3p^2\right] \tag{8a}$$

$$\text{Anion:} \quad \mathcal{A}\left[c_1 2s^2 2p^{n+1} - c_2 2s^2 2p^{n-1} 3p^2\right] \tag{8b}$$

In addition, for the $^3P(2s^2 2p^2)$ state of carbon, the $(2s^2 \rightarrow 2p^2)$ near-degeneracy effect,[31] arising because of the unoccupied 2p orbital, was included in the zero-order wavefunction by adding the configuration:

$$c_3 2p^4 \alpha\beta\alpha\alpha \qquad (8c)$$

For the CI calculations the [4s,4p] basis was augmented with 3 sets of d-functions. The first two functions were taken from a two-term Gaussian expansion of a Slater 3d function.[32] These exponents were then scaled together to minimize the energy for the neutral in terms of an MCSCF+1+2 wavefunction. Then a more diffuse exponent was added and optimized for oxygen and fluorine to describe the anion. This was done by allowing all single and double excitations out of one of the doubly occupied 2p orbitals, based upon the MCSCF orbital set of the anion. Since for carbon there is not an equivalent procedure to follow, the third exponent was chosen in the same ratio as optimized for fluorine. These exponents are given in Table IV.

An f-function was also added to the fluorine basis and optimized for both the atom and the anion in HF+1+2 and MCSCF+1+2 calculations. The exponent was found not to be a strong function of the state or orbital set and, therefore, the optimum values for ^2P and ^1S were averaged ($\zeta_f = \underline{1.9167}$).

For the most part the CI wavefunctions consisted of all single and double excitations from either the HF

TABLE IV. Optimized 3d and 4f Exponents for carbon, oxygen and fluorine

	Carbon	Oxygen	Fluorine
ξ_{3d}	1.0886	2.2887	3.0238
	0.3223	0.6777	0.8954
	0.0954	0.2651	0.2651
ξ_{4f}			1.9167

reference configuration (HF+1+2) or from the MCSCF reference configurations (MCSCF+1+2). These calculations were partitioned to include first the (sp) space, then the effect of adding the d and f-functions was examined. For all three systems full-CI's within just the (p) space were performed to test the adequacy of the $(2p^2\text{->}3p^2)$ MCSCF description, and for carbon and oxygen selected full-CI calculations are also reported. The 1s(HF) orbital was kept frozen in all of the calculations, and symmetric orbital sets were used.

IV. CALCULATION OF THE EA'S OF CARBON, OXYGEN AND FLUORINE

A. Carbon

The results for carbon are summarized in Table V. Carbon is somewhat anomalous because of the near-degeneracy effect[31] found in the $^3P(2s^22p^2)$ state of the atom but not in the negative ion. Since this effect is ignored at the HF level, the energy of the ^3P state is artificially high, resulting in a larger EA than would be the case if HF treated both the atom and anion equivalently. If the $(2s^2\text{->}2p^2)$ near-degeneracy effect is included in the ^3P wavefunction, the GVB description of carbon,[33] this state is lowered by 0.47eV giving an EA of only 0.06eV.

Allowing the 2p orbitals to radially correlate by including $2p^2$ to $3p^2$ excitations, lowers the ^3P state by 0.12eV. This correlation lowers the ^4S state by 0.49eV, larger than expected based on the effect in the ^3P state. Full CI's within the (p) space improve the MCSCF energy of

TABLE V. Hartree-Fock, MCSCF and [a]CI calculations on the ^3P state of the carbon atom and the ^4S state of the carbon anion. Basis set: [4s,4p,3d], units are as indicated.

	$^3P(2s^22p^2)$ hartree	ΔHF eV	$^4S(2s^22p^3)$ hartree	ΔHF eV	EA eV
Hartree-Fock	-37.6880	0.0	-37.7076	0.0	0.53
MCSCF $(2s^2 \rightarrow 2p^2)$	-37.7054	0.47			0.06
$(2p^2 \rightarrow 3p^2)$	-37.6924	0.12	-37.7256	0.49	
[b]CI (p) Full	-37.6924	0.12	-37.7269	0.52	
MCSCF $(2s^2 \rightarrow 2p^2)+(2p^2 \rightarrow 3p^2)$	-37.7095	0.58			0.44
[c]CI (sp)					
HF+1+2	-37.7293	1.12	-37.7588	1.39	0.80
MCSCF+1+2	-37.7296	1.13	-37.7607	1.45	0.84
Full	-37.7297	1.13	-37.7611	1.46	0.85
[d]CI (spd)					
HF+1+2	-37.7740	2.34	-37.8114	2.83	1.02
MCSCF+1+2	-37.7747	2.36	-37.8144	2.91	1.08
Full	-37.7755	2.38			
[a,e]CI Yoshimine & Sasaki					
HF+1+2					1.11
HF+1+2+3+4					1.13
[f]Experiment					1.27

[a] The 1s orbital remained doubly-occupied in all calculations.

[b] Full CI within the (p) space.

[c] Excitations allowed only in the (sp) space.

[d] Excitations allowed in the (spd) space.

[e] From reference 2.

[f] 'Recommended' value from reference 1.

the ^4S state only slightly, having no effect on the ^3P state, demonstrating the adequacy of the $(2p^2{\rightarrow}3p^2)$ MCSCF description for carbon. The result of incorporating both effects, near-degeneracy and radial $2p^2$ correlation in the ^3P wavefunction is a lowering of 0.58eV, just the sum of the individual effects, and results in an MCSCF EA of 0.44eV for carbon.

The orbitals obtained from the HF and MCSCF calculations were used in CI+1+2 and full CI calculations within the (sp) space. The total lowerings (relative to HF) obtained from the full-CI calculations are 1.13eV for the ^3P state and 1.46eV for the ^4S state, predicting an EA of 0.85eV. The MCSCF+1+2 calculations lower both states by essentially the full-CI result, 1.13eV for C and 1.45eV for C^-. HF+1+2 calculations within (sp) give a similar ^3P lowering but are 0.07eV higher for the ^4S state, predicting the EA to be 0.80eV. Thus, about 57% of the EA of carbon is obtained by full correlation within the (sp) space. Enlargement of the (sp) basis would improve this to perhaps 65-70%, leaving about 0.4eV which can be ascribed to higher angular momentum terms.

CI calculations within the (spd) space are also reported in Table V. A full-CI was only possible for the ^3P state, lowering it by 2.38eV relative to HF. The MCSCF+1+2 and HF+1+2 lowerings for this state are similar, being only 0.02 and 0.04eV higher than the full-CI result. The energy of the anion is affected more than the neutral by the higher-order excitations in the MCSCF+1+2 calculation, picking up 0.08eV over the HF+1+2 energy and giving an EA of 1.08eV. The HF+1+2 EA is 1.02 eV. While about 0.2eV of the EA is still unaccounted for at this level, a comparison to the CI calculations of Y&S[2] show that our HF+1+2 EA is only 0.09eV less than theirs, thus providing an estimate of the basis set limitations within our calculation. Since the MCSCF+1+2 wavefunction contains quadruple excitations relative to the HF configuration, the EA can be compared to the HF+1+2+3+4 result, being only 0.05eV less than this value. If the basis set error is on the order of at least 0.1eV, a more complete basis would yield an MCSCF+1+2 EA larger than obtained by Y&S and about 0.1eV smaller than experiment.

B. Oxygen

Calculations on the oxygen $^3P(2s^2 2p^4)$ neutral atom and the $^2P(2s^2 2p^5)$ negative ion are summarized in Table VI. HF finds the anion to be unbound (as was also the case for the FOCI description[23]). The $(2p^2 \rightarrow 3p^2)$ radial correlation effect lowers the ^3P state by 0.91eV, and the anion by 1.92eV. Now the energy of the anion lies below the atom giving the correct physical description at zero-order with an EA of 0.46eV.

Full-CI's within the (p) space are more important in oxygen than in carbon resulting in an additional lowering of 0.17eV for the atom and 0.47eV for the anion over the

TABLE VI. Hartree-Fock, MCSCF and [a]CI calculations on the ^3P state of the oxygen atom and the ^2P state of the oxygen anion. Basis set: [4s,4p,3d], units are as indicated.

	$^3P(2s^22p^4)$ hartree	ΔHF eV	$^2P(2s^22p^5)$ hartree	ΔHF eV	EA eV
Hartree-Fock	-74.8077	0.0	-74.7875	0.0	-0.55
MCSCF $(2p^2 \rightarrow 3p^2)$	-74.8411	0.91	-74.8580	1.92	0.46
[b]CI (p) Full	-74.8474	1.08	-74.8754	2.39	0.76
[c]CI (sp)					
HF+1+2	-74.8774	1.90	-74.9057	3.22	0.77
MCSCF+1+2	-71.8792	1.94	-74.9132	3.42	0.92
Full	-74.8794	1.95	-		
[d]CI (spd)					
HF+1+2	-74.9544	3.99	-74.9871	5.43	0.89
MCSCF+1+2	-74.9575	4.07	-74.9976	5.72	1.09
[a,e]CI Yoshimine & Sasaki					
HF+1+2					1.04
HF+1+2+3+4					1.17
[f]Experiment					1.46

[a] The 1s orbital remained doubly-occupied in all calculations.

[b] Full CI within the (p) space.

[c] Excitations allowed only in the (sp) space.

[d] Excitations allowed in the (spd) space.

[e] From reference 2.

[f] 'Recommended' value from reference 1.

MCSCF ($2p^2 \to 3p^2$) energies. This is because more than one effect must be described by the 2p and 3p MCSCF orbitals once the 2p orbitals become doubly occupied. For the neutral, correlation of the intra-p^2 pair as well as the inter-p^2 pairs must be represented by the two orbitals. For the anion, in addition to these, the effect of one diffuse electron correlating with four tighter electrons is also present. All of these effects are averaged in the MCSCF procedure but are more fully represented by additional p-functions, as demonstrated by the full-CI (p) energies.[34]

Full-CI calculations within the (sp) space could only be done for the neutral because of the size of the configuration list, lowering the ^3P state by 1.95eV relative to HF. As was found for carbon, the MCSCF+1+2 and HF+1+2 correlation energies for this state are only slightly higher, 1.94 and 1.90eV respectively. The energy of the anion is lowered by 3.42eV for MCSCF+1+2, while it is 0.2eV smaller for HF+1+2. Thus, the effect of the triple and quadruple excitations upon the energy of the anion is becoming pronounced. The HF+1+2 EA is 0.77eV. The MCSCF+1+2 EA is 0.92eV, 63% of the experimental value.

For the CI calculations within the entire (spd) virtual space, the higher-order excitations begin to show an effect on the energy of the neutral, HF+1+2 being 0.12eV above the MCSCF+1+2 energy. For the anion this effect is even larger, 0.29eV. The HF+1+2 EA is 0.89eV, 0.15eV less than that of Y&S, again an indication of basis set limitations. The MCSCF+1+2 EA is 1.09eV, only 0.08eV less than that of Y&S, but still in error by 0.37eV with experiment. Correcting for limitations in the basis set, we estimate the MCSCF+1+2 limit for the EA of oxygen to be more than 1.24eV.

C. Fluorine

Calculations on the $^2P(2s^2p^5)$ atom and $^1S(2s^22p^6)$ anion of fluorine are summarized in Table VII. HF, while properly predicting the stability of F^-, accounts for less than half of the experimental EA of 3.40eV. Radial ($2p^2$->$3p^2$) correlation differentially lowers the ^1S anion by 1.16eV, resulting in an MCSCF EA of 2.51eV. Full-CI calculations within the (p) space show the same trend as for oxygen reducing the energy of the anion more than that of the neutral, giving an EA of 2.78eV. CI's within the (sp) and (spd) spaces also show the trend that the higher-order terms included in the MCSCF+1+2 wavefunction are more important for the anion than the neutral; a differential effect of 0.18eV for (sp) and 0.25eV for (spd). Within the (sp) space the MCSCF+1+2 calculations account for 87% of the EA of fluorine. Within the (spd) space, the MCSCF+1+2 EA is 3.16eV, HF+1+2 being 2.91eV. Thus, in the [4s,4p,3d] frozen core basis the HF+1+2 EA is only 0.09eV less than that of Y&S, while the MCSCF+1+2 EA is

TABLE VII. Hartree-Fock, MCSCF and [a]CI calculations on the ^2P state of the fluorine atom and the ^1S state of the fluorine anion. Basis set: [4s,4p,3d,1f], units are as indicated.

	$^2P(2s^22p^5)$ hartree	ΔHF eV	$^1S(2s^22p^6)$ hartree	ΔHF eV	EA eV
Hartree-Fock	-99.4067	0.0	-99.4563	0.0	1.35
MCSCF ($2p^2$-$3p^2$)	-99.4646	1.58	-99.5570	2.74	2.51
[b]CI (p) Full	-99.4724	1.79	-99.5746	3.22	2.78
[c]CI (sp)					
HF+1+2	-99.5043	2.66	-99.6068	4.09	2.79
MCSCF+1+2	-99.5070	2.73	-99.6163	4.35	2.97
[d]CI (spd)					
HF+1+2	-99.5948	5.12	-99.7016	6.68	2.91
MCSCF+1+2	-99.5992	5.24	-99.7153	7.05	3.16
CI (spdf)					
HF+1+2	-99.6159	5.69	-99.7229	7.25	2.91
MCSCF+1+2	-99.6202	5.81	-99.7369	7.64	3.18
[a,e]CI Yoshimine & Sasaki					
HF+1+2					3.00
HF+1+2+3+4					3.15
[f]Experiment					3.40

[a] The 1s orbital remained doubly-occupied in all calculations.

[b] Full CI within the (p) space.

[c] Excitations allowed only in the (sp) space.

[d] Excitations allowed in the (spd) space.

[e] From reference 2.

[f] 'Recommended' value from reference 1.

actually 0.01eV better. Addition of an f-function shows no differential effect for the HF+1+2 EA, while the MCSCF+1+2 EA is only improved by 0.02eV. If the basis set error is about 0.1eV, the EA obtained with the MCSCF+1+2 wavefunction should be about 0.1eV less than the experimental value.

V. DISCUSSION

The importance of the differential p^2 correlation energy in determining the electron affinity of an atom is best illustrated by comparing isoelectronic systems. These energies relative to HF, are given in Table VIII for the systems: C^-, $N(^4S)$; O^-, F (^2P); and F^-, $Ne(^1S)$, at various levels of calculation (oxygen ^3P is also included for completeness). Comparing the anion and isoelectronic neutral, it is clear that correlation of the p-electrons is larger in the anion than the neutral, even though the p-orbitals contract as Z increases and so an opposite trend might be expected. For carbon the ^3P state shows a p^2 repulsion energy of 0.12eV/pair. If the effect in the anion were the same, the lowering in the ^4S state would be 0.36eV (0.12 x 3 pairs), while it is, in fact, 0.13eV larger. This can be associated with the extra correlation energy due to the diffuse electron. Note though, that the effect for nitrogen atom is 0.34eV, as predicted from the pair energy for carbon. The importance of this differential radial correlation increases

TABLE VIII. MCSCF and [a]CI correlation energies relative to Hartree-Fock for the isoelectronic series: $^4S(2s^22p^3)$ of C^- and N; $^2P(2s^22p^5)$ of O^- and F; and $^1S(2s^2p^6)$ of F^- and Ne. All units are in eV.

	MCSCF $(2p^2\rightarrow 3p^2)$	[b]CI(p) Full	[c]CI(sp) HF+1+2	[c]CI(sp) MCSCF+1+2	[c]CI(sp) Full
$^4S(2s^22p^3)$					
C^-	0.49	0.52	1.39	1.45	1.46
[d,e]N	0.34	0.35	1.12	1.14	1.14
Δ	0.15	0.17	0.27	0.31	0.32
$^3P(2s^22p^4)$					
O	0.91	1.08	1.90	1.94	1.95
$^2P(2s^22p^5)$					
O^-	1.92	2.39	3.22	3.42	
F	1.58	1.79	2.66	2.73	
Δ	0.34	0.60	0.56	0.69	
$^1S(2s^22p^6)$					
F^-	2.74	3.22	4.09	4.35	
[d,f]Ne	2.33	2.55	3.50	3.61	
Δ	0.41	0.67	0.59	0.74	

[a] The 1s orbital remained doubly occupied in all CI calculations.

[b] Full CI within the p-space.

[c] Excitations allowed only in the (sp) space.

[d] Calculated using the (11s,7p/4s,4p) basis from reference 29.

[e] E_{HF}=-54.4000 hartree.

[f] E_{HF}=-128.5431 hartree.

with the number of p electrons, where for F^- the effect accounts for 0.41eV more correlation energy than found in neon.

Table IX summarizes the errors in the calculated EA's at various levels for HF-based and MCSCF-based wavefunctions. Since in every case the difference between atom and anion is the addition of one more electron, it is reasonable that the differential correlation energy be similar from atom to atom. This is consistent with the concept that the addition of an electron to a system should cost about 1eV in correlation energy. Thus, the error in the uncorrelated EA should be about 1eV. But for HF, as previously mentioned, these errors range from little more than 0.5eV to over 2eV as the p-orbitals become doubly occupied. The FOCI wavefunction, by removing the degeneracy and polarization effects but not the differential p^2 correlation increases this error to 2.01±0.85eV. The MCSCF description which includes the differential $(2p^2 \rightarrow 3p^2)$ radial correlation (and the near-degeneracy effect in the ^3P state of carbon), results in EA's which do reflect this trend, being in error by 0.91±0.09eV, even though the p-orbitals are doubly occupied in oxygen and fluorine. Thus, the nonrelativistic electron affinity (Equation 1) may be more consistently represented by:

$$EA = \Delta E_o + \Delta E_{corr} \qquad (9)$$

TABLE IX. Errors in the calculated electron affinities of carbon, oxygen and fluorine, EA(expt)-EA(i). All units are in eV.

	Carbon	Oxygen	Fluorine	Mean Error
Hartree-Fock	0.74	2.01	2.05	1.40 ± 0.66
[a]Schaefer FOCI	1.16	2.58	2.87	2.01 ± 0.85
HF+1+2 (sp)	0.47	0.69	0.61	0.58 ± 0.11
(spd)	0.25	0.57	0.49	0.41 ± 0.16
(spdf)			0.49	
[b]Y&S HF+1+2	0.16	0.42	0.40	0.29 ± 0.13
[c]MCSCF	0.83	1.00	0.89	0.91 ± 0.09
MCSCF+1+2 (sp)	0.43	0.54	0.43	0.49 ± 0.05
(spd)	0.19	0.37	0.24	0.28 ± 0.09
(spdf)			0.22	
[b]Y&S HF+1+2+3+4	0.14	0.29	0.25	0.21 ± 0.08

---

[a] From reference 23.

[b] Frozen K-shell values taken from reference 2.

[c] Calculated using equations 8a, b and c.

where ΔE_o is the difference between the MCSCF energies of the neutral and anion, and ΔE_{corr} is on the order of 1eV.

Comparing the CI calculations based upon the HF wavefunction to those based upon the $(2p^2 \rightarrow 3p^2)$ MCSCF wavefunction also points up the consistency of the MCSCF approach. While the CI+1+2 error within the (sp) space is 0.58±0.11eV for the HF-based calculations, this is reduced to 0.49±0.05eV for those based upon the MCSCF wavefunction. CI's within the (spd) space result in HF+1+2 errors of 0.41±0.16eV, which is reduced to 0.28±0.09eV if the MCSCF reference wavefunction is used.[35] These results can be compared to the results of Y&S, 0.29±0.13eV for the HF+1+2 errors. Including higher-order excitations, HF+1+2+3+4, which are most comparable to our MCSCF+1+2 calculations, Y&S have an error of 0.21±0.09eV, only 0.07eV less than ours despite the far larger basis sets and configuration lists. Note that the importance of the higher-order terms for the description of the anion increases with the number of p-electrons.

VI. CONCLUSIONS

The zero-order MCSCF wavefunction which includes the differential radial correlation due to the diffuse nature of the (Z+1)st electron in the negative ion, properly predicts the stability of H^-, Li^-, and O^-. This wavefunction gives a consistent error of approximately 1eV in the calculated EA. At higher levels, CI+1+2 calculations based upon these orbitals and configurations provide a consistent method for introducing triple and quadruple excitations (away from the HF configuration) into the wavefunction. With only a [4s,4p,3d] basis we have calculated the HF+1+2 EA's of carbon, oxygen and fluorine to within 0.12eV of the large basis set calculations of Y&S.[2] If the configuration list is based on the MCSCF generating configurations and orbital set, this difference is reduced to 0.07eV, where for fluorine the resulting EA is slightly better than obtained in the near basis set limit HF+1+2+3+4 calculations of Y&S. The MCSCF+1+2 EA's differ from those determined experimentally by about 0.2eV.

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[34] Other forms of MCSCF wavefunctions were examined where, for example, (2s2p->3s3p) or ($2s^2$->$3s^2$) type configurations were included. The orbital characters were affected very little by these additions and CI's based upon these orbitals gave essentially the same energies and EA's as the ($2p^2$->$3p^2$) wavefunction.

[35] The results for carbon and fluorine are in slightly better agreement than for oxygen. This may be due to the stability of the 1/2-filled and filled 2p shells of C^- and F^-.

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[35] The results for carbon and fluorine are in slightly better agreement than for oxygen. This may be due to the stability of the 1/2-filled and filled 2p shells of C^- and F^-.

Part C: TRANSITION METAL ATOMS

I. INTRODUCTION

There is much interest currently in obtaining a consistent theoretical description of the electronic states arising from the s^2d^n, sd^{n+1}, and d^{n+2} configurations of the transition metal atoms.[1-4] While Hartree-Fock (HF) calculations are known to inadequately represent these low-lying states, it has not been well-understood what level of description is required. This inability of the HF model to reproduce the atomic separation has important consequences for the description of the bonding between transition metal atoms and other atoms and molecules. In particular, for manganese through copper, the atomic dissociation limits for small molecular species are biased in favor of the s^2d^n state in the HF picture by as much as 1.3eV compared to experiment, raising serious doubts as to the validity of interpretations based on molecular calculations which do not go beyond the HF model. We have examined the differential correlation effects within the lowest lying states corresponding to the s^2d^n, sd^{n+1}, and d^{n+2} configurations of the first row transition metal atoms using MCSCF and CI approaches (nonrelativistic) with the intention of:

1. Characterizing the major valence correlation effects in these states, and,
2. Developing a compact yet accurate multiconfiguration description for each of the states.

A. Background

The metal atoms typically have a s^2d^nground state sd^{n+1} as the first excited state, and the d^{n+2} state several eVs higher. Experimentally[5] the excitation energies (ΔE) follow two trends, decreasing with Z for d^1 to d^5 (half-filled shell), increasing abruptly at d^6, then decreasing again to d^{10} (filled shell). The sd^{n+1}-s^2d^n ΔE's denoted by $\Delta(n+1)$, are plotted in Figure 1a. Note that at Cr(d^5) and Cu(d^{10}) the two states invert, sd^{n+1} becoming more stable, i.e., the ground state.

Numerical HF results[6] are also presented in Figure 1b as the error with respect to experiment (solid lines). While the general trends are reproduced by HF, the ΔE in Sc-Cr is underestimated by $\sim$0.3eV favoring the sd^{n+1} state, and overestimated in Mn-Cu by $\sim$1.0eV favoring the s^2d^n state. These trends are more consistent if viewed in terms of the number of singlet-coupled electron pairs in each state which are not expected to be represented well in the HF description. In Mn-Cu the two states have the same number of singlet-coupled pairs, i.e., the same multiplicity, and so the HF level of description should be comparable for both states. In Sc-Cr on the other hand, the s^2d^n state always has the one $4s^2$ singlet-coupled pair whereas the sd^{n+1} state, being high spin coupled, has no singlet pairs. Thus, a description for the first half of the row comparable with that of the second half would require correlation of the $4s^2$ pair. The dashed

Figure 1.

$4s3d^{n+1}$-$4s^{2}3d^{n}$ excitation energies of scandium to copper, $[E(sd^{n+1})-E(s^{2}d^{n})]$. All units are in eV.

a) Experimental values (reference 5).

b) Error in the numerical HF excitation energy[6], $[\Delta_{HF} - \Delta E_{EXPER}]$ (solid line). The dashed line is the HF error corrected for the $(4s^{2},4p^{2})$ near degeneracy effect, ΔE_{HF} + 0.78eV(avg).

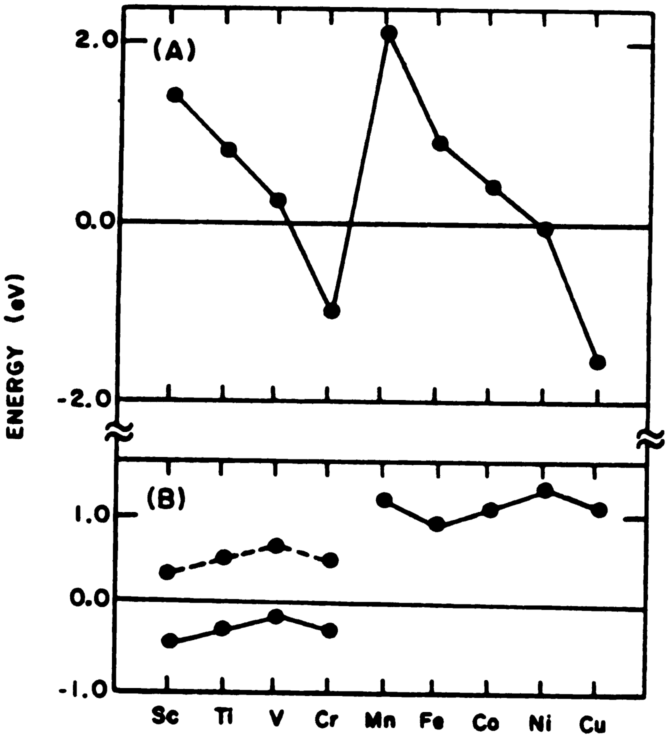

Figure 1.

line gives the ΔE's for Sc-Cr including this correlation (to be discussed in detail later). Now the calculated trend is clear; the ΔE's are consistently overestimated, favoring the s^2d^n state by $\sim$0.5eV for Sc-Cr, and $\sim$1.0eV for Mn-Cu. For the d^{n+2}-s^2d^n ΔE, $\Delta(n+2)$, the same type of HF trends are observed, the error being $\sim$1.4eV for Sc-V and $\sim$3.5eV for Cr-Cu.

Clearly, the inclusion of electron correlation is necessary to properly represent the excitation energies of the low-lying states of the transition metal atoms. A most puzzling point is that is the sd^{n+1} and d^{n+2} states which are less accurately described, even though for d^2-d^5 the electrons all occupy different orbitals and all are high spin coupled. It is this problem which our paper addresses, first by examining in detail the differential correlation effects in terms of a valence MCSCF wavefunction, and then by comparing the ΔE's obtained with this approach to valence CI and experimental values.

B. Basis Set

The primitive Gaussian basis set used in the following calculations, (14s,11p,6d), is that of Wachters[7] augmented with two additional p functions to describe the 4p orbital and one additional, diffuse d function to describe the 3d orbital of the sd^{n+1} and d^{n+2} states.[6] This set was contracted to [5s,4p,3d] using the general contraction scheme of Raffenetti.[8] Since the contraction was based on the atomic orbitals for the s^2d^n state we expect a slight bias toward this state. The HF ΔE's, $\Delta(n+1)$ and $\Delta(n+2)$, for this basis are compared to numerical results in Table I. In general, the basis set error is on the order of $\sim$0.1eV for $\Delta(n+1)$ and $\sim$0.15eV for $\Delta(n+2)$.

For Sc-Cr CI calculations were carried out in which a full set of single-component f-functions was added to the basis and the exponent optimized for each state of the atom based upon a CI wavefunction which included all single and double excitations with respect to the MCSCF configurations. The optimal f-exponents changed significantly from one atom to another but not between states of the same atom; consequently an average f-exponent was used for each atom: Sc(0.27), Ti(0.45), V(0.77), Cr(1.14).

The [5s,4p,3d,1f] basis was examined further for titanium where an additional function of each symmetry type was added and the exponent was optimized in CI calculations with the 1s-3p core orbitals frozen. The additional functions were found to have no significant effect on the s^2d^2 to sd^3 excitation energy.[9]

II. VALENCE CORRELATION EFFECTS IN THE EARLY TRANSITION METAL ATOMS, Sc-Cr

Since energy differences are the quantities related to experimental observables, the important correlations are those which are differential between the states

TABLE I. A comparison of numerical and Gaussian basis set of calculations of the Hartree-Fock $sd^{n+1}-s^2d^n$, $\Delta(n+1)$, and $d^{n+2}-s^2d^n$, $\Delta(n+2)$, excitation energies of scandium to copper. All quantities are in eV.

	$\Delta(n+1)$			$\Delta(n+2)$		
	numerical[a]	Gaussian	Δ	numerical[a]	Gaussian	Δ
Sc	1.00	1.10	0.10	4.47	4.63	0.16
Ti	0.54	0.63	0.09	4.25	4.41	0.16
V	0.12	0.21	0.09	3.27	3.44	0.17
Cr	-1.27	-1.17	0.10	5.75	5.90	0.15
Mn	3.32	3.38	0.06	9.15		
Fe	1.80	1.86	0.06	7.46		
Co	1.53	1.55	0.02	7.05		
Ni	1.28	1.30	0.02	5.47		
Cu	-0.37	-0.34	0.03			

[a] From reference 6

of the atoms. There are three types of pair correlations which arise in the (4s,3d) valence shell:

1. s^2 correlation of the $4s^2$pair (largely the near degeneracy effect)
2. d^2 correlation of the 3d electrons
3. sd correlation between the 4s and 3d electrons

We have used an MCSCF wavefunction to describe the s^2 and d^2 correlation effects. The sd correlation effect was not represented at this level but was, however, included in subsequent CI calculations (discussed in more detail later).

Correlation of the $4s^2$ pair is clearly a differential effect, occuring only in the s^2d^n state. The most important correlating configurations are those which allow angular correlation of the 4s pair represented by a double excitation from 4s into the 4p orbitals. This is the third-row analog of the well-know near degeneracy effect found in first-row atoms.[10] While the magnitude of this effect decreases with Z in the first row as the 2p orbitals become occupied, the 4p orbitals for the states of interest in the metal atoms are unoccupied, so the effect would be expected to remain relatively constant across the row. Inclusion of this effect favors, i.e., differentially lowers the energy of the s^2d^n state.

The d^2 pair correlation effect, on the other hand, occurs in all states of the atoms. We have found that radial correlation of the 3d electrons is by far the most important contribution to the energy[11] and thus, have used correlating configurations which are double excitations from $3d^2$ into $4d^2$, for all 3d pairs[12]. This effect would be expected to be proportional to the number of pairs of d-electrons, $i(i-1)/2$ for d^i, favoring the states in the following order:

$$d^{n+2} > sd^{n+1} > s^2d^n.$$

Since the d-orbitals are known to contract with increasing Z, the d^2 correlation effects would also be expected to increase with Z.

Thus, the valence MCSCF wavefunctions used in the following calculations include angular correlation of the $4s^2$ pair and radial correlation of the $3d^2$ pairs:

$$s^2d^n \quad : \quad c_1 4s^2 3d^n + c_2 4p^2 3d^n + c_3 4s^2 3d^{n-2} 4d^2 \qquad \text{(1a)}$$

$$sd^{n+1} \quad : \quad c_1 4s 3d^{n+1} + c_2 4s 3d^{n-1} 4d^2 \qquad \text{(1b)}$$

$$d^{n+2} \quad : \quad c_1 3d^{n+2} + c_2 3d^n 4d^2 \qquad \text{(1c)}$$

A. Scandium and Titanium

Scandium and titanium, being the simplest transition metal atoms, serve as a useful point to begin discussion of the above effects without the added complication which more d-electrons present. Scandium has a $^2D(4s^23d)$ ground state with the $^4F(4s3d^2)$ first excited state 1.43eV higher. The present HF calculations predict an excitation energy of 1.10eV, 0.10eV above the HF limit and 0.33eV below the experimental value (Table II). The valence MCSCF wavefunction for the s^2d^1 state contains no d^2 correlation term since there is only one d-electron. Addition of the $4p^2$ configuration lowers the energy by 0.75 eV. The MCSCF wavefunction for the sd^2 state has one configuration in addition to the HF configuration to describe the correlation between the two d-electrons. The d^2 correlation energy for this state is 0.21eV. The resulting excitation energy, 1.64eV, now favors the s^2d^1 state by 0.21eV. Improvement of the core basis as judged from numerical HF calculations could reduce the difference with experiment to about 0.1eV.

Titanium has a $^3F(4s^23d^2)$ ground state with the $^5F(4s3d^3)$ first excited state 0.81eV above it (Table III). The HF ΔE is 0.63eV, again 0.09eV above the HF limit, but underestimating the experimental value by 0.18eV. The s^2d^2 state has both s^2 and d^2 correlation terms. The s^2 correlation accounts for a 0.77eV lowering relative to HF, slightly larger than for scandium. The d^2 correlation in s^2d^2 is only 0.09eV. The combination of both s^2 and d^2 correlation is essentially additive, 0.85. In the sd^3 state of Ti the d^2 correlation energy is 0.49eV. The valence MCSCF gives an ΔE of 0.99, 0.19eV above experiment.[13]

While the d^2 state of titanium (s^2d^2) shows a lowering of 0.09eV for one $3d^2$ pair, the effect in scandium (sd^2) is 0.21eV, 2.5 times larger. Further, the

TABLE II. Calculated and experimental energies for the s^2d^1, sd^2 and d^3 states of the scandium atom. Basis set: [5s, 4p, 3d, 1f]. Units are as indicated.

	$^2D(4s^23d)$		$^4F(4s3d^2)$			$^4F(3d^3)$		
	Energy hartree	ΔHF eV	Energy hartree	ΔHF eV	$\Delta(s^2d)$ eV	Energy hartree	ΔHF eV	$\Delta(s^2d)$ eV
HF	-759.7251	0.0	-759.6847	0.0	1.10	-759.5551	0.0	4.63
MCSCF								
$3d^2$-$4d^2$	--		-759.6924	0.21		-759.5833	0.77	
Full[a]	-759.7527	0.75	--		1.64	--		4.61
CI								
HF+1+2	-759.7625	1.02	-759.7005	0.43	1.69	-759.5929	1.03	4.62
MCSCF+1+2	-759.7636	1.05	-759.7007	0.44	1.71	-759.5987	1.19	4.49
Full[b]	-759.7638	1.05	-759.7007	0.44	1.72	-759.5991	1.20	4.48
Experimental[c]					1.43			4.18

[a] MCSCF wavefunctions defined by equations 1a-c

[b] Full-CI for 3 valence electrons

[c] From reference 5

TABLE III. Calculated and experimental energies for the s^2d^2, sd^3, and d^4 states of the titanium atom. Basis set: [5s, 4p, 3d, 1f]. Units are as indicated.

	$^3F(4s^23d^2)$		$^5F(4s3d^3)$			$^5D(3d^4)$		
	Energy hartree	ΔHF eV	Energy hartree	ΔHF eV	$\Delta(s^2d^2)$ eV	Energy hartree	ΔHF eV	$\Delta(s^2d^2)$ eV
HF	-848.3927	0.0	-848.3697	0.0	0.63	-848.2306	0.0	4.41
MCSCF								
$3d^2$-$4d^2$	-848.3961	0.09	-848.3877	0.49		-848.2761	1.24	
$4s^2$-$4p^2$	-848.4210	0.77	--			--		
Full[a]	-848.4241	0.85	--		0.99	--		4.03
CI								
HF+1+2	-848.4377	1.22	-848.4009	0.85	1.00	-848.2909	1.64	4.00
MCSCF+1+2	-848.4396	1.27	-848.4019	0.88	1.03	-848.2974	1.82	3.87
Full[b]	-848.4399	1.28	-848.4020	0.88	1.03	-848.2982	1.84	3.86
Experimental[c]					0.81			3.55

[a] MCSCF wavefunctions defined by equations 1a-c.

[b] Full-CI for 4 valence electrons

[c] From reference 5

d^2 correlation energy in the sd^3 state of Ti, 0.49eV, is much larger than the 0.27eV (0.09eV/pair x three pairs) that would be predicted on the basis of a simple pair dependence of the correlation energy.

B. Differential Trends

The results of the s^2 and d^2 correlation effects for the early transition metal atoms are summarized in Table IV. Here we use the symbol $\varepsilon^n_{4s^2\to 4p^2}$ to denote the energy lowering, relative to the HF energy, obtained from the $(4s^2,4p^2)$ correlations of the $4s^2 3d^n$ states. Similarly, $\varepsilon^n_{3d^2\to 4d^2}$ represents the $(3d^2,4d^2)$ energy lowering of those states with n d-electrons.

Columns 1-3 show the effect of including $4p^2$ and $4d^2$ configurations in the $4s^2 3d^n$ wavefunction. As mentioned earlier, $\varepsilon^n_{4s^2\to 4p^2}$ is relatively constant being 0.78 ± 0.03eV. For the $4s^2 3d^n$ states $\varepsilon^n_{3d^2\to 4d^2}$ increases approximately quadratically with the number of d-electrons following the simple pair formula:

$$\varepsilon^n_{3d^2\to 4d^2} = \Delta\varepsilon_{dd}\,\frac{n(n-1)}{2} \tag{2}$$

where $\Delta\varepsilon_{dd} = 0.087\text{eV}$, and corresponds to the energy lowering associated with correlation of a parallel spin 3d electron pair. Note that it is also approximately the pair energy calculated for the s^2d^2 state of titanium. The

TABLE IV. Valence MCSCF $(4s^2, 4p^2)$, $(3d^2, 4d^2)$ correlation energy differences from Hartree-Fock. All quantities are in eV.

	$4s^2 3d^n$			$4s3d^{n+1}$	$3d^{n+2}$
	Full[a]	$4s^2 \rightarrow 4p^2$	$3d^2 \rightarrow 4d^2$	$3d^2 \rightarrow 4d^2$	$3d^2 \rightarrow 4d^2$
Sc	0.75	0.75	0.0	0.21	0.77
Ti	0.85	0.77	0.09	0.49	1.24
V	1.03	0.79	0.27	0.84	1.69
Cr	1.28	0.80	0.52	1.21	2.48
Mn	1.55	0.81	0.79	1.85	
Fe	2.03	0.82	1.29	2.48	
Co	2.53	0.83	1.81	3.16	
Ni	3.07	0.84	2.37	3.86	
Cu	3.67	0.84	2.99	4.59	

[a] MCSCF wavefunction defined by equation 1a.

first column shows the results of incorporating both effects into an MCSCF wavefunction (Equation 1a). As can be seen, the d^2 and s^2 energies are essentially additive as would be expected if the orbitals are indeed concentrated in different regions of space and the correlation effects noninterfering.

If the same type of d^2 correlation energy were associated with the (n+1) electrons of the sd^{n+1} states of the atoms, $\varepsilon^{n+1}_{3d^2\rightarrow 4d^2}$ would simply be equal to $\varepsilon^{n}_{3d^2\rightarrow 4d^2}$ of Z+1. Comparing columns 3 and 4 shows that this is not the case. Consistent with the results given above for Sc and Ti, the d^2 correlation energy for the sd^{n+1} state in all cases is larger than for the s^2d^n state with the same number of d-electrons. Apparently a different type of correlation is involved with the (n+1) electrons of the sd^{n+1} state than the simple pair repulsions between the n electrons in the s^2d^n state.

We have found the d^2 correlation energy for the sd^{n+1} state to follow a form which is the sum of two terms. The first term represents the correlations between the n d-electrons as in the ground state; the second describes the extra energy of the $(n+1)^{st}$ electron correlating with each of the other n:

$$\varepsilon^{n+1}_{3d^2\rightarrow 4d^2} = \Delta\varepsilon_{dd}\,\frac{n(n-1)}{2} + \Delta\varepsilon_{dd'}\,n \qquad (3)$$

The difference between the d^2 correlation in the two states should, therefore, be linear in n:

$$\Delta E_{3d^2\to 4d^2} = \Delta\varepsilon_{dd'}\ n \tag{4}$$

where the slope of the line gives this extra energy associated with the $(n+1)^{st}$ electron. Figure 2 shows a plot of the d^2 correlation energies for the two states. The energy lowering in the s^2d^n state is represented by the diamonds. The dotted line is a plot of equation (2) with $\Delta\varepsilon_{dd} = 0.087\text{eV}$. The observed good agreement between the calculated energy lowerings and dotted line, rms = 0.005eV, validates the simple pair model of this correlation effect. The d^2 correlation energy for the sd^{n+1} state, $\varepsilon^{n+1}_{3d^2\to 4d^2}$, is represented by the circles. The difference between these values (squares) is seen to be linear in n, where the value of the slope, $\Delta\varepsilon_{dd'}$, is 0.18eV, with rms=0.04 (solid line). The dashed line, associated with the sd^{n+1} state, is simply the sum of the solid and dotted lines.

C. Orbital Interpretation

From the above discussion, it is clear that the d^2 correlation effects in the sd^{n+1} states are unusually large. An understanding of the unique nature of this extra correlation energy is given by contrasting these states to the analogous sp^{n+1} states of the first row atoms. In carbon, for example, the excitation $s^2p^2\to sp^3$ places a 2s electron into a 2p orbital. The shielding of the nuclear charge

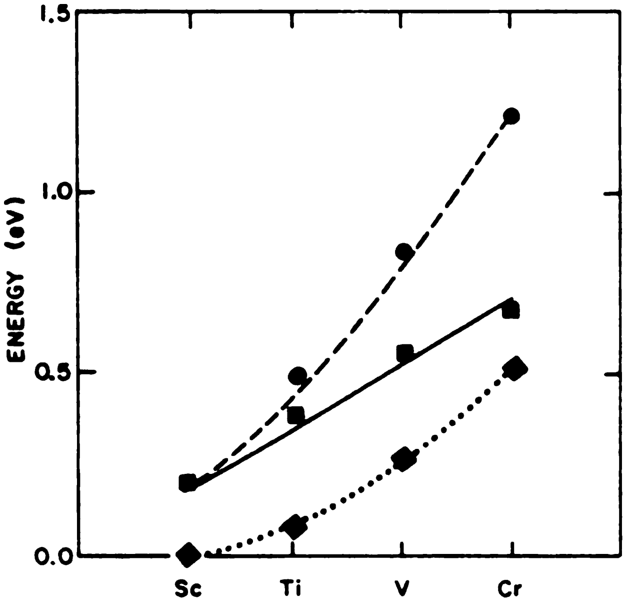

Figure 2.

Calculated ($3d^2,4d^2$) energy lowering relative to HF for the s^2d^n (diamonds) and sd^{n+1} (circles) states of scandium to chromium, [$E_{HF}-E_{MCSCF}$]. The dotted line through the s^2d^n points corresponds to the formula, 0.087 x n(n-1)/2 (rms=0.005eV). The squares correspond to the calculated differential energy lowering between the two states, while the solid line corresponds to the equation 0.18 x n (rms=0.04eV). The dashed line is the sum of the solid and dotted lines. All units are in eV.

by the 2s and 2p electrons is essentially equivalent according to Slater's rules,[14] so that this excitation is not expected to greatly change the net potential felt by the 2p electrons. For carbon the p^2 radial correlation energy for the $^3P(2s^22p^2)$ state is calculated to be 0.12eV using an MCSCF wavefunction which includes the $3p^2$ configurations. If the pair effects were transferable, the p^2 correlation energy for the $^5S(2s2p^3)$ state would simply be three times this amount, or 0.36eV. The calculated energy lowering of 0.30eV is only slightly less.

In the transition metals, on the other hand, the excitation s^2d^n to sd^{n+1} removes an 'outer' 4s electron, placing it into an 'inner' 3d orbital. In this case, Slater's rules state that the 4s electrons do not shield electrons in the 3d shell, however, 3d electrons do partially shield one another. If the (n+1)st d-electron were put into an orbital equivalent to the other n there would be a decrease in the net potential felt by all of the d-electrons, resulting in an expansion of the entire 3d shell. This is, indeed, what happens in a HF wavefunction.[6] Alternatively, the (n+1)st electron can be placed in a somewhat more diffuse orbital, 3d', which does not shield the other n 3d electrons as effectively, and, thus, does not decrease the net potential which they feel. It is this later model that explains the anomalous d^2 correlation effects in the sd^{n+1} states noted above.

This type of description for the d^{n+1} states of the transition metal atoms was first proposed by Froese Fischer[15] in discussing the ionization potential of copper $3d^{10}(^1S)nl$, where she suggested that the last 3d electron should be treated differently from the previous nine, $3d^9 3d'(^1S)nl$. This was further discussed for the $^7P(3d^5 4p)$ state of chromium[11] where, by allowing the fifth 3d electron to be nonequivalent to the other four, the improper HF ordering of the two septet P states arising from $3d^5 4p$ and $3d^4 4s4p$ is corrected.

In support of this picture of the 3d correlation effects we compare the calculated d orbitals of the $4s^2 3d^2$ state of Ti to those of the $4s3d^2$ state of Sc. In order to meaningfully interpret orbitals from an MCSCF calculation it is simplest to first transform them into an equivalent independent particle wavefunction involving nonorthogonal orbitals.[16] This is analogous to the natural orbital to nonorthogonal pair orbital transformation used to interpret generalized valence bond wavefunctions.[17]

In the following, $3d_i$ and $4d_i$ denote the various components of the orthogonal 3d and 4d natural orbitals obtained from the MCSCF calculations, while d_i and d_i' denote the nonorthogonal orbitals of the equivalent independent particle wavefunction. The necessary orbital transformation can then be written:

$$\begin{aligned} &\mathscr{A}[c_1 3d_i 3d_j - c_2 4d_i 4d_j]\,\alpha\alpha \\ &= [2(1+S^2)]^{-\frac{1}{2}}\,\mathscr{A}[d_i d'_j + d_i' d_j]\alpha\alpha \end{aligned}$$

where,

$$d = [(1+S)/2]^{\frac{1}{2}}\, 3d + [(1-S)/2]^{\frac{1}{2}}\, 4d$$

$$d' = [(1+S)/2]^{\frac{1}{2}}\, 3d - [(1-S)/2]^{\frac{1}{2}}\, 4d$$

$$S = \langle d|d'\rangle = (c_1-c_2)/(c_1+c_2)$$

To make the independent particle nature of this wavefunction more evident we define a projection operator $\mathscr{P}_F$ which eliminates all but the F component of a many electron wavefunction. With this definition, the wavefunction for the ^3F state of Ti may be written as:

$$\mathscr{P}_F \mathscr{A} d_i d'_j \alpha\alpha$$

where now the physical interpretation of these orbitals is clear; one electron is bound in orbital d_i and the second electron is bound in a nonequivalent orbital, d'_j. The projection operator then assures that the wavefunction will have the correct spatial symmetry.

The overlap between the nonorthogonal orbitals, d and d' is high when the contribution of the 4d correlating orbital is low, resulting in two orbitals very similar to the HF orbital[18] (if S=1, $d=d'=3d_{HF}$). Comparing these orbitals to $3d_{HF}$ is then a measure of the breakdown of the single configuration representation of the 3d orbitals inherent to the HF wavefunction. In Figures 3 and 4 the radial amplitudes of the d, d' and $3d_{HF}$ orbitals are plotted as a function of the distance from the nucleus, R.

The Ti s^2d^2 nonorthogonal d orbitals (dashed lines) and the HF orbital (solid line) are shown in

Figure 3. The essential equivalence of these orbitals is reflected in their high overlap, S=0.91, and in the small deviation of the expectation value of R, <R>, from that of the HF orbital: 1.20, 1.82, and 1.46 a_o for d, d' and $3d_{HF}$, respectively. Contrast this with the sd^2 orbitals of Sc plotted in Figure 4. Here the nonequivalence of the d and d' orbitals is reflected in the lower overlap, S=0.81, and in the larger deviation of <R> from HF: 1.52 and $3.06a_o$ compared to $2.13a_o$ for $3d_{HF}$. The nonorthogonal d orbital in the sd^2 excited state of scandium is actually very similar in radial extent to the 3d orbital in the s^2d^1 ground state ($<R>=1.68a_o$).

Thus, an orbital picture emerges which ascribes a different type of binding to the 3d electrons in the s^2d^n and sd^{n+1} states of the transition metal atoms:

- The s^2d^n states have n 3d-electrons in essentially equivalent orbitals with $\Delta\varepsilon_{dd}$ = 0.087eV correlation energy for each pair of d-electrons.
- The sd^{n+1} states have n 3d-electrons bound approximately the same as in the ground state with the same correlation energy, $\Delta\varepsilon_{dd}$ for the $\frac{n(n-1)}{2}$ pairs; and one electron, the $(n+1)^{st}$, in a more diffuse orbital with an additional $\Delta\varepsilon_{dd'}$ = 0.18eV correlation energy for

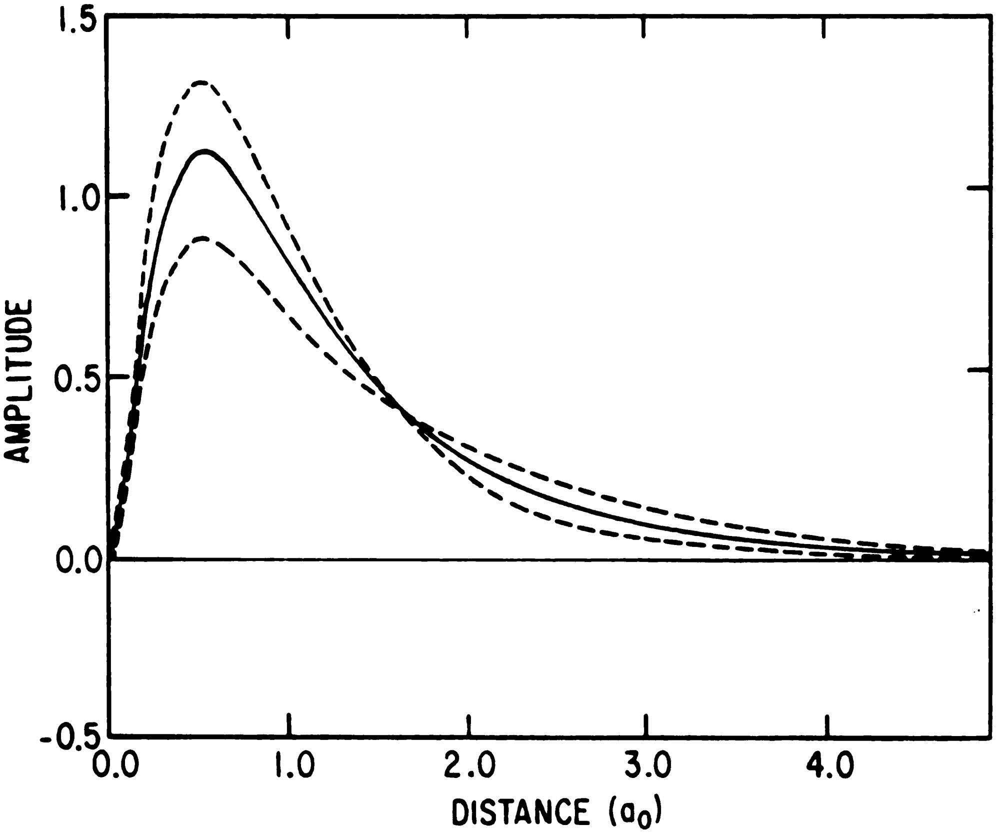

Figure 3.

Radial plots of the Hartree-Fock (solid) and nonorthogonal d-orbitals (dashed curves) for the $^3F(4s^2 3d^2)$ state of titanium.

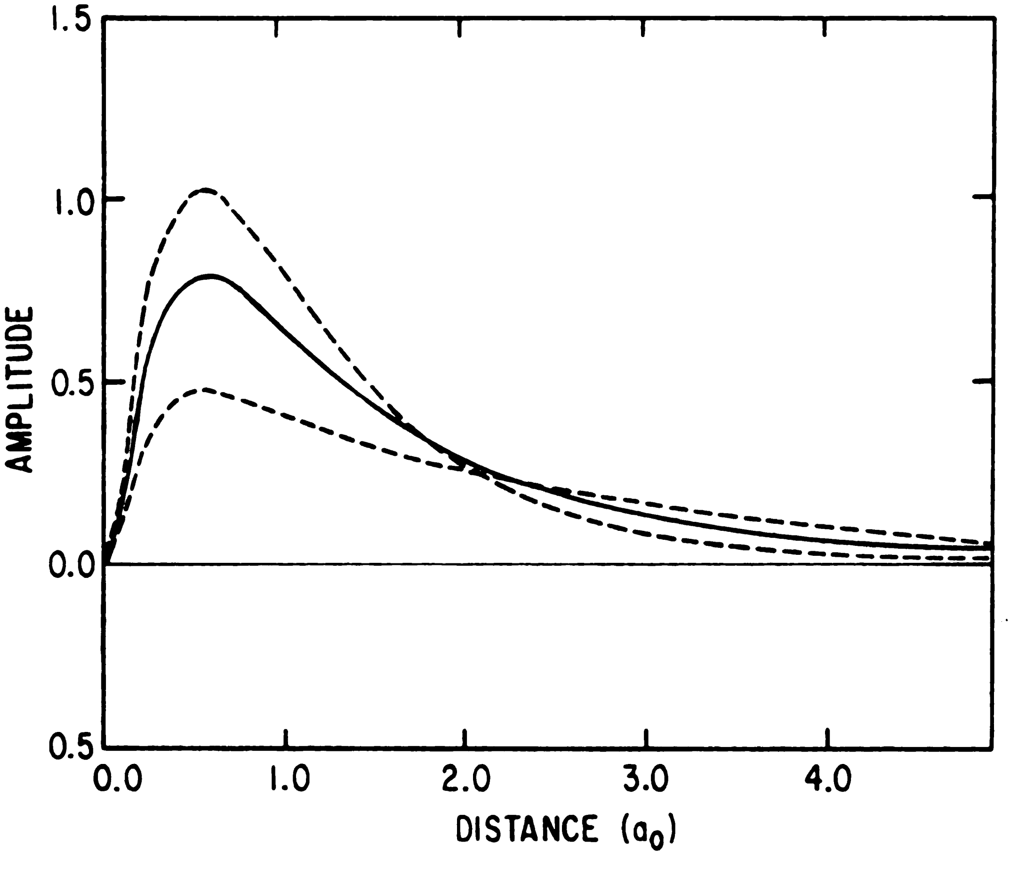

Figure 4.

Radial plots of the Hartree-Fock (solid) and nonorthogonal d-orbitals (dashed curves) for the $^4F(4s3d^2)$ state of scandium.

each of the n other d-electrons
with which it correlates.

The HF description, restricted to a single configuration wavefunction, is unable to allow for the diffuse 3d' orbital in the sd^{n+1} state, resulting instead in equivalent 3d orbitals, all of which expand relative to those of the s^2d^n state. The valence MCSCF wavefunction, which lifts this restriction, finds that n electrons are bound as in the s^2d^n ground state, with only the $(n+1)^{st}$ electron occupying a more diffuse orbital.

D. CI Calculations

While the valence MCSCF wavefunction presents a consistent picture of the differential s and d correlations within the s^2d^n and sd^{n+1} states of the atoms, its utility as a practical method for use in electronic structure calculations depends upon its ability to track the energy differences obtainable in a full valence CI. In the following section, we compare the excitation energies obtained at each level in order to determine the additional correlation effects which have been neglected or underestimated in the valence MCSCF wavefunction.

Valence CI calculations within the entire virtual space were carried out for scandium to chromium which included all single and double excitations with respect to the HF reference configuration (HF+1+2), or the MCSCF reference configurations (MCSCF+1+2), constructed from the

MCSCF orbitals for each state (Tables II, III, V, VI). For both Sc and Ti full valence CI calculations are reported as well. As previously noted, for the CI calculations the basis set was expanded to include an f-function.

Discussing first the s^2d^n and sd^{n+1} states it is seen from Table VII that the MCSCF calculations faithfully represent the ΔE's obtained from the CI calculations, the differences ranging from 0.04 to 0.07eV. Note that HF+1+2 gives ΔE's closer to experiment than either the MCSCF+1+2 or the full-CI,[19] but all three are quite comparable and well-represented by the valence MCSCF wavefunction.

In order to verify that the s^2 and d^2 differential pair correlation energies are well-represented by the valence MCSCF wavefunction, pair CI calculations were carried out consisting of single and double excitations from the 4s or 3d orbitals into the virtual space for the ^5D and ^7S states of chromium. In addition, the sd correlation energy was estimated from a similar CI calculation by allowing simultaneous single excitations from the 4s and 3d orbitals into the virtuals. These results are summarized in Table VIII where the difference with E_{HF} is given for MCSCF, and CI calculations in which excitations were allowed within the (s,p,d) and (s,p,d,f) virtual space. Comparing the energies of the MCSCF wavefunction with the CI within the (s,p,d) space, it is noted that there is less than 0.1eV improvement in either the s^2 or d^2

TABLE V. Calculated and experimental energies for the s^2d^3, sd^4 and d^5 states of the vandium atom. Basis set: [5s,4p,3d,1f]. Units are as indicated.

	$^4F(4s^23d^3)$		$^6D(4s3d^4)$			$^6S(3d^5)$		
	Energy hartree	ΔHF EV	Energy hartree	ΔHF eV	$\Delta(s^2d^3)$ eV	Energy hartree	ΔHF eV	$\Delta(s^2d^3)$ eV
HF	-942.8678	0.0	-942.8602	0.0	0.21	-942.7414	0.0	3.44
MCSCF								
$3d^2$-$4d^2$	-942.8777	0.27	-942.8912	0.84		-942.8037	1.69	
$4s^2$-$4p^2$	-942.8966	0.79	--			--		
Full[a]	-942.9058	1.03	--		0.40	--		2.78
CI								
HF+1+2	-942.9255	1.57	-942.9117	1.40	0.38	-942.8245	2.26	2.75
MCSCF+1+2	-942.9286	1.65	-942.9137	1.45	0.41	-942.8322	2.46	2.62
Experimental[b]					0.24			2.46

[a] MCSCF wavefunctions defined by equations 1a-c.

[b] From reference 5

TABLE VI. Calculated and experimental energies for the s^2d^4, sd^5, and d^6 states of the chromium atom. Basis set: [5s,4p,3d,1f]. Units are as indicated.

	$^5D(4s^23d^4)$		$^7S(4s3d^5)$			$^5F(3d^6)$		
	Energy hartree	ΔHF eV	Energy hartree	ΔHF eV	$\Delta(s^2d^4)$ eV	Energy hartree	ΔHF eV	$\Delta(s^2d^4)$ eV
HF	-1043.2891	0.0	-1043.3323	0.0	-1.17	-1043.0724	0.0	5.90
MCSCF								
$3d^2$-$4d^2$	-1043.3082	0.52	-1043.3766	1.21		-1043.1637	2.48	
$4s^2$-$4p^2$	-1043.3184	0.80	--			--		
Full[a]	-1043.3360	1.28	--		-1.10	--		4.69
CI								
HF+1+2	-1043.3648	2.06	-1043.4046	1.97	-1.08	-1043.2091[b]	3.72	4.24
MCSCF+1+2	-1043.3695	2.19	-1043.4077	2.05	-1.04	-1043.2258[b]	4.17	3.91
Experimental[c]					-1.00			3.40

[a] MCSCF wavefunctions defined by equations 1a-c

[b] Converged only by deleting the 4s orbital from the virtual space

[c] From reference 5

TABLE VII. $4s3d^{n+1}-4s^{2}3d^{n}$ calculated and experimental excitation energies for scandium to chromium. All units are in eV.

	Sc	Ti	V	Cr
HF	1.10	0.63	0.21	-1.17
MCSCF[a]	1.64	0.99	0.40	-1.10
CI: HF+1+2	1.69	1.00	0.38	-1.08
MCSCF+1+2	1.71	1.03	0.41	-1.04
Full[b]	1.72	1.03		
Experimental:				
Relativistic[c]	1.43	0.81	0.24	-1.00
'Non-Relativistic'[d]	1.31	0.67	0.07	-1.21

[a] MCSCF wavefunctions defined by equations 1a and 1b.

[b] Full-CI for (n+2) valence electrons

[c] From reference 5

[d] Corrected for differential relativistic effects taken from numerical relativistic HF calculations (reference 27) for each state.

TABLE VIII. $4s^2$, $3d^2$ and 4s3d pair correlation energy differences from Hartree-Fock for the chromium atom. All units are in eV.

		HF+1+2			
	MCSCF	(spd) [a]	ΔMCSCF	(spdf) [6]	ΔMCSCF
$^5D(4s^2 3d^4)$					
$4s^2$	0.80	0.87	0.07	0.88	0.08
$3d^2$	0.52	0.54	0.02	0.90	0.38
4s3d	--	0.26	0.26	0.48	0.48
$^7S(4s3d^5)$					
$3d^2$	1.21	1.26	0.05	1.79	0.58
4s3d	--	0.09	0.09	0.21	0.21
$^5D(3d^6)$					
$3d^2$	2.48	3.11	0.63	3.72	1.24

[a] Single and double excitations restricted to the (spd) virtual space.

[b] Single and double excitations allowed within the entire (spdf) virtual space.

correlation energy for either state. So inclusion of other s,p or d functions does not affect the description of these correlation effects which are indeed well-represented by the valence MCSCF wavefunction. The sd correlation effect is seen to favor the s^2d^n state, the state with the most s-electrons. This implies that all three pair effects included in a single and double CI within the (s,p,d) virtual space should increase the ΔE relative to the MCSCF energy, which, in fact, it does by 0.2eV.[20] If f-excitations are allowed in the CI, the s^2 description is still unaffected, but now the energy lowerings from d^2 and sd excitations are significantly larger. Relative to the spdf-CI then, the MCSCF calculation for the s^2d^4 state neglects correlation effects worth 0.94eV while for the sd^5 state the difference is 0.79eV. Thus, the difference between the MCSCF and spdf-CI ΔE is only 0.15eV.

Thus, without f-functions the sd^{n+1}-s^2d^n excitation energy will increase at the CI+1+2 level over the valence MCSCF energy because the differential sd correlation, favoring the s^2d^n state, is now included. Including f-functions has little effect on the s^2 correlation energy but increases *both* the d^2 and the sd pair correlation energies, leading to essentially the same ΔE as obtained at the valence MCSCF level. While the lowering from the sd excitations shows a differential effect in the pair-CI calculation, it should be noted that the three effects, taken together, are not completely additive, implying that the results in Table VIII overestimate this effect. Secondly, this correlation description is not expected to change the qualitative features of the orbitals significantly, thus supporting its exclusion at the MCSCF level.

It is appropriate at this point to discuss the calculations on the d^{n+2} states of Sc-Cr. In general, the d^{n+2} states are expected to be more difficult to describe than the sd^{n+1} states using a valence MCSCF wavefunction which makes use of only 3d and 4d orbitals. Now three nonorthogonal orbitals, d, d', and d'', may well be required to represent the diffuse nature of the $(n+1)^{st}$ and $(n+2)^{nd}$ d-orbitals.[21] Although the d^2 valence MCSCF energy lowerings relative to HF, $\varepsilon^{n+2}_{3d^2 \to 4d^2}$, are larger than seen for sd^{n+1} (Table IV), CI's within the (3d,4d,5d) space indicate that the 5d orbital also plays an important role in describing the d^2 correlation effect, i.e., the 3d and 4d MCSCF orbitals alone are not sufficient. Comparing these results to other levels of description (Table IX), it is seen that the valence MCSCF wavefunction is a much better description of the d^{n+2} state than is the HF wavefunction, leading in all cases to ΔE's less than 0.2eV above those obtained from CI's in which the entire virtual space is included. We note that a large part of the difference between the MCSCF and full virtual CI+1+2 results can be accounted for by allowing excitations from the MCSCF wavefunction into a third set of d-functions (5d).

TABLE IX. $3d^{n+2}-4s^{2}3d^{n}$ calculated and experimental excitation energies for scandium to chromium. All units are in eV.

	Sc	Ti	V	Cr
HF	4.63	4.41	3.44	5.90
MCSCF[a]	4.61	4.03	2.78	4.69
CI:				
HF+1+2	4.62	4.00	2.75	4.24[b]
MCSCF+1+2				
(3d,4d,5d)[c]	4.53	3.86	2.59	3.92
all virtuals[d]	4.49	3.87	2.62	3.91[b]
Full-CI[e]	4.48	3.86	--	--
Experimental:				
Relativistic[f]	4.18	3.55	2.46	3.40
'Non-Relativistic'[g]	4.00	3.33	2.18	3.09

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[a] MCSCF wavefunctions defined by equations 1a and 1c.

[b] The d^{6} state converged only by deleting the 4s orbital from the virtual space.

[c] Single and double excitations of the 3d electrons restricted to the (3d,4d,5d) space.

[d] Single and double excitations of all (n+2) valence electrons allowed into the entire virtual space.

[e] Full-CI for the (n+2) valence electrons.

[f] From reference 5.

[g] Corrected for differential relativistic effects taken from numerical relativistic HF calculations (reference 27) for each state.

As indicated by the CI calculations, the valence MCSCF wavefunction provides a compact representation of the differential s^2 and d^2 correlation effects between the s^2d^n, sd^{n+1}, and d^{n+2} states of Sc-Cr. While this form of the wavefunction is not as accurate for the d^{n+2} state, it is still a far better description than the HF wavefunction provides. For all of these states, the valence MCSCF description condenses the major valence correlation effects into a form which lends itself to molecular calculations.

E. Experimental Excitation Energies

Comparing the calculated ΔE's $\Delta(n+1)$ and $\Delta(n+2)$, to the experimental values for Sc-Cr (Tables VII and IX), indicates that even with full valence correlation of the (4s,3d) electrons the ΔE's are overestimated, favoring the s^2d^n state by ∿0.2eV for $\Delta(n+1)$, and ∿0.3eV for $\Delta(n+2)$. Note that the error is much larger, 0.52eV, for the d^6-s^2d^4 ΔE of Cr due to the presence of the doubly-occupied d-orbital in the upper state.

III. VALENCE CORRELATION EFFECTS IN THE LATE TRANSITION METAL ATOMS, Mn-Cu

We have examined the differential valence correlation effects between the s^2d^n and sd^{n+1} states of manganese through copper in terms of the valence MCSCF wavefunction (Equations 1a-c) discussed previously. The same type of s^2 and d^2 correlations were incorporated into the MCSCF orbitals as in the first half of the row except now, since the d-orbitals are doubly-occupied, there are four types of d-d interactions: $(\alpha\beta)_{ii}$, $(\alpha\beta)_{ij}$, and $(\beta\beta)_{ij}$, as well as the $(\alpha\alpha)_{ij}$ term from before. Thus, configurations which allow $3d_i^2 \rightarrow 4d_i^2$ and $3d_i^2\ 3d_j^2 \rightarrow 3d_i 4d_i 3d_j 4d_j$, as well as $3d_i 3d_j \rightarrow 4d_i 4d_j$, were included in the calculations.

A. Differential Trends

The results of the s^2 and d^2 differential correlation effects for the late transition metal atoms are summarized in Table IV. The s^2 correlation in the s^2d^n state was again found to be essentially constant and approximately equal to that for the early transition metal atoms, 0.82 ± 0.02eV. As in the first half of the row, the s^2 and d^2 correlation energies are found to be nearly additive. Because the d^2 correlation effects are now complicated by the additional interactions due to the presence of the β-electrons, they are best understood by considering all of the α,β interactions within the n and (n+1) d-electrons. Since both states have five α-electrons, there will always be $5(4)/2$ $\alpha\alpha$-interactions. In addition, for the s^2d^n state, there are (n-5) doubly-occupied orbitals so there will be:

(n-5)	$(\alpha\beta)_{ii}$ interactions,
4(n-5)	$(\alpha\beta)_{ij}$ interactions,
and, (n-5)(n-6) /2	$(\beta\beta)_{ij}$ interactions.

For the sd^{n+1} state there are (n-4) doubly-occupied orbitals, with the corresponding number of interactions, resulting in the differential energy expression:

$$\Delta E_{3d^2 \rightarrow 4d^2} = \varepsilon_{ii}(\alpha\beta) + 4\varepsilon_{ij}(\alpha\beta) + (n-5)\varepsilon_{ij}(\beta\beta)$$

This expression is linear in n as with the first half of the row (Equation 4), but has an additional constant term, due to the correlations of the $(n+1)^{st}$ β-electron with the five α-electrons. In Figure 5, $\Delta E_{3d^2 \rightarrow 4d^2}$ is plotted as a function of n for Sc-Cr as well as Mn-Cu. As predicted, these differences are linear in n, the line for Mn-Cu shifted upward relative to Sc-Cr because of the additional constant term. Note that the slopes of each are similar, being 0.18 and 0.14 eV (rms=0.02) for the first and second halves respectively, indicating that the correlation energy of the $(n+1)^{st}$ electron with the other n electrons is similar for Sc-Cr and Mn-Cu. This d-d' interaction energy for the second half is also ∿0.1eV higher than that found in the s^2d^n state, implying again that the $(n+1)^{st}$ electron is loosely bound.

B. CI Calculations on the Nickel Atom

Because of its experimental and theoretical importance,[22] we have carried out valence CI calculations (HF+1+2) for the s^2d^8 and sd^9 states of the nickel atom, within the [5s,4p,3d] basis, using the orbitals obtained

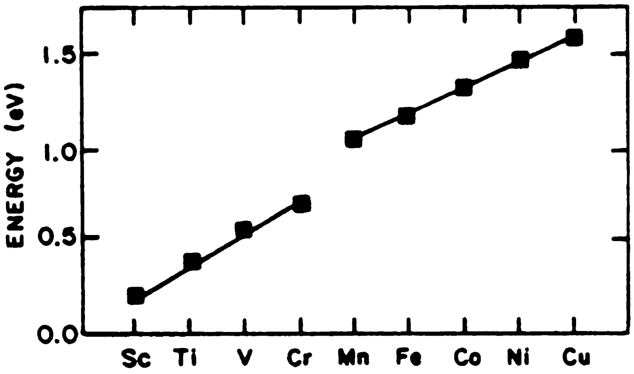

Figure 5.

Differential ($3d^2$, $4d^2$) energy lowerings for the s^2d^n and sd^{n+1} states of scandium to copper as calculated in this work. All units are in eV.

from the valence MCSCF calculations. These results are summarized in Table X. The valence MCSCF wavefunction predicts an sd^9-s^2d^8 ΔE of 0.51eV while HF+1+2 gives a value of 0.42. Similar valence HF+1+2 calculations by Martin,[2] in which the HF orbitals were used as the expansion basis, resulted in an energy separation of 0.32eV. This separation increased to 0.46eV upon uncontracting the 3s and 3p core orbitals, whereupon, addition of an f-function to describe (4s,3d) correlation, was found to lower this ΔE to 0.30eV. These results are consistent with the conclusions for the first half of the row that the valence MCSCF wavefunction does present a reasonable description of the valence correlation in the s^2d^n and sd^{n+1} states even when doubly occupied d-orbitals are involved.

C. Experimental Excitation Energies

The excitation energies calculated with the valence MCSCF wavefunction are compared to the experimental values in Table XI. While the error for HF ranges from 1.0 to 1.3eV, this has been reduced using the valence MCSCF approach to 0.5-0.2eV for Fe-Cu.[23] This error is larger than seen in Sc-Cr but is still reasonable since it is estimated that single and double valence CI calculations would give similar results.

TABLE X. Calculated and experimental energies for the s^2d^8 and sd^9 states of the nickel atom. Basis set: [5s,4p,3d]. Units are as indicated.

	$^3F(4s^23d^8)$		$^3D(4s3d^9)$		
	Energy hartree	ΔHF eV	Energy hartree	ΔHF eV	$\Delta(s^2d^8)$ eV
HF	-1506.8214	0.0	-1506.7736	0.0	1.30
MCSCF					
$3d^2$-$4d^2$	-1506.9084	2.37	-1506.9155	3.86	
$4s^2$-$4p^2$	-1506.8522	0.84	--		
Full[a]	-1506.9341	3.07	--		0.51
CI					
HF+1+2	-1506.9533	3.59	-1506.9377	4.47	0.42
Experimental[b]					-0.03

[a] MCSCF wavefunctions defined by equations 1a and b.

[b] From reference 5

TABLE XI. $4s3d^{n+1}-4s^{2}3d^{n}$ calculated and experimental excitation energies for manganese to copper. All units are in eV.

	Mn	Fe	Co	Ni	Cu
HF	3.38	1.86	1.55	1.30	-0.34
MCSCF[a]	3.07	1.40	0.93	0.51	-1.26
Experimental:					
Relativistic[b]	2.14	0.88	0.42	-0.03	-1.49
'Non-Relativistic'[c]				-0.38	

[a] MCSCF wavefunctions defined by equations 1a and 1b.

[b] From reference 5.

[c] Corrected for differential relativistic effects taken from numerical relativistic HF calculations (reference 2) for each state.

IV. OTHER CONSIDERATIONS

Since the valence correlated energies of the s^2d^n and sd^{n+1} states of the transition metal atoms are still in error by ∿0.2eV for Sc-Cr and ∿0.5 for Mn-Cu compared to the experimental ΔE's, there must be other differential effects which are of importance. The two major effects which have been neglected are:

-- Correlation effects involving the 'core' (3s,3p) electrons

-- Relativistic effects

A. Core Correlations

While true core electrons would be expected to be unaffected by changes within the valence electron occupancy, the (3s,3p,3d) orbitals are all concentrated in similar regions of space so that changes in the 3d occupancy could induce a differential effect in correlation of the 3s and 3p electrons. There are three types of correlation effects which could arise:

1. The (3s,3p,3d) near degeneracy effect
2. Core/valence dynamic correlation
3. Correlation of the 3s and 3p electrons, including space and spin polarization effects.

The near degeneracy effect observed in the N=3 shell is analogous to the effect in (4s,4p) discussed previously only now excitations into the empty 3d orbital are involved. It can be represented by a CI wavefunction which allows double excitations from (3s,3p) into 3d. As with the first row, this effect will decrease as the d-orbitals become occupied. It will favor the state with the fewest d-electrons, s^2d^n, since the more d 'holes' there are, the more orbitals available for correlation. This effect is evident in the paper by Guse, *et al.*[3] (labeled as a differential core-core correlation effect).

The core/valence dynamic correlation effect describes the instantaneous correlation of the core and valence electrons. It is represented by simultaneous single excitations of (3s,3p) and (3d,4s) into the virtual space. This effect would be largest for the state with the most d-electrons, since it is the 3d's which should interact most strongly with the (3s,3p) electrons decreasing the sd^{n+1}-s^2d^n excitation energy. Preliminary calculations[24] show that a second tight f-function is needed to describe this correlation properly[25] as the dominant configurations are those which involve 3p,3d→nd,4f.

Spatial and spin polarization effects among the 3s and 3p electrons can be induced by the asymmetric charge distribution of the 3d and 4s electrons. Munch and Davidson, in calculations on the $^4F(s^2d^3)$ state of vanadium,[26] noted the importance of the single excitation 3p→f, which describes the polarization of the 3p shell by the asymmetric d shell. Thus, a second f-function is also needed to describe spatial polarization of the 3p electrons as well as the dynamic correlation between core and valence. These effects will be state-dependent since the orbital occupancies vary considerably from Sc-Cu. For example, the Cr $^7S(sd^5)$ state should show no spatial effects but spin polarization due to the six α-electrons may be important; whereas for Ni $^1S(d^{10})$ both effects will be zero. It is not clear what kinds of differential trends will emerge due to these effects.

Thus, two competing effects occur in the correlation of the n=3 shell: the (3s,3p,3d) near degeneracy effect favoring the s^2d^n state; and the dynamic correlation of the 3s and 3p electrons with the valence 4s and 3d, favoring the sd^{n+1} and d^{n+2} states. A third effect, spatial and spin polarization within the (3s,3p) electrons may also be important but not clearly favoring either the ground or excited states. Data taken from Guse, *et al.*[3] imply that correlation of the core electrons increases in importance from Sc-Cu.

B. Relativistic Effects

Relativistic HF calculations have been carried out by Martin and Hay[27] for Sc-Cr to determine the differential effects between the s^2d^n, sd^{n+1} and d^{n+2} states of the transition metal atoms. Their results indicate that in all cases the relativistic energies lower the s^2d^n states. The differential effect for $\Delta(n+1)$ is 0.1eV for Sc, increasing to 0.2eV for Cr. The differential effect for $\Delta(n+2)$ is 0.2eV for Sc, increasing to 0.3eV for Cr. It appears that this trend prevails across the row so that for nickel the relativistic effect has increased the sd^9-s^2d^8 splitting by 0.35eV[2]. Because this effect is large, the calculated nonrelativistic ΔE's should actually be compared to 'nonrelativistic experimental' values, given in Tables VII, IX and XI, where the experimental values have been corrected for the differential relativistic effects taken from Martin and Hay's numerical HF calculations. With the s^2d^n state being differentially lowered by these effects, the ΔE's which are comparable to the calculated values are all smaller in magnitude than the reported values and consequently, the error in the calculated values is even larger.

V. CONCLUSIONS

A reasonable description of the differential valence correlation effects within the s^2d^n, sd^{n+1}, and d^{n+2} states can be obtained at the MCSCF level by using a wavefunction which incorporates $(3d^2, 4d^2)$ radial correlation, and $(4s^2, 4p^2)$ angular correlation effects. This simple wavefunction reproduces well the results of a single and double excitation valence CI calculation including f-functions in the basis. The ΔE's obtained from the simple MCSCF wavefunction are in error by 0.2eV for Sc-Cr and 0.5eV for Mn-Cu for the sd^{n+1}-s^2d^n excitation energies.

An interpretation which is consistent with these results is that in the sd^{n+1} and d^{n+2} states of the transition metal atoms the $(n+1)^{st}$ and $(n+2)^{nd}$ 3d-electrons are not bound as tightly to the nucleus as the other n electrons. These states are more appropriately described as:

$$4s3d^{n+1} \longrightarrow 4s3d^{n}3d'$$

$$3d^{n+2} \longrightarrow 3d^{n}3d'3d''$$

signifying that n electrons are bound as in the s^2d^n ground state with the additional d-electrons occupying more diffuse orbitals, 3d' and 3d'', nonorthogonal to the other 3d orbitals.

If relativistic effects are included in the description of each state, the error in the excitation energy appears to increase. This implies that a highly accurate description of the splittings of the low-lying states of the transition metal atoms requires that differential correlation involving the (3s,3p) 'core' electrons also be taken into account.

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[18] The HF orbital is approximately an occupation number weighted average of d and d'.

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[20] This increase in the ΔE(eV) for the rest of the row is: Sc(0.13), Ti(0.11), V(0.19).

[21] The d' and d'' orbitals may be similar in radial extent.

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REPRINT

On the orbital description of the $4s3d^{n+1}$ states of the transition metal atoms[a)]

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The diverse and complex chemistry of the first row transition metal atoms is in large part due to the near degeneracy of the 4*s* and 3*d* orbitals. Thus, depending on the molecular environment, the formal configuration of the transition metal atom may be $4s^2 3d^n$, $4s3d^{n+1}$, or $3d^{n+2}$. Clearly then, it is important that the theoretical methods used to study transition metal compounds be able to accurately predict the relative energies of these atomic states. Despite its widespread use in calculations on molecules containing transition metal atoms, the Hartree–Fock method does not satisfy this criterion, e.g., for the nickel atom Hartree–Fock calculations[1] place the $^3D(4s3d^9)$ state 1.28 eV and the $^1S(3d^{10})$ state 5.47 eV above the $^3F(4s^2 3d^8)$ state, whereas the experimental separations are −0.03 eV and 1.71 eV.[2]

In calculations on the ground and low-lying excited states of the titanium atom, we have found that the Hartree–Fock descriptions of the $4s3d^3$ and $3d^4$ states are inadequate. These calculations indicate that the "$(n+1)$st" 3*d* orbital of the $4s3d^{n+1}$ states and the "$(n+1)$st" and "$(n+2)$nd" 3*d* orbitals of the $3d^{n+2}$ states of the transition metal atoms are functionally inequivalent to the other 3*d* orbitals, being much more diffuse. Thus, the proper orbital configurations of these states are $4s3d^n 3d'$ and $3d^n 3d' 3d''$.

The primitive basis set used in the calculations on the titanium atom, (14*s*11*p*6*d*), is that of Wachters[3] augmented with two additional *p* functions to describe the 4*p* orbital and one additional, diffuse *d* function to describe the 3*d* orbital of the $4s3d^3$ state.[4] Hartree–Fock (HF) calculations with this basis set predict a ^5F–^3F splitting of 0.55 eV; numerical HF calculations[1] give a nearly identical result, namely, 0.54 eV. For the subsequent atomic calculations the primitive set was contracted to [6*s*6*p*3*d*] using the general contraction scheme of Raffenetti.[5]

If one of the 3*d* orbitals in the $^5F(4s3d^3)$ state of titanium is functionally different from the remaining two 3*d* orbitals, the resulting *projected Hartree–Fock* (PHF) wave function has the form (with the core orbitals deleted)

TABLE I. Summary of Hartree–Fock (HF) and multiconfiguration Hartree–Fock (MCHF) calculations on the $^5F(4s3d^3)$ and $^3F(4s^2 3d^2)$ states of the titanium atom.

	$^5F(4s3d^3)$	$^3F(4s^2 3d^2)$
E_{HF} (hartree)	−848.3715	−848.3918
$\Delta E_{HF}(^5F-{}^3F)$ (eV)	0.55	···
E_{MCHF} (hartree)	−848.3882	−848.4202
c_1	0.90	0.96
c_2	0.43	0.29
$E_{MCHF}-E_{HF}$ (eV)	−0.45	−0.77
$\Delta E_{MCHF}(^5F-{}^3F)$ (eV)	0.87	···

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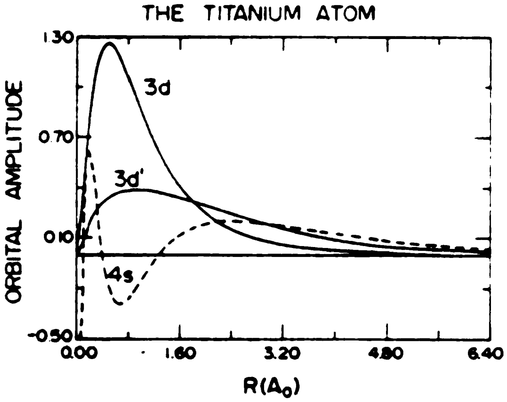

FIG. 1. Radial plots of the 4s, 3d, and 3d' orbitals of the $^5F(4s3d^3)$ state of the titanium atom obtained from multiconfiguration Hartree–Fock calculations.

$$\Psi_{\mathrm{PHF}}(^5F) = \hat{\mathcal{P}}\mathcal{A}\,4s3d^2 3d'\alpha\alpha\alpha\alpha, \tag{1a}$$

where $\hat{\mathcal{P}}$ is a projection operator which insures that the wave function has the proper spatial symmetry. Noting that

$$3d' = c_{3d}3d + c_{4d}4d\ ,$$

(1a) can be rewritten as a *multiconfiguration Hartree–Fock* (MCHF) wave function

$$\Psi_{\mathrm{MCHF}}(^5F) = c_1\mathcal{A}\,4s3d^3\alpha\alpha\alpha\alpha + c_2\mathcal{A}\,4s3d^2 4d\,\alpha\alpha\alpha\alpha\ . \tag{1b}$$

It is in this form that calculations were carried out with the BISON-MC program.[6] There is, of course, a simple relationship between the two sets of coefficients (c_{3d}, c_{4d}) and (c_1, c_2) and, correspondingly, between the two wave functions (1a) and (1b).

The energy computed with (1), along with the HF results, are given in Table I. The size of the energy lowering, 0.45 eV, and the large value of c_2, 0.43, reflects the unusual strength of this correlation effect even though the electrons involved are in spatially different 3d orbitals and are high spin coupled. The 4s, 3d, and 3d' orbitals obtained from the MCHF calculations are plotted in Fig. 1. The difference in the spatial extension of the 3d and 3d' orbitals is clearly evident. The 3d' orbital is much more diffuse than the 3d orbital (the overlap being only 0.76) and is more like the 4s orbital in radial extent.

In earlier HF calculations on the transition metal atoms Hay[4] found that the 3d orbitals of the $4s3d^{n+1}$ states were more diffuse than those of the $4s^2 3d^n$ states. In fact, as noted above, basis sets appropriate for the $4s3d^n$ states must be augmented with an additional, more diffuse d function to properly describe the $4s3d^{n+1}$ states. From the present calculations we see that this uniform expansion of the 3d orbitals is a consequence of the equivalence restriction in the HF calculations and, when projection effects are properly taken into account, only one of the 3d orbitals becomes diffuse. To a good approximation the 3d orbital of the $4s3d^3$ state of titanium obtained from the HF calculation is an occupation number weighted average of the 3d and 3d' orbitals.

Turning now to the ground state, $^3F(4s^2 3d^2)$, of the titanium atom, we use the MCHF wave function,

$$\Psi_{\mathrm{MCHF}}(^3F) = c_1\mathcal{A}\,4s^2 3d^2\alpha\beta\alpha\alpha + c_2\mathcal{A}\,4p^2 3d^2\alpha\beta\alpha\alpha\ , \tag{2}$$

where the second configuration accounts for the 4s–4p near degeneracy effect. The results of the HF and MCHF calculations on the ^3F state of titanium are also summarized in Table I. Use of (2) decreases the energy of the ^3F state by 0.77 eV over that obtained with a single configuration.

Using (1) for the ^5F state of titanium and (2) for the ^3F state, we obtain a ^5F–^3F splitting of 0.87 eV, in good agreement with the experimental separation of 0.81 eV.[2]

In her MCHF calculations on the copper atom, Froese-Fischer[7] noted that inclusion of the $4s3d^9 4d$ configuration in the calculations on the $^2S(4s3d^{10})$ state led to a dramatic decrease in the energy of this state (> 2 eV). Further, she noted that the resulting wave function was equivalent to a PHF wave function of the form $4s3d^9 3d'$. Thus, both the present titanium calculations and the copper calculations of Froese-Fischer[7] argue for the importance of a PHF description of the $4s3d^{n+1}$ states of the transition metal atoms.

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[b] Participant in the Laboratory-Graduate Participantship Program administered by the Argonne Center for Educational Affairs.

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Part C: TRANSITION METAL ATOMS