c axis in the case of the doped $CsUO_2(NO_3)_3$. $g_{\perp}$ is very sensitive to the wave function of the ground state. That is, small distortions in the sample give a large distribution in the value of $g_{\perp}$, and this will broaden the resonance signals and eventually the signals will fall below the limit of detection as H_{dc} is rotated away from the c axis. For the doped $Cs_2UO_2Cl_4$ crystal the parameter A is very sensitive to the wave function, and Fig. 9 gives a plot of A versus the spin-orbit mixing parameter θ_1. A becomes important to the linewidth of the EPR signals as H_{dc} is rotated toward the c axis. Small distortions in the sample correspond to large changes in A at $\theta_1 = 118°$. When the H_{dc} is rotated toward the Np-O axis from the perpendicular position of the Np-O axis, the EPR signals broaden and eventually fall below the limit of detection due to large deviations in A from small distortions of the sample.

CONCLUSION

The two values for the nuclear moment of Np^{237} reported here are $2.90\mu_B$ and $2.1\mu_B$. It is very difficult to estimate the error in these calculations. Eisenstein and Pryce's estimation of $\pm 20\%$ error due to the uncertainty of the wave function seems to be reasonable. This means that our measurements will be $2.9 \pm 0.6\mu_B$ and $2.1 \pm 0.4\mu_B$. These two values are more or less in agreement, and their average value also agrees with the value of $2.7\mu_B$ reported by Hutchison and Weinstock. The ground-state wave functions used in the two samples are not the same. For $CsUO_2(NO_3)_3$, the wave function has a large part of a $m_J = \pm\frac{5}{2}$ state and for $Cs_2UO_2Cl_4$, the important part of the wave function is $m_J = \pm\frac{1}{2}$. A major remaining problem is that both samples contain the NpO_2^{2+} complex, yet the ground state changes from $m_J = \pm\frac{1}{2}$ to $m_J = \pm\frac{5}{2}$. This effect is not understood by the authors. It is possible that a wrong ground state has been chosen for the $Cs_2UO_2Cl_4$, or the bond distance of Np-O has changed enough in the two samples to give different ground states. The reported U-O distances vary from 1.67 Å[9] to 1.91 Å.[10,11] It is quite possible that the Np-O bond distances are different in the two samples.

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[9] D. T. Cromer and P. E. Harper, Acta Cryst. 8, 846 (1955).

[10] W. H. Zachariasen, Acta Cryst. 1, 277 (1948).

[11] W. H. Zachariasen, Acta Cryst. 1, 281 (1948).

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Limited-Basis-Set Hartree-Fock Theory of NiF_6^{4-}

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Restricted self-consistent-field molecular-orbital calculations have been carried out for four states of the octahedral cluster NiF_6^{4-} *in vacuo* and with 38 point charges representing the perovskite lattice $KNiF_3$. For a contracted Gaussian-basis set with 15 more members than a minimal set, *all integrals* were computed. The value found for the ligand field splitting, 4670 cm^{-1}, is 35% smaller than the observed value. The Racah parameters do not reflect the expected decrease associated with cluster formation. The covalency estimates, $f_s \cong 0.18\%$ and $f_\sigma \cong 1.26\%$, are three times smaller than the observed values. Thus, as measured by the results, the calculation is neither significantly better nor significantly worse than previous calculations, which, however, include many ill-understood assumptions. In addition, our calculations indicate that omission of the Madelung potential from next-nearest neighbors is not a grievous approximation; that free-ion d orbitals suffer only small distortions in the cluster; and that $p\pi$ bonding in states with partly open t_{2g} orbitals is much smaller than $p\sigma$ bonding. This calculation is to be regarded as a precursor. An attempt is made to extract the implications so that selection of the least sensitive assumptions may be made for subsequent calculations.

INTRODUCTION

TRANSITION metal-fluoride clusters in predominantly ionic crystal lattices are a particularly useful substrate for testing first-principles calculations of electronic structure. The low-lying set of states provide an unusually large number of accessible experimental data. The observables are quite sensitive to experimentally accessible changes in the local environment. Since theories of the observables are primarily associated with a small set of the electrons of the cluster, their successes and deficiencies can be assessed more readily than theories of grossly averaged observables such as molecular polarizability. In particular, transferred hyperfine interactions measure covalent electron transfer almost directly.

Such clusters are intrinsically interesting because of the large practical and theoretical importance of magnetic-impurity effects in crystals. They may also be considered the "monomers" for extensively studied ferromagnetic and antiferromagnetic lattices. Following

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the initial successes of crystal-field theory and parametric ligand-field theory, attention has been focused on *ab initio* calculations of the ligand-field parameters. By now, it is accepted that simplified theories of the electronic interactions are qualitatively correct but not adequate. Minor improvements in theory have been known to result in poorer agreement with experiment. Orbital overlap and covalency significantly affect most observables for transition metal complexes. Since theories of superexchange invariably involve estimates of unpaired electron density on bridging anions between interacting cations, it is important that covalent behavior be understood better.

Partly for historical reasons, the nickel hexafluoride molecule-ion cluster NiF_6^{4-} has become the prototype for theoretical studies of the bonding in this class of systems. It was one of the earliest for which a fairly complete assignment of the optical $d \leftarrow d$ transitions was available,[1] and for which the transferred hyperfine interactions were fully analyzed.[2] The ground state and two of the first three excited states can be represented formally by single-determinant wave functions, so that some trivial but tedious ligand-field algebra can be avoided. A pioneering attempt[3] to account for the observed parameters with the theory of linear combination of atomic orbitals (LCAO) of covalency accompanied the experimental observations. It was subsequently much criticized in several attempts[4–8] to remove the most questionable approximations. In the earliest work[9] on first-principles description of transition-metal ligand clusters, the objective was to calculate the cubic ligand-field splitting 10 *Dq*. More recently,[3–8] more emphasis has been placed on transferred hyperfine effects. Relatively little attention has been given to electron-repulsion contributions to term separations. Usually spin-orbit coupling and orbital contributions to gyromagnetic tensors are not treated, since they may be regarded as finer effects which cannot be convincingly addressed until the grosser features are resolved. It is the objective of this paper to extend these studies by as complete molecular-orbital calculations as are presently feasible.

Until now, the extremely large number of electron-repulsion integrals necessarily involved has precluded the possibility of even approximate Hartree-Fock self-consistent-field (SCF) calculations. In addition to direct computational savings, minimal-basis-set estimations are organizationally much simplified. For all symmetries with only doubly occupied orbitals, orbital transformations exist so that it is correct to calculate on the assumption of complete ionicity, if overlap effects are correctly accounted for.[10] Since overlaps between orbitals on different ligands are very small, they are ignored and localized orbitals, taken as the free-ion orbitals, may be substituted for cumbersome symmetry orbitals. Independent of the choice between a molecular-orbital or a Heitler-London (HL) approach, the formal expression for the conventional covalency parameter appears as a perturbation-type formula

$$\lambda \approx \frac{(\varphi|h|\chi) - S_{\varphi\chi}(\chi|h|\chi)}{(\chi|h|\chi) - (\varphi|h|\varphi)}, \tag{1}$$

where $S_{\varphi\chi}$ is the overlap integral between the central-ion d orbital ϕ, and a symmetrized ligand orbital χ, and where h is some effective Hamiltonian. The problem reduces to choosing suitable orbitals and a suitable effective Hamiltonian. The result is particularly sensitive to the denominator of Eq. (1), which may be interpreted as the excitation energy from a central-ion orbital to a ligand orbital. Quite commonly, an ionic Hamiltonian, which is viewed as the starting point of an iterative self-consistent calculation, is employed. Watson and Freeman suggest in their analysis that "a proper evaluation of covalent effects cannot be had without inclusion of the overlap and covalent terms in the Hamiltonian."[4] The issue is as much one of the *plausibility* as the correctness of calculated results. To advance beyond first-order theories by the previous methods[3–8] would require an inordinate effort in the evaluation of matrix elements, not only because of their increased number, but because of severe numerical differencing. Even the calculations with zeroth-order Hamiltonians and minimal basis sets become quite complicated, so that the influences of the many interactions are difficult to trace. The approximations and assumptions made are generally plausible and reasonable. Nevertheless, it becomes obscure to what extent the failure or success of such calculations to account for the observed properties should be attributed to the electronic-structure models adopted or to numerical deficiencies introduced by specific secondary assumptions. With Hartree-Fock SCF calculations we are able both to evaluate all matrix elements exactly (within the accuracy implied by computer round-off errors) and to maintain a simple enough model so that its limitations can be readily analyzed. Since it has been indicated that configuration interaction cannot be ignored,[7] the present calculations might be considered a precursor for Cl calculations including all integrals.

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[1] K. Knox, R. G. Shulman, and S. Sugano, Phys. Rev. **130**, 512 (1963).

[2] R. G. Shulman and S. Sugano, Phys. Rev. **130**, 506 (1963).

[3] S. Sugano and R. G. Shulman, Phys. Rev. **130**, 517 (1963).

[4] R. E. Watson and A. J. Freeman, Phys. Rev. **134**, 1526 (1964).

[5] E. Simanek and Z. Sroubek, Phys. Status Solidi **4**, 251 (1964).

[6] S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **20**, 1155 (1965).

[7] J. Hubbard, D. E. Rimmer, and F. R. A. Hopgood, Proc. Phys. Soc. (London) **88**, 13 (1966).

P. O. Offenhartz, J. Chem. Phys. **47**, 2951 (1967).

This is reviewed by Shulman and Sugano (Ref. 3).

[10] Commonly such overlaps are tacitly ignored when a core-potential assumption is made. Watson and Freeman (Ref. 4) comment upon this approximation in some detail. For the atomic SCF solutions quoted below, the overlap between the Ni^{++} $3s$ function and the $p\sigma(a_{1g})$ symmetry orbital on the fluorides is 0.13—hardly negligible. That between $p\sigma$ orbitals on adjacent ligands is about 0.06.

The $NiF_6{}^{4-}$ cluster has 86 electrons. An SCF calculation that approaches the Hartree-Fock limit would at the moment be unreasonably costly. For a Gaussian-type atomic-orbital basis, such a calculation would involve at least (4×10^8) repulsion integrals. While this is probably feasible, it is an order of magnitude larger than any single computation attempted in this laboratory to date. With our limited information about the probability of significant undetected arithmetic errors in 10^{11} computer operations, the risk of an erroneous calculation presently seems too large. It was thought that a limited calculation, with (3×10^7) repulsion integrals could be used to isolate some physical trends and prepare the way for more elaborate future calculations. It will be shown that a basis of this size, if carefully chosen, can test several typical assumptions involved in "chemical" reasoning and in the validity of minimal-basis-set calculations. Since less complete calculations than that reported in this paper will continue to be valuable in the future, whatever trends one can isolate may be of use in them and in qualitative descriptions of paramagnetic clusters.

In this spirit, some points of inquiry are as follows:

1. On the assumption that LCAO theory with minimal basis sets can provide an adequate qualitative description, how do the atomic orbitals best suited for such a description differ from free-ion orbitals? Expansion or contraction of the metal ion-radial functions has been discussed,[4–8,11] but not settled. Experimental evidence from term splittings, hyperfine interactions, and neutron-diffraction form factors show only that a simple scale change, without shape modification, is unlikely.

2. It is well known that the Slater-Racah electron-repulsion parameters B and C required to fit the optical energy-level spacings are smaller for transition metal ions in molecular clusters than they are for the free ions. We do not anticipate that for the type of calculation reported we will obtain values which compare well with experimental values.[12] However, comparison with free-ion Hartree-Fock calculations with the atomic-orbital basis corresponding to the cluster calculation might be expected so show repulsion reduction, which is associated with electron delocalization.

3. After several other contributions[11] are included, the isotropic part of the hyperfine interactions is proportional to the product of the fractional unpaired spin density f_s in a $2s$ orbital at the F^- site and the probability density $[\delta(r)]_{2s}$ of the $2s$ orbital at that nucleus. Similarly, the anisotropic part f_σ-f_π involves the expectation of another singular operator $\langle r^{-3}\rangle_{2p}$. Generally, these singular operators are estimated from free-ion wave functions. To what extent should molecular estimates be changed? Of course, eventually it is desirable to evaluate all matrix elements of these operators within the cluster for accuracy. However, at the moment, the orbital basis is not extensive enough to expect much success with this procedure, and computer programs are not available to accomplish it.

4. How good is the assumption that $d \leftarrow d$ optical spectra may be estimated without reference to the crystal lattice beyond the nearest neighbors of the central ion? Certainly EPR spectra are sensitive to charge compensation in next-nearest-neighbor sites.

MOLECULAR-ORBITAL FORMALISM

In the $KNiF_3$ lattice, the Ni^{++} ion lies at the center of an octahedron of F^- ions (Fig. 1). The nuclear separation R is 20.07 nm.[13] The next shell of ions consist of eight K^+ ions located at the coordinates $(\pm R, \pm R, \pm R)$, six Ni^{++} ions at $(\pm R, 0, 0)$ and the permutations of this coordinate triple, and 24 F^- ions located at the permutations of the triple $(\pm R, R, 0)$. Below, we report two SCF calculations: In that for the "unadorned cluster" the $NiF_6{}^{4-}$ is treated without reference to the host lattice; in the adorned-cluster calculation, the next shell is represented by point charges at the nuclear sites.[14] Such representation is subject to the same type of criticisms as those directed at point-charge crystal-field theory. Clearly, if superexchange phenomena are of interest its adequacy must be examined. In the present case, since covalency is itself small, inaccuracy in the second shell should be unimportant. Furthermore, the assumption was self-checking; we found that inclusion of the second shell made only insignificant changes.

All the states of interest are derived from states of the free Ni^{++} ion belonging to the d^8 configuration. It is convenient to make the formal description in terms of a d^2-hole configuration.[15] Transitions are observed[3] from the ground ${}^3A_{2g}$ state to the ${}^3T_{2g}$ state, to both ${}^3T_{1g}$ states and to the lowest ${}^1E_g$ and ${}^1T_{1g}$ states of this configuration. The spectrum is fairly well described by three parameters, the cubic crystal-field splitting 10 Dq, and the Slater-Racah parameters B and C. For comparison with experiment, hopefully enough states to estimate these parameters will be calculated. Now, the SCF procedure implemented in IBMOL[16] is applicable only to systems for which the total energy may be

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[11] W. Marshall and R. Stuart, Phys. Rev. **123**, 2048 (1961).

[12] Hartree-Fock calculations by R. E. Watson [Phys. Rev. **118**, 1036 (1960); **119**, 1934 (1960)] for free transition-metal ions yield term splittings much larger than those observed. The discrepancy is ascribed to correlation effects.

[13] A. Okazaki and Y. Suemene, J. Phys. Soc. Japan **16**, 671 (1961).

[14] To represent more of the crystal in this fashion would exceed the present limitation of the molecular-orbital computer program to 50 nuclear centers.

[15] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, London, 1964), pp. 245ff.

[16] E. Clementi and D. R. Davis, J. Comput. Phys. **2**, 223 (1957); A. Veillard, IBM Technical Report, 1968 (unpublished; available upon request).

written[17]

$$E=\sum_{\lambda i} N_{\lambda i}H_{\lambda ii}+\sum_{\lambda i}\sum_{\mu j} N_{\lambda i}N_{\mu j}(a_{\lambda\mu}J_{\lambda i,\mu j}-\tfrac{1}{2}b_{\lambda\mu}K_{\lambda i,\mu j}), \quad (2)$$

where not more than one open shell of any symmetry occurs. This expression is biquadratic in the expansion coefficients of the molecular orbitals in terms of symmetrized basis orbitals. The only energy minimization permitted is by variation of the expansion coefficients (which are implicit in the integrals H, J, and K). Within the d^2 configuration, only the degenerate states ${}^3A_{2g}$, ${}^3T_{2g}$, and ${}^1T_{1g}$ arise once and once only. For each of these, it is possible to choose a state that may be written as a single determinant, from which the occupation numbers and the vector coupling coefficients are easily evaluated. For the other states, which in ligand-field theory require a diagonalization for determination of the energy, a parameter-free energy expression cannot be written. However, it is possible to calculate for a single-determinant state which is not an eigenstate of the octahedral Hamiltonian. If the state is "close" to an eigenstate, then the molecular orbitals derived will be insignificantly distorted from those of the eigenstate, and Racah parameters may be estimated. For the comparison with experiment, we have used[18]

$$\begin{aligned} E({}^3T_{2g})-E({}^3A_{2g})&=10Dq\,,\\ E({}^1T_{1g})-E({}^3T_{2g})&=12B+2C\,,\\ E({}^3T_{1g}te)-E({}^3T_{2g})&=12B\,. \end{aligned} \quad (3)$$

Represented as determinants of holes in complete shells, the corresponding wave functions, for which vector-coupling coefficients are easily written, are

$$\begin{array}{ll} {}^3A_{2g}\,, & |\theta\alpha\epsilon\alpha| \\ {}^3T_{2g}\,, & |\theta\alpha\zeta\alpha| \\ {}^1T_{1g}z\,, & |\epsilon\zeta|\,(\alpha\beta-\beta\alpha) \\ {}^3T_{1g}(te)z\,, & |\epsilon\alpha\zeta\alpha|\,. \end{array} \quad (4)$$

For the concomitant atomic calculations, the comparison with experiment can be made with

$$\begin{aligned} E({}^1G)-E({}^3F)&=12B+2C\,,\\ F({}^3T_{1g}te)-E({}^3F)&=12B\,. \end{aligned} \quad (5)$$

Here the cluster state denoted in Eq. (4) by ${}^3T_{1g}te$ has 80% ${}^3P$ character and 20% ^{3}F character. Although for the free ion there is no difficulty in calculating the ${}^3P$ state directly, we have chosen to use the same state for homogeneity in comparison with the cluster calculation.

In the extraction of covalency estimates from our wave functions, the argument of Watson and Feeman[4] as to the distinction between antibonding electrons and unpaired bonding electrons is irrelevent, since we constrain the wave function to strict spin pairing. It is also pertinent to note that the concept of bonding-antibonding pairing begins to lose its relevance as the basis set becomes larger than minimal. The point may be otherwise demonstrated by noting that in a spin-pairing wave function, the algebraic form of the unpaired-antibonding orbitals is identical to that of their unoccupied counterparts, in terms of which covalency may validly be estimated.[4] It may, of course, be better to remove the spin-pairing constraint. The arguments in favor of unrestricted Hartree-Fock theory are well known. This alternative was not presently available, so that such a calculation has been deferred.

BASIS FUNCTIONS

As has already been mentioned, a major concern in the present calculation was the selection of a set of basis orbitals flexible enough to provide preliminary illumination of some of the questions posed, but not so large that unreasonable costs were incurred. To approach the SCF energy limit with Gaussian orbitals would require at least a (13*s*, 9*p*, 4*d*) basis to represent the nickel ion and a (10*s*, 6*p*) basis for each fluorine ion (232 orbitals and 3.6×10^8 integrals). Instead, the limited calculation undertaken has (8*s*, 4*p*, 3*d*) and (6*s*, 3*p*) bases (128 orbitals and 3×10^7 integrals). In calculations of this magnitude, one should also consider cumulation of round-off errors. The internal arithmetic of each integral has been calculated with double precision, so that an accuracy of 10^{-9} a.u. is attained. Numerical experiments with long lists of integrals have shown us that the correct SCF energies are attained if the accuracy on the integrals is greater than 10^{-6} a.u. This insures that the results reported here are significant.

It is common knowledge that Gaussian orbitals, particularly *s*-type ones, are ill adapted to representation of orbital singularities near their nuclear center. This difficulty may be overcome by including in the set many basis orbitals with large orbital exponents. We have made no attempt in this direction, but in fact somewhat deemphasized accuracy near the nucleus in favor of accuracy near the "bonding region" of the function. Details of the optimization of the atomic Gaussian basis appear in Appendix B, together with the wave functions.

The approach has several possible adverse consequences:

1. Total energies do not approach Hartree-Fock limits, nor is the virial theorem accurately satisfied. It is hoped that the present results are insensitive to these difficulties, since only small redistributions of probability of the electron density differentiate the excited states of interest.
2. The present calculations cannot be used to estimate orbital expectations $\langle\delta(r)\rangle$ and $\langle r^{-3}\rangle$. It will be necessary to adopt the usual stratagem of estimation of these integrals from separate atomic SCF calculations.

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[17] Here λ and μ denote symmetry classifications. The integrals H, J, and K are the usual one-electron, Coulomb, and exchange contributions evaluated on molecular orbitals i and j. Each vector coupling coefficients $a_{\lambda\mu}$ or $b_{\lambda\mu}$ is unity if either λi or μj refers to a doubly occupied orbital. $N_{\lambda i}$ is the orbital occupation number.

[18] See Ref. 15, p. 410.

TABLE I. Contracted SCF calculation for $Ni^{++}(^3F)$.

Basis functions[a] (normalized)

$S=0.06803s_1+0.32505s_2+0.49577s_3+0.25450s_4$
$S'=s_5$
$S''=s_6$
$S'''=0.61649s_7+0.42625s_8$
$P=0.34953p_1+0.77191p_2$
$P'=p_3$
$P''=p_4$
$D=0.34340d_1+0.80073d_2$
$D'=d_3$

Orbital energies and eigenvectors

1*s*	2*s*	3*s*	2*p*	3*p*	3*d*
−306.1102	−38.3952	−5.5248	−33.2340	−3.8929	−1.3421
0.99834	−0.44570	0.17665	0.94038	−0.37185	0.71880
0.00267	0.77278	−0.48270	0.14148	0.45502	0.46820
0.00241	0.41656	−0.55133	−0.03047	0.65706	
−0.00103	−0.05457	1.45175			

[a] Subscripts refer to Gaussian orbital numbers in Table X.

This is implicit if we accept as "experimental" data the conventional covalency parameters, since the experiments measure normalized products of these singular operators with the covalency parameter (if one has accepted a LCAO picture).

3. The most troublesome difficulty is that single-electron atomic-orbital energies may be inaccurate. In perturbation theories of covalency (see above) such orbital energies have a first-order effect. One may hope that, if the inaccuracies of the Ni^{++} atomic orbitals are similar to those for F^-, this problem will be minimized. However, this happy possibility is unlikely, because *d* orbitals are less sensitive to this source of error than *p* or *s* orbitals.

The computational time required for the transformation to symmetry orbitals increases at least linearly with the length of the integral list and at least linearly with the length of the transformed-integral list. Much economy is possible by replacing the individual Gaussians in the orbital lists with appropriate linear combinations of Gaussians, called "contracted" Gaussians.[19] If the contraction coefficients are carefully chosen, the set of contracted orbitals can be almost as good as the original set of Gaussians as a basis for the atomic SCF computation, even though there are fewer degrees of freedom. A method for choosing contractions suggests itself naturally. Because of orthogonality constraints, certain ratios of expansion coefficients in the atomic wavefunctions are similar. For instance, in the F^- function in Appendix B, the ratio of the first two coefficients in the 1*s* function is 3.96; for the 2*s* function the corresponding ratio is 4.37. These functions contribute much more to the 1*s* orbital than to the 2*s* orbital, so that the former ratio is adopted. The contracted functions used, and the atomic ground-state wave functions on these bases, are presented for Ni^{++} in Table I and F^- in Table II. Besides the economy of transformation on contracted orbitals, their advantages over direct use of Gaussian orbitals are that 2×10^6 integrals can be stored on a single reel of magnetic tape but 3×10^7 cannot, and that final qualitative interpretation of the wave functions is far more readily performed.

In Table III there are listed, for comparison with Hartree-Fock limit calculations, orbital and total energies for contracted and uncontracted bases used in

TABLE II. Contracted SCF calculation for F^-.

Basis functions[a] (normalized)

$S=0.21665s_1+0.85761s_2$
$S'=0.79983s_3+0.28201s_4$
$S''=0.58568s_5+0.48031s_6$
$P=0.21865p_1+0.54245p_2+0.50526p_3$

Orbital energies and eigenvectors

1*s*	2*s*	2*p*
−25.7625	−1.0992	−0.17351
0.50255	−0.12582	1.0
0.61980	−0.24807	
−0.06502	1.09032	

[a] Subscripts refer to Gaussian orbital numbers in Table XI.

TABLE III. Atomic-orbital energies.

	Hartree-Fock limit[a]	"Uncontracted" $Ni^{++}(^3F)$	"Contracted"
1*s*	−306.3316	−306.2291	−306.1102
2*s*	−38.6182	−39.0190	−38.3952
2*p*	−33.6460	−33.1988	−33.2340
3*s*	−5.5854	−5.6557	−5.5248
3*p*	−3.9873	−3.8888	−3.8929
3*d*	−1.4177	−1.3360	−1.3421
Total *E*	−1506.0286	−1494.5022	−1492.9448
		$F^-(^1S)$	
1*s*	−25.8294	−25.7157	−25.7625
2*s*	−1.0744	−1.0925	−1.0992
2*p*	−0.1808	−0.1557	−0.1735
Total *E*	−99.4594	−98.5884	−98.5219

[a] Hartree-Fock limit from Ref. 25.

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[19] E. Clementi, Chem. Rev. 68, 341 (1968).

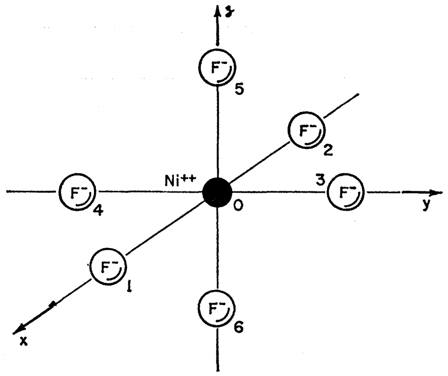

FIG. 1. NiF_6^{4-} cluster showing numbering scheme.

this calculation. It is seen that the quality of the solutions for the two ions as measured by the relative errors in the total energy is uniform, and that contraction has relatively little effect on the total energies. The orbital energies are quite close to those of the Hartree-Fock limits. In particular, the excitation from a free-ion Ni^{++} d orbital to a F^- p orbital is only 7% different from the Hartree-Fock limit result. This excitation represents the Koopman's theorem energy for the process $Ni^{++}F^- \rightarrow Ni^+F$ in the limit of infinite internuclear separation.

TABLE IV. Symmetry orbitals.

Symmetry type	Degrees of freedom	Number of basis functions	Orbitals
a_{1g}	2	3	$S_1+S_2+S_3+S_4+S_5+S_6$
		4	S_0
		1	$-Z_5+Z_6-X_1+X_2-Y_3+Y_4$
$e_g\theta$	2	3	$2S_5+2S_6-S_1-S_2-S_3-S_4$
		1	$-2Z_5+2Z_6+X_1-X_2+Y_3-Y_4$
		2	$(2Z^2-X^2-Y^2)_0$
$e_g\epsilon$	2	3	$S_1+S_2-S_3-S_4$
		1	$-X_1+X_2+Y_3-Y_4$
		2	$(X^2-Y^2)_0$
$t_{2g}\xi$	1	1	$Z_3-Z_4+Y_5-Y_6$
		2	$(YZ)_0$
$t_{2g}\eta$	1	1	$X_5-X_6+Z_1-Z_2$
		2	$(XZ)_0$
$t_{2g}\zeta$	1	1	$X_3-X_4-Y_1+Y_2$
		2	$(XY)_0$
$t_{1u}x$	2	3	S_1-S_2
		1	$-X_1-X_2$
		1	$X_3+X_4+X_5+X_6$
		3	X_0
$t_{1u}y$	2	3	S_3-S_4
		1	$-Y_3-Y_4$
		1	$Y_1+Y_2+Y_5+Y_6$
		3	Y_0
$t_{1u}z$	2	3	S_5-S_6
		1	$-Z_5-Z_6$
		1	$Z_1+Z_2+Z_3+Z_4$
		3	Z_0
$t_{1g}\xi$	0	1	$-Y_5-Z_4+Y_6+Z_3$
$t_{1g}\eta$	0	1	$X_5-Z_1-X_6+Z_2$
$t_{1g}\zeta$	0	1	$Y_1-X_3-Y_2+X_4$
$t_{2u}x$	0	1	$-X_3-X_4+X_5+X_6$
$t_{2u}y$	0	1	$-Y_1-Y_2+Y_5+Y_6$
$t_{2u}z$	0	1	$-Z_1-Z_2+Z_3+Z_4$

TABLE V. SCF energies (in a.u.).

$Ni^{++}+6F^-$		NiF_6^{4-} Cluster		Adorned cluster
^3F	−2084.0659	$^3A_{2g}$	−2084.4339	−2093.1803
		$^3T_{2g}$	−2084.4117	−2093.1590
$^3T_1(te)$	−2083.9947	$^3T_{1g}(te)$	−2084.3418	−2093.0890
^1G	−2083.9489	$^1T_{1g}$	−2084.2970	−2093.0441

Thus it does not seem that limitation of the basis set will seriously affect the covalency estimate through the mechanism of orbital energy inaccuracy.

Prior to the SCF calculation, symmetry orbitals must be constructed as the basis for a representation of the octahedral group. These are indicated in Table IV, which is supplemented by Fig. 1 to indicate the numbering and axis system. The phases of the ligand functions have been chosen so that overlaps with the central-ion orbitals are all positive. In Table IV, the degrees of freedom give the difference between the number of basis orbitals and the number of occupied orbitals in the ground state. Since the $d \leftarrow d$ transitions move electrons from filled to half-filled orbitals, the number of degrees of freedom does not change for excited states. Except for the nonbonding orbitals, we have arranged that each symmetry type has at least one degree of freedom. Clearly, it is only appropriate to make as many deductions about the functions as there are degrees of freedom.

RESULTS

The total energy calculations, given in Table V, are analyzed into the ligand-field parameters in Table VI. 10 Dq, although of the correct sign, is $\frac{1}{3}$ too small. As is found for SCF calculations of free ions, the repulsion integrals B and C are too large for all of the calculations. The larger part of the error may be ascribed to correlation effects. The experimental trend, that the repulsion should be decreased in the cluster system over that of the free ion, is not reflected in our SCF calculations. This suggests that the calculated d functions are insufficiently delocalized. Inclusion of effects from the next shell of ions slightly decreases the crystal-field splitting.

The expansion coefficients for the wave functions are reported in Table VII. Orbitals belonging to degenerate rows of irreducible representations are omitted. Included on the right for convenience are indications of

TABLE VI. Comparison with experiment.

	NiF_6^{4-} Cluster	Adorned cluster	Expt. (Ref. 2)
10Dq	4870 cm^{-1}	4670 cm^{-1}	7250 cm^{-1}
B	1280	1280	955
C	4910	5040	4234
		Ni^{++}	
B	1300		1030
C	5020		4850

TABLE VII. ${}^3A_{2g}$ wave functions for NiF_6^{4-}.

Symmetry	Orbital 1	2	3	4	5	6	7	8	Classification
a_{1g}				0.99835	0.00267	0.00242	−0.00104	0.00004	Ni 1*s*
a_{1g}	0.00004	−0.00035	0.00060	−0.44567	0.77256	0.41720	−0.05527	0.00242	Ni 2*s*
a_{1g}	0.50257	0.61956	−0.06473	−0.00011	0.00073	−0.00237	0.00263	0.00196	F 1*s*
a_{1g}	−0.00034	−0.00114	0.00437	0.17653	−0.48234	−0.55086	1.45025	0.00739	Ni 3*s*
a_{1g}	−0.12480	−0.24661	1.08778	−0.00493	−0.01449	0.01401	−0.04586	0.03208	F 2*s*
a_{1g}	0.00901	0.01723	−0.08031	−0.01573	0.04469	0.06280	−0.18947	1.00847	F $p\sigma$
e_g	0.50243	0.62034	−0.06605	−0.00234	−0.00185	0.00615			F 1*s*
e_g	−0.12601	−0.24857	1.08977	0.01484	0.01089	0.00882			F 2*s*
e_g	0.00022	0.00021	0.00023	0.98590	0.05939	0.04562			F $p\sigma$
e_g	0.00941	0.01728	−0.08016	−0.19493	0.72910	0.46019			Ni *d*
t_{2g}	0.85647	0.33593	0.22474						bonding
t_{2g}	−0.51922	0.62745	0.42258						antibonding
t_{1u}		−0.00028	0.00046	0.00121	0.00029	0.94035	0.14163	−0.03067	Ni 2*p*
t_{1u}	0.50252	0.61986	−0.00651	−0.00024	0.00157	0.00033	−0.00121	0.00202	F 1*s*
t_{1u}	0.00156	0.00418	−0.01690	−0.02384	−0.00635	0.37109	−0.45383	−0.65560	Ni 2*p*
t_{1u}	−0.12570	−0.24808	1.08988	0.01717	0.00738	0.01241	−0.01779	−0.02001	F 2*s*
t_{1u}	0.00439	0.00832	−0.03845	0.82259	0.52172	0.02816	−0.04053	−0.05697	F $p\sigma$
t_{1u}	−0.00304	−0.00595	0.02826	0.57513	−0.85614	0.00873	−0.11682	−0.02130	F $p\pi$
t_{1g}	1.0								
t_{2u}	1.0								

the primary atomic-orbital contributions. In the interpretation of these wave functions, it must not be overlooked that linear normalized transformations of doubly occupied orbitals do not change the wave function. Within a symmetry type, such rearrangement does not introduce any extra expansion coefficients. Thus, the $p\sigma$ contribution in the tabulated $t_{1u}(F_{2s})$ orbital can be eliminated; $t_{1u}(F_{p\sigma})$ and $t_{1u}(F_{p\pi})$ can be rearranged to separate the σ and π orbitals. It can be shown that when orbitals of different symmetries are also combined, the wave functions can be written in terms of localized orbitals which are the atomic orbitals. Only small nonlocal contributions enter. These can be interpreted largely as orthogonality contributions. In particular, the doubly occupied t_{2g} orbitals may be written as entirely localized and nonbonding functions.

It is appropriate to comment on the wave functions within the degrees of freedom permitted. The commentary is made by direct examination of the functions.

1. a_{1g}. The Ni^{++} orbitals are not significantly changed from those of the free ion. Except for orthogonality contributions, the fluoride $p\sigma$ orbitals do not bond.

2. e_g. For comparison with the observed superhyperfine interaction, half-filled orbitals may be written approximately as

$$\varphi_e - 0.195\chi_\sigma - 0.079\chi_s. \qquad (6)$$

Here φ_e is the Ni^{++} *d* orbital, χ_σ is the symmetrized F^- $p\sigma$ orbital, and χ_s the symmetrized F^- 2*s* orbital. The overlap and covalency contributions almost cancel, so that the function (6) is normalized when ϕ_e is the normalized *d* orbital. Thus the two calculated spin densities

$$f_\sigma^c = 1.26\% \quad \text{and} \quad f_s^c = 0.18\% \qquad (7)$$

are both about three times smaller than the values reported by Shulman and Sugano.[2] The *d*-orbital contribution to the e_g orbital is slightly contracted from the corresponding free-ion orbital.

3. t_{2g}. In these orbitals, the *d*-orbital contribution is slightly expanded from the corresponding free-ion orbital.

4. t_{1u}. The two degrees of freedom for this symmetry may be expended in the comments that neither the Ni 3*p* orbital nor the symmetrized F 2*s* orbital is significantly changed from that in the free ion.

For the ${}^3T_{2g}$ state, the closed-shell wave functions are not very different from those of the ground state, and are therefore not tabulated. The half-filled orbitals are

$$\begin{aligned} e_g\theta = {} & 0.0094(2S_5+2S_6-S_1-S_2-S_3-S_4) \\ & +0.0173(2S_5'+2S_6'-S_1'-S_2'-S_3'-S_4') \\ & -0.0801(2S_5''+2S_6''-S_1''-S_2''-S_3''-S_4'') \\ & -0.1951(-2Z_5-2Z_6+X_1-X_2-Y_3+Y_4) \\ & +0.7288(2Z^2-X^2-Y^2)_0 \\ & \qquad +0.4606(2Z'^2-X'^2)_0 \end{aligned} \qquad (8)$$

and

$$t_{2g}\zeta(2) = -0.0925(X_3-X_4-Y_1+Y_2) +0.7208(XY)_0+0.4666(XY)_0'. \qquad (9)$$

In both open orbitals, the *d* function is slightly contracted from the free-ion function. For the closed orbitals, the *d* function is slightly expanded. The occupation of the $p\pi$ orbital in $t_{2g}\zeta(2)$ is more nearly similar to that of the ligand *s* orbital in $e_g\theta(2)$ than of the $p\sigma$ orbital.

Inspection of the orbitals of the ${}^3T_{1g}$ and ${}^1T_{1g}$ state confirms the trends already indicated. For open shells, the *d* function is slightly contracted; for closed shells, slightly expanded from the free-ion functions. The open-shell wave functions are substantially similar to those given. Inspection of the adorned-cluster wave functions does not reveal significant changes in the wave functions

TABLE VIII. Gross atomic populations.

		s	p_x	p_y	p_z	$d_{xx}=d_{yy}$	d_{zz}	d_{xy}	$d_{xz}=d_{yz}$	Total
$^3A_{2g}$	Ni	6.0000	4.0001	4.0001	4.0001	0.6803	0.6802	1.9999	1.9999	26.04
	F1, F2	3.9995	1.9937	2.0000	2.0000					9.99
	F3, F4	3.9995	2.0000	1.9937	2.0000					9.99
	F5, F6	3.9995	2.0000	2.0000	1.9937					9.99
$^3T_{2g}$	Ni	6.0000	4.0001	4.0001	4.0001	1.1701	0.6803	1.0040	1.9999	26.02
	F1, F2	3.9998	1.9984	1.9990	2.0000					9.99
	F3, F4	3.9998	1.9990	1.9984	2.0000					9.99
	F5, F6	3.9995	2.0000	2.0000	1.9937					9.99
$^3T_{1g}$	Ni	6.0000	4.0001	4.0001	4.0000	0.8455	1.3331	1.0048	1.9998	26.02
	F1, F2	3.9996	1.9943	1.9988	2.0000					9.99
	F3, F4	3.9996	1.9988	1.9943	2.0000					9.99
	F5, F6	4.0000	2.0000	2.0000	2.0000					10.00
$^1T_{1g}$	Ni	6.0001	4.0001	4.0001	4.0000	0.8470	1.3331	1.0053	1.9998	26.03
	F1, F2	3.9995	1.9936	1.9987	2.0000					9.99
	F3, F4	3.9995	1.9987	1.9936	2.0000					9.99
	F5, F6	4.0000	2.0000	2.0000	2.0001					10.00

compared to those indicated for the bare cluster in Table VII and Eqs. (8) and (9).

For an easier understanding of the electron distribution, we can now turn to Mulliken's population analysis.[20] Given a molecular orbital ψ_i occupied by N_i electrons

$$\psi_i=\sum_r \sum_{k_r} C_{ik_r}\chi_{k_r}, \qquad (10)$$

where r is an atom and χ_{kr} is the kth atomic orbital associated with that atom, the partial gross atomic population of this kth orbital on the atom r is defined as

$$N(k_r)=\sum_i N(i,k_r), \qquad (11)$$

where $N(i,k_r)$ is the contribution to $N(k_r)$ from the ith occupied molecular orbital, and is defined as

$$N(i,k_r)=N_i(C_{ik_r}{}^2+\sum_{l_s\neq k_r} C_{ik_r}C_{il_s}S_{k_r,l_s}). \qquad (12)$$

The gross atomic population of atom r is the sum of all the $N(k_r)$ for all the orbitals belonging to the atom r. Another useful measure is the partitioning of the gross atomic population according to the type of the basis functions (s, p_x, p_y, p_z, etc.).

TABLE IX. Relative populations of inner d orbitals to outer d orbitals. ⁑=Population entirely derived from half-filled molecular orbitals. *=Population derived partly from filled, partly from half-filled molecular orbitals.

	$xx=yy$	zz	xy	$xz=yz$
$^3A_{2g}$	⁑1.929	⁑1.929	1.778	1.778
$^3T_{2g}$	*1.867	⁑1.926	⁑1.863	1.775
$^3T_{1g}$	*1.916	1.831	⁑1.923	1.750
$^1T_{1g}$	*1.884	1.835	⁑1.869	1.755
$Ni^{++}(^3A_{2g})$	⁑1.926	⁑1.926	1.822	1.822
$Ni^{++}(^3T_{1g})$	*1.897	1.767	⁑1.991	1.799
$Ni^{++}(^1T_{1g})$	*1.869	1.869	⁑1.936	1.805

We report in Table VIII the gross atomic population for each center, together with its partitioning according to the type of basis function. The numerical results are given to five significant figures, corresponding to the accuracy of the population-analysis calculation. Usually the trend of a change, for instance, from one state to another, will be given by the fourth significant figure. It should be emphasized that such small changes are meaningful only on a relative basis. Absolute meaning should not be attached to the four or five figures because of the approximate nature of our wave function and because of some arbitrariness in the way the population analysis distributes the electrons between the atoms.

Before more extensive commentary, the results which are given in Table VIII deserve two more explanations. First, one will notice that the populations are given for the six types of d functions d_{xx}, d_{xy}, d_{xz}, d_{yy}, d_{yz}, and d_{zz} because the population analysis is performed on the basis functions, not on the symmetry-adapted functions. Second, the six fluorine atoms are no longer strictly equivalent for the $^3T_{2g}$, $^3T_{1g}$, and $^1T_{1g}$ states. This is because we have calculated one state of a degenerate triplet in each case. There is no requirement that these states have the full symmetry of the Hamiltonian.

The most striking result is that the total population for each atom is very close to that for the free ion. For instance, in the $^3A_{2g}$ state, the net charge is $+1.9594$ on the nickel atom and -0.9932 on each fluorine. This indicates a small amount of electron transfer from the fluorine ion to the nickel ion. Note that most of the charge transferred (and even the totality for the $^3A_{2g}$ state) comes from the $2p\sigma$ orbital of the fluorine.

A more detailed analysis of the d-orbital populations is reported in Table IX for the cluster states as well as for the corresponding states of the Ni^{++} free ion. Here are given the ratios of the populations of the portions of the d orbitals closer to the nucleus to those of the expanded portions (the sum of these parts occurs in

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[20] R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955).

Table VIII). Ratios for orbitals from which the population is entirely derived from half-filled molecular orbitals are marked ⁑; those derived partly from filled and partly from half-filled molecular orbitals are marked *. The numbers may be compared with 1.847, the corresponding ratio for the ground state of Ni^{++}, which was calculated under the constraint that all d orbitals have the same radial dependence. Examination of this table confirms the observation made by direct inspection of the wave functions. There is a tendency for half-filled orbitals to be somewhat contracted, and for doubly filled orbitals to be somewhat expanded, relative to the free ion. All changes are small.

COMMENTARY

The major indications of our calculation are the following:

(i) If a point-charge representation of the crystal outside the cluster is plausible, the calculations show that only small errors are made in the vacuum-cluster approximation and that it is primarily 10 Lq that is affected. However, it is so easy to include a point-charge model that we see little reason to continue with the vacuum approximation for calculations avoiding drastic approximations in the integrals.

(ii) It seems that d orbitals from free-ion calculations are not much distorted in the cluster. There is a slight tendency for half-filled orbitals to be somewhat contracted, and doubly filled ones somewhat expanded. This may be an artifact of the constraint to identical radial behavior of all d orbitals in the atomic calculation. Uniform expansion of d functions required by Marshall and Stuart[11] to account for neutron form factors, is not confirmed.

(iii) There is very little difference between corresponding orbitals for different multielectron states, apart from the effect of orbital filling already noted.

(iv) The reported calculations do not reflect reduction of repulsive term splittings. This may be associated with unchanged d-orbital radii and insufficient covalency in the wave function. Such an association should be partially confirmed by a calculation with an extended basis (see above). Alternatively, one must suppose that there are appropriate changes from state to state in the correlation energy.

(v) The calculated ligand-field splitting, 4670 cm^{-1}, for the adorned cluster is 35% too small. Since the wave functions hardly change when the point-charge shells representing the crystal are added, it is reasonable to say that the Madelung potential is an additive contribution of about -200 cm^{-1} to 10 Dq. Then our result may be compared to corrected estimates for the LCAO-molecular orbital method,[3] $\sim$2600 cm^{-1}, and the HL method,[7] $\sim$5200 cm^{-1}. If one accepts the Hamiltonian approximations of Hubbard *et al.*,[7] this indicates that there is little to choose between a SCF and a HL method of estimating 10Dq. However, it seems a more likely extrapolation that correct evaluation of the Hamiltonian combined with interaction with a few configurations is necessary for accurate evaluation of 10Dq. In any case, the implication drawn by Hubbard *et al.*, that their low estimate of 10Dq is related to underestimated covalency, does not seem tenable.

(vi) The t_{2g} orbital of the excited state [Eq. (9)] shows that $p\pi$ bonding is about four times smaller than $p\sigma$ bonding in e_g orbitals (measured as % fractional occupation). These calculations support the notion that covalency tends to be proportional to the square of the corresponding overlap integral. [The d-ligand overlap of the e_g orbital in Eq. (9) is 0.106; for the t_{2g} orbital it is 0.053.] In the ground state of Ni^{++} clusters, only σ and s bonding are important; for Mn^{++} clusters, only π bonding is important. However, all three types of bond contribute for the ground state of Co^{++} and in low enough symmetry environments can be separated.[21] This experiment supports a relationship between overlap and covalency, and suggests that the cancellation of the anisotropic contributions to $MnF_6{}^{4-}$ transferred hyperfine structure is a pecularity associated with Mn^{2+}. There are numerous indications in the literature of a special role for the d^5 configuration.[7] We are considering a SCF calculation for $MnF_6{}^{4-}$ using the integrals for $NiF_6{}^{4-}$. Although the inner orbitals may not be well suited to Mn^{++}, the calculation is easy and inexpensive, and should be qualitatively instructive.

(vii) The SCF covalency estimates are a factor of 3 too small. In contrast, the approximate CI results[7] tend to be too large with errors of the same order of magnitude. It is unfortunate that HL calculations with all integrals accurately evaluated do not yet exist for comparison.

(viii) Because of the severely limited nature of the basis set employed, no statement can be made about suitability of free-ion estimates of the singular integrals $\langle\delta(r)_{2s}\rangle$ and $\langle r^{-3}\rangle_{2p}$. However, now that it is possible to calculate wave functions with self-consistency of all electrons, it is time that all contributions to the hyperfine splittings be calculated by summation of the integrals over all orbitals. The tails of the Ni^{++} and neighboring F^- orbitals overlap into the region of the F^- nucleus and contribute significantly to the hyperfine interaction. Direct calculation will be of even more importance for unrestricted SCF wave functions than for spin-paired functions. Unfortunately, the simple connection between covalency and hyperfine splitting vanishes in the calculation advocated. Possibly a simple relationship may be re-established with Mulliken population analysis.

The reported calculations have been made with restricted Hartree-Fock theory on a limited basis set. There are three constraints implied, namely, that inadequacy of the basis set does not allow sufficient freedom of charge motion, that restricted Hartree-Fock

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[21] H. M. Gladney, Phys. Rev. **146**, 253 (1966).

theory does not recognize that exchange forces are different for spin-up and spin-down electrons, and that certain types of orbital relaxation accompanying covalency can be represented only by admixture of key configurations. Each of these limitations is potentially serious and should be further addressed. Unfortunately, comparison with previous work is only of limited value, because of the complicated approximations previously necessary. Comparison by extension seems more promising. In particular, unrestricted Hartree-Fock calculations could be made economically using our integral lists as input.[22] Configuration interaction extensions allowing for the most important relaxations probably require some supplementation of the basis set. IBMOL has the capability of extending integral lists without recalculating values already available. But a calculation which simply extends the basis and calculates all the new integrals would be costly. However, since the excited configurations enter only weakly, one might contemplate neglecting many of the additional multicenter integrals, but continue to use all integrals implied by the ground configuration. At the moment, we are not planning either extension ourselves, but urge their consideration.

To increase the size of the calculation by a factor of 5 seems within our capability in the near future. Uniformly applied, this expansion would permit about 190 Gaussian atomic orbitals (instead of 128) and about 81 "contracted" Gaussians (instead of 59). The number of symmetry orbitals would be nearly the same as the number of contracted Gaussians. However, one can expect that the atomic basis need not be expanded too much. With an F^- basis of (8,4) and a Ni^{++} basis of (11,6,4), the atomic total energies should be within about 0.1% of the Hartree-Fock limit (instead of 1%). For the cluster, this implies 173 Gaussians and 1.1×10^8 integrals. A major difficulty with the credibility of the present calculation is that the orbitals did not have enough freedom to relax, so that whatever increase in the contracted-orbital basis can be afforded is desirable. We suggest contracted bases of (3,2) for the F^- ions and (5,4,3) for the Ni^{++} ion, leading to 89 contracted orbitals (8×10^6 integrals on tape) and 86 symmetry orbitals. Then for the symmetries a_{1g}, e_g, t_{2g}, t_{1u}, t_{2g}, and t_{2u} the degrees of freedom will be 4, 4, 3, 5, 1, and 1, respectively, instead of 2, 2, 1, 2, 0, and 0. Since the inner orbitals do not change for cluster formation, most of the increased freedom can be allowed for the strongly overlapped orbitals. We believe that this size basis will be adequate in that the major questions will be directed at other features of the calculation (spin polarization, configuration interaction, estimation of hyperfine interactions from SCF solutions).

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APPENDIX A: COMPUTATIONS

The calculations reported in this paper were made primarily with two programs, both of which are well documented elsewhere. The atomic SCF solutions used primarily to select basis functions with optimized orbital exponents were accomplished partly with a version of the University of Chicago atomic SCF program adapted for Gaussian orbitals, partly with a program developed in this laboratory.[23] The cluster calculations were performed by IBMOL,[16] a program for LCAO restricted self-consistent field calculations with a Gaussian atomic-orbital basis and any nuclear geometry.

The $NiF_6{}^{4-}$ cluster calculation differs from most of the problems for which IBMOL is being used. About half of the repulsion integrals have one or more d-orbital factors in the integrand; most of the previous work required only s and p orbitals. Also, the symmetry group of the Hamiltonian is larger than has been common, with the consequence that many symmetry orbitals are combinations of four or six atomic orbitals, so that the symmetry transformation may be expected to become costly. This is offset by the extensive factoring of the Hamiltonian matrices and the corresponding time saving in the SCF calculation. One of us (HMG) further improved the programming of the relevant sections of IBMOL over what has been previously reported. For electron-repulsion integrals with d orbitals, direct use of the general formula given by Wright[24] was abandoned in favor of partial hand elaboration of the formula into a series of special cases. Complete elaboration of the formula, as is employed by IBMOL for integrals with only s and p functions, seemed inappropriate because of the very large number of special formulas implied. But several factorizations, including one corresponding to three Cartesian axes and one separating the radial factors from the angular, replace much of the arithmetic by a series of quickly executed branch points. While these new formulas were being coded, several efficiencies were discovered affecting integrals on s and p orbitals also. The modified integral package, tested on subsets of orbitals from proposed $NiF_6{}^{4-}$ bases, required about 45% of the time previously reported for integrals on a basis of s, p, and d orbitals.

It is significant that the organization of IBMOL into independent integrals, symmetry transformation, and SCF sections makes the calculation of several states on

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[22] On request to the authors, either the tape of integrals over contracted-basis orbitals or that of integrals over symmetry orbitals will be available for further calculations.

[23] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965); B. Roos, C. Salez, A. Veillard and E. Clementi, IBM Technical Report, 1968 (unpublished; available upon request).

[24] J. P. Wright, Quarterly Progress Report, Solid State and Molecular Theory Group, MIT, No. 50, 1963, p. 35 (unpublished).

the same basis set not much more time consuming than the calculation of a single state. Our computations were performed on an IBM SYS/360, Model 65. In the integral calculation and symmetry-transformation sections, for which the machine was limited only by central processing unit speed, about 17 and 3 h, respectively, were expended. Generation of a supermatrix tape for each symmetry state calculated required only negligible expenditure. Each SCF calculation required about 10 min. No special difficulty was encountered in the SCF section. Convergence was achieved without the use of any special extrapolation procedure.

APPENDIX B: ATOMIC HARTREE-FOCK SOLUTIONS

For the ground state of Ni^{++}, first of all a wave function with nine *s* orbitals, five *p* orbitals, and four *d* orbitals, fully optimized as to orbital exponents, was obtained. Then the *s* orbital with the largest exponent and the corresponding *p* orbital were eliminated, and the remaining innermost orbitals were reoptimized. Finally, the number of *d* orbitals was reduced to three and the *d* exponents were optimized without further adjustment of the *s* and *p* exponents. Hopefully, this procedure yields, with a limited basis set, an atomic wave function which is reasonably accurate far from the nucleus, with good representations of the *d* orbitals. Of course, the total energy thus calculated, −1494.502 a.u., is not optimal for this size basis, and expectations of operators singular at the nucleus cannot be accurately calculated with this wave function. For comparison, the accurate Hartree-Fock energy, −1506.029 a.u., calculated by Clementi[25] may be cited.

TABLE X. SCF wave function of $Ni^{++}(^3F)$.

Basis functions (Gaussian orbital exponents)

	s	*p*	*d*
1	3545.32	80.8868	10.872
2	583.599	17.9736	2.6068
3	171.800	3.6472	0.65590
4	61.4553	1.29997	
5	16.4320		
6	4.9993		
7	2.6371		
8	0.965939		

Orbital energies and eigenvectors

1*s*	2*s*	3*s*	2*p*	3*p*	3*d*
−306.2291	−39.0190	−5.6557	−33.1988	−3.8888	−1.3360
0.06793	−0.02157	0.00812	0.32870	−0.13152	0.24600
0.32458	−0.11308	0.04341	0.72591	−0.28510	0.57302
0.49505	−0.25653	0.10138	0.14141	0.45290	0.47111
0.25413	−0.12745	0.05874	−0.03039	0.65852	
0.00160	0.81850	−0.53625			
0.00580	0.42515	−0.46729			
−0.00453	−0.11141	0.86935			
0.00103	0.02269	0.60108			

TABLE XI. SCF wave function of $F^-(^1S)$.

Basis functions (Gaussian orbital exponents)

	s	*p*
1	238.282	5.7863
2	39.7169	1.2415
3	11.8581	0.24547
4	2.2204	
5	1.1534	
6	0.32901	

Orbital energies and eigenvectors

1*s*	2*s*	2*p*
−25.7157	−1.0925	−0.1557
0.10816	−0.02553	0.21864
0.42815	−0.11572	0.54244
0.51051	−0.20855	0.50529
0.18391	−0.02078	
−0.10026	0.61687	
0.01900	0.50857	

The functions for F^- were similarly treated. The estimated Hartree-Fock energy, −98.5884, compares badly with the accurate value, −99.4593. The presence of six fluoride ions in the cluster necessitated such drastic curtailment in this preliminary calculation.

The atomic wave functions are reported in Tables X and XI.

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[25] E. Clementi, IBM J. Res. Develop. Suppl. **9**, 1 (1965).