Covalency Effects in KNiF₃. III. Theoretical Studies

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For the $(NiF_6)^{4-}$ complex in $KNiF_3$ we have constructed molecular orbitals (MO) which are linear combinations of the Ni^{2+} and F^- Hartree-Fock atomic orbitals. These LCAO-MO, introduced by Van Vleck, are of the form $\Psi = N^{-1/2}(\varphi - \lambda\chi)$ in which φ is the Ni^{2+} $3d$ function and χ a linear combination of the suitable F^- functions. The orbitals were assumed to be solutions of Schrödinger's equation $h\Psi = E\Psi$, where the Hamiltonian was $h = -\Delta/2 + V_M + V_L$. The terms V_M and V_L describe the Coulombic and exchange interactions with the metal ion and ligands, respectively. Matrix elements of the form $\langle \Psi | h | \Psi \rangle$ were evaluated numerically on an IBM 7090. Assuming λ and the overlap between φ and χ to be small, the energy was minimized and the parameters λ were determined. For the $2p\sigma$ bonding and the $2s$ bonding the calculated values were $N_e^{-1/2}\lambda_\sigma = 0.383$ and $N_e^{-1/2}\lambda_s = 0.109$ which agreed very well with the values $N_e^{-1/2}\lambda_{p\sigma} = 0.337$ and $N_e^{-1/2}\lambda_s = 0.116$ determined in the nuclear magnetic resonance experiment. The molecular orbitals were used to calculate the cubic crystal field splitting $10Dq = (\Psi_e | h | \Psi_e) - (\Psi_t | h | \Psi_t)$ which is the promotion energy of an electron from a t_{2g} orbital to an e_g orbital. The calculated value of $10Dq = 6350$ cm^{-1} agreed quite well with the observed value of $10Dq = 7250$ cm^{-1} considering the accuracy of the calculation. Furthermore, the reduction of the spin-orbit parameter and the Racah parameter B from their free-ion values are satisfactorily explained by the molecular orbital approach. The physical interpretation of these results is emphasized. In particular, the only contributions to $10Dq$ with the correct sign come from the off-diagonal matrix elements associated with the covalency; the amount of π electron admixture is shown to be large; one novel physical mechanism partly responsible for the large π bonding is the crystal field splitting of the F^- $p\sigma$ and $p\pi$ levels by the Ni^{2+} ions; expanding the Ni^{2+} radial function is shown to be unnecessary for some purposes and incorrect for the remainder. Details of the calculation are presented and implications of the LCAO-MO model discussed.

I. INTRODUCTION

IN most applications of crystal field theory the cubic field splitting $10Dq$ has been a parameter adjusted to fit the experimental data. However, several attempts have been made to calculate $10Dq$ from first principles.

The first attempts to calculate $10Dq$ by Van Vleck[1] and Polder[2] used a point charge or point-dipole approximation for the ligands and calculated the splitting of the d-electron levels in the field of the ligands. The case chosen by Van Vleck and by many of the subsequent authors was Cr^{3+} surrounded by six water molecules with their negative oxygens pointing towards the Cr^{3+}. These calculations gave the proper sign for $10Dq$ since it is obvious that a negative charge at the corners of the octahedron raises the energy of the e_g electrons, which point towards the negative charges, above the energy of the t_{2g} electrons which point between them. Furthermore, by using Slater orbitals for the $3d$-electron functions the values of $10Dq$ were quite close to the experimental measurements. This harmony lasted until the calculations were extended by Kleiner.[3] Instead of representing the ligands by a negative-point charge, Kleiner included the delocalization of the oxygen ligand

electrons by using Slater orbitals for the oxygen electrons. This too was a semiclassical calculation in which the d electron's energy in the field of the ligands was calculated. Unfortunately, the value of $10Dq$ calculated in this way had the wrong sign, because the positive nuclear charge attracted the e_g electrons more than the ligand electrons repelled them. A major advance in the problem was made by Tanabe and Sugano[4] who did a quantum-mechanical calculation based on a purely ionic model. They used the same physical model as Kleiner, i.e., delocalized electrons on the ligand, but they orthogonalized the d electrons to the ligands which meant that their wave functions were composed of d-electron functions plus some admixture of ligand $2s$ and $2p$ functions. Furthermore, they included quantum-mechanical exchange integrals between the d electrons and the ligand electrons in addition to the Coulomb integrals considered by Kleiner. They did obtain a value of $10Dq$ of the proper sign but the result involved some ambiguity because reliable $3d$ wave function were unavailable at that time. Phillips[5] acting on a suggestion of Herring's claimed that the point-charge approximation was correct because all the additional terms calculated by Tanabe and Sugano would cancel. Freeman and

[1] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).
[2] D. Polder, Physica **9**, 709 (1942).
[3] W. H. Kleiner, J. Chem. Phys. **20**, 1784 (1952).

[4] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **11**, 864 (1956).
[5] J. C. Phillips, J. Phys. Chem. Solids **11**, 226 (1959).

Watson[6] repeated Kleiner's calculation using Watson's[7] Hartree-Fock wave functions and concluded that the point-charge model only agrees with experiment when Slater functions are used. Thus, Phillips' claim that the point-charge model can explain the observed crystal field is only correct if one used such diffuse-starting wave functions as Slater's. Freeman and Watson showed that by calculating Kleiner's correction with Hartree-Fock functions the result was no longer a negative value of $10Dq$ but rather a very small value which could be slightly greater than zero with reasonable assumptions.

All these treatments, both semiclassical and quantum mechanical, are confined to the ionic model. However, as shown by the nuclear magnetic resonance (NMR) experiments presented in the previous paper,[8] it now is necessary to go a step further away from the ionic model. In this paper, we present the details of a molecular orbital (MO) calculation from first principles of both the cubic crystalline field-splitting $10Dq$ and the linear combination of atomic orbital (LCAO) wave functions in $KNiF_3$. The values calculated agree with the experimental results presented in the previous two papers.[8,9] As a result of this calculation our understanding of the physical origins of the crystalline field and of the covalency is quite different from the traditionla picture.

From the calculation we have come to the following conclusions:

1. The semiclassical view of the crystalline field splitting, which considers the ligands as perturbations upon the metal ion, is merely one contribution which in $KNiF_3$ is small and has the wrong sign.

2. The major contribution to $10Dq$ arises from the covalency.

3. The π bonding is described by large π admixtures into the molecular orbitals—admixtures which are almost as large as the σ-bonding terms.

4. The π bonding is important wherever the wave functions themselves are important, i.e., in hyperfine interactions, in optical intensities, and in magnetic-exchange interactions, but it is not as important as the σ bonding when the bond energy is involved, i.e., in bond distances, bond energies, etc.

II. MOLECULAR ORBITAL FORMALISM IN IONIC CRYSTALS

In molecular orbital theory, the MO wave functions, Ψ, and orbital energies, E, are obtained by solving the Hartree-Fock equation

$$h\Psi = E\Psi, \tag{2.1}$$

where h is the Hartree-Fock Hamiltonian for one

electron. It should be noted that, in general, the Hamiltonian involves coefficients of molecular orbitals, γ, appearing below. The usual way of solving this Hartree-Fock equation is to fix γ in the Hamiltonian and then vary γ in the wave functions so as to minimize the energy; finally, after iteration, γ in the Hamiltonian should be equal to γ in the wave functions. As a starting point one assumes that the antibonding and bonding wave functions, respectively,

$$\Psi^a = N^{-1/2}(\varphi - \lambda\chi), \tag{2.2}$$

and

$$\Psi^b = N'^{-1/2}(\chi + \gamma\varphi), \tag{2.3}$$

are the exact eigenfunctions of (2.1). In (2.2) and (2.3), φ is a normalized wave function localized at the metal ion, χ is a normalized MO wave function for the surrounding atom system, λ and γ are numerical coefficients, and N's are normalization constants. This is equivalent to assuming that the antibonding orbital energy is already maximized by λ in (2.2) and the bonding orbital energy is already minimized by γ in (2.3). Inserting (2.2) into (2.1) and integrating after the multiplication by φ or χ from the left, we obtain

$$E^a = \frac{1}{1-\lambda S}[(\varphi|h|\varphi) - \lambda(\varphi|h|\chi)], \tag{2.4}$$

$$= \frac{1}{1-\lambda^2}[(\varphi|h|\varphi) - \lambda^2(\chi|h|\chi)], \tag{2.5}$$

where S is the overlap integral between φ and χ. Here, without any loss of generality, we assume φ and χ to be real. Similarly, inserting (2.3) into (2.1), we obtain

$$E^b = \frac{1}{1+\gamma S}[(\chi|h|\chi) + \gamma(\varphi|h|\chi)], \tag{2.6}$$

$$= \frac{1}{1-\gamma^2}[(\chi|h|\chi) - \gamma^2(\varphi|h|\varphi)]. \tag{2.7}$$

In our problem, the Ψ_t's have just the forms given in (2.2) and (2.3), but the Ψ_e's have more complicated forms as shown in (2.1) and (2.5) of part I. Even for the latter, a simple extension of (2.4) and (2.5) is possible if χ, S, and λ are replaced by χ_e, S_e, and λ_e, respectively, which are defined as follows;

$$\chi_e = \mu_s\chi_s + \mu_\sigma\chi_\sigma,$$

$$S_e = \mu_s S_s + \mu_\sigma S_\sigma, \tag{2.8}$$

$$\lambda_e = \lambda_s/\mu_s = \lambda_\sigma/\mu_\sigma,$$

where

$$\mu_s^2 + \mu_\sigma^2 = 1.$$

Therefore, we can use the expressions (2.4) and (2.5) for both the e_g and t_{2g} antibonding molecular orbitals in our problem.

The cubic crystalline field-splitting parameter,

[6] A. J. Freeman and R. E. Watson, Phys. Rev. **120**, 1254 (1960).

[7] R. E. Watson, Phys. Rev. **118**, 1036 (1960).

[8] R. G. Shulman and S. Sugano, Phys. Rev. **130**, 506 (1963), referred to as part I.

[9] K. Knox, R. G. Shulman, and S. Sugano, preceding paper [Phys. Rev. **130**, 512 (1963)], referred to as part II.

$\Delta \equiv 10Dq$, is defined as

$$\Delta = E_e{}^a - E_t{}^a. \tag{2.9}$$

Assuming λ and S to be small quantities of the order of ϵ ($\epsilon \ll 1$) and neglecting quantities smaller than ϵ^2, we arrive at the expression,

$$\Delta = [(\varphi_e|h|\varphi_e) - (\varphi_t|h|\varphi_t)]$$
$$- [\lambda_e(\varphi_e|h|X_e) - \lambda_t(\varphi_t|h|X_t)]$$
$$+ [(\lambda_e S_e - \lambda_t S_t)(\varphi_e|h|\varphi_e)], \tag{2.10}$$

where $\lambda_t = \lambda_\pi$ and $X_t = X_\pi$. Here we have used the important fact, shown below, that the difference $[(\varphi_e|h|\varphi_e) - (\varphi_t|h|\varphi_t)]$ is of the same order as $\lambda(\varphi|h|\chi)$, which has the order of ϵ^2 when the order of $(\chi|h|\chi)$ is unity. By using relations (2.6) of part I, (2.10) can be rewritten as follows:

$$\Delta = [(\varphi_e|h|\varphi_e) - (\varphi_t|h|\varphi_t)]$$
$$+ [(\lambda_s S_s + \lambda_\sigma S_\sigma - \lambda_\pi S_\pi)(\varphi_e|h|\varphi_e)]$$
$$- [S_s(\varphi_e|h|X_s) + S_\sigma(\varphi_e|h|X_\sigma) - S_\pi(\varphi_t|h|X_\pi)]$$
$$- [\gamma_s(\varphi_e|h|X_s) + \gamma_\sigma(\varphi_e|h|X_\sigma)$$
$$- \gamma_\pi(\varphi_t|h|X_\pi)]. \tag{2.11}$$

The first line of (2.11) involves the point-charge term, Kleiner's correction, and the exchange interaction between metal and ligand electrons. The second term comes from the renormalization. The third line comes from the nonorthogonality between metal and ligand orbitals, and the fourth and fifth lines come from the covalency which is measured by γ as mentioned in Sec. 2 of part I. Phillips[5] argued that the terms in the third line would cancel Kleiner's correction and the exchange terms in the first line. It is numerically shown later that this argument is approximately correct, although the main contribution to Δ comes from the fourth and fifth lines, the covalency term, not from the point-charge term which is much smaller than the covalency contribution.

For the t_{2g} orbitals, λ_π is determined by Eq. (2.4) and (2.5), with the result that

$$\lambda_\pi = [-(\varphi_t|h|X_\pi) + S_\pi(\varphi_t|h|\varphi_t)]$$
$$\times [(\varphi_t|h|\varphi_t) - (X_\pi|h|X_\pi)]^{-1}. \tag{2.12}$$

Similarly, by equating (2.6) and (2.7), we have

$$\gamma_\pi = [-(\varphi_t|h|X_\pi) - S_\pi(X_\pi|h|X_\pi)]$$
$$\times [(\varphi_t|h|\varphi_t) - (X_\pi|h|X_\pi)]^{-1},$$
$$= \lambda_\pi - S_\pi, \tag{2.13}$$

as required [(2.6) of part I] by the orthogonality between the bonding and antibonding orbitals. In deriving (2.12) and (2.13), we have neglected small terms of order $\epsilon^n (n \geq 2)$.

For the e_g orbitals, we cannot determine λ_s and λ_σ from (2.4) and (2.5). In this case, we determine γ_s, γ_σ, and $\gamma_{s\sigma}$ from the expressions for $E_{es}{}^b$ and $E_{e\sigma}{}^b$ similar to (2.6) and (2.7). $E_{es}{}^b$ and $E_{e\sigma}{}^b$ are the orbital energies of the $\Psi_{es}{}^b$ and $\Psi_{e\sigma}{}^b$ bonding orbitals in (2.5) of part I,

respectively. Neglecting again small terms of higher order, we obtain

$$\gamma_s = [-(\varphi_e|h|X_s) + S_s(X_s|h|X_s)]$$
$$\times [(\varphi_e|h|\varphi_e) - (X_s|h|X_s)]^{-1}, \tag{2.14}$$

$$\gamma_\sigma = [-(\varphi_e|h|X_\sigma) + S_\sigma(X_\sigma|h|X_\sigma)]$$
$$\times [(\varphi_e|h|\varphi_e) - (X_\sigma|h|X_\sigma)]^{-1}. \tag{2.15}$$

and

$$\gamma_{s\sigma} = (X_s|h|X_\sigma) \times [(X_s|h|X_s) - (X_\sigma|h|X_\sigma)]^{-1}. \tag{2.16}$$

By using relations (2.6) of part I, λ_s and λ_σ are now obtained from (2.14) and (2.15), respectively.

III. HAMILTONIAN

The Hartree-Fock Hamiltonian for a single electron in our problem is

$$\mathcal{3C} = h + V_{\text{crys}}, \tag{3.1}$$

in which h is the Hamiltonian of a specific $[\text{NiF}_6]^{4-}$ molecule and V_{crys} represents the effects arising because the molecule is embedded in a crystal. Assuming that the electron of interest is localized in the molecule for which h is given, we are interested in V_{crys} in the region of the molecule. Neglecting the periodicity of crystals is one of the fundamental assumptions employed in Bethe's crystalline field theory.[10] Experimentally it is well known that a cubic crystalline field parameter is insensitive to the surroundings beyond the nearest neighbor ions or ligands: For example, the cubic crystalline field parameters in the $\text{Ni}(\text{NH}_3)_6{}^{2+}$ and $\text{Ni}(en)_6{}^{2+}$ systems are almost the same, 10 300 and 10 800 cm^{-1}, respectively.[11] Theoretically it is easily shown that the cubic-field potential around the central metal ion arising from distant ions beyond the nearest neighbors is very small compared with that arising from the nearest neighbor ions: The ratio of the former part of the crystal field to the latter is only 0.023 in the NaCl-type crystal. Therefore, the potential inside the hole, which is originally occupied by the $[\text{NiF}_6]^{4-}$ molecule, is fairly flat around the center. Folds of the potential of cubic symmetry inside the hole deepen as one approaches the edge of the hole, but we can show that at the points where the nearest neighbor fluorines are located, the depth of the potential fold is still shallow.[12] From these experimental and theoretical considerations, we now assume that V_{crys} is a constant in the region of the $[\text{NiF}_6]^{4-}$ molecule. In other words, we adopt the physical model that the molecule is placed in a flat

[10] H. Bethe, Ann. Physik 3, 133 (1929).
[11] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan 9, 766 (1954).
[12] The potential at the center of the hole is obtained by subtracting the point-charge potential due to the nearest neighbor fluorines from minus the Madelung potential at the nickel site. This gives the depth of the potential well, −0.7666 in atomic units, at the center. The potential at the points originally occupied by the nearest-neighbor fluorines is roughly estimated by subtracting the point-charge potential due to the Ni²⁺F₅⁻ originally accomodated in the hole from the Madelung potential at the fluorine site. This gives the depth of the potential well, −0.7763, at the points of interest.

bottom potential well. This simplification enables us to neglect V_{crys} as this merely shifts the origin of the energy scale.

The Hamiltonian h is

$$h = h_0 + h', \qquad (3.2)$$

where h_0 is the Hamiltonian of a purely ionic $\text{Ni}^{2+}\text{F}_6^-$ complex in which the overlaps are ignored ($S=0$) and h' is a correction due to the deviation from this semi-classical ionic model. Following Tanabe and Sugano,[4] the Hamiltonian h_0 is given by

$$h_0 = -\tfrac{1}{2}\Delta + V_M + V_L, \qquad (3.3)$$

in which $-\Delta/2$ is the kinetic energy operator, V_M is the Coulomb and exchange interaction operator of all the Ni^{2+} electrons and the Ni^{2+} nucleus of the form:

$$V_M = V_{\text{core}} + V_d^{\text{Coul}} + V_d^{\text{ex}}, \qquad (3.4)$$

where V_{core} comes from the nucleus and the core electrons up to and including the $3p$ shell. We have used

$$V_{\text{core}} = -(10 + 31.0\ e^{-4.73r})/r, \qquad (3.5)$$

which is obtained[13] by an analytical fit to Watson's Hartree-Fock core potential of Ni^{2+}. V_d^{Coul} and V_d^{ex} come from seven d electrons with the configuration $\xi_\pm{}^0\eta_\pm{}^0\zeta_+{}^0 u_+{}^0 v_+{}^0$, where ξ^0, η^0, ζ^0, u^0, and v^0 are the abbreviations for the atomic orbitals φ_ξ, φ_η, φ_ζ, φ_u, and φ_v given in (2.3) of part I. Subscripts $+$ and $-$ indicate spins accommodated. Rewriting (2.9) we have

$$\Delta(\equiv 10Dq) = E(t_2{}^5 e^3\ {}^3T_2) - E(t_2{}^6 e^2\ {}^3A_2), \qquad (3.6)$$

where E's are the energies of the states indicated in the brackets. The detailed electron configurations of the ζ component of the $^3T_2$ state and of the $^3A_2$ state are

$$\xi_\pm \eta_\pm \zeta_\pm u_+ v_+ \quad \text{for} \quad {}^3A_2 \quad \text{with} \quad M_s=1,$$
$$\xi_\pm \eta_\pm \zeta_+ u_+ v_\pm \quad \text{for} \quad {}^3T_2\zeta \quad \text{with} \quad M_s=1.$$

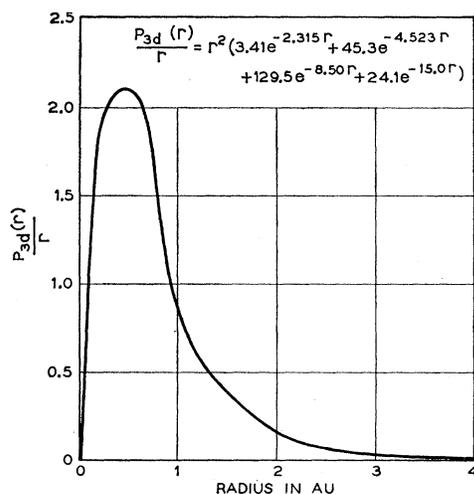FIG. 1. Normalized radial part of the Ni^{2+} $3d$ function, $R_{3d}(r)$ (in atomic units) from Watson, where $R_{3d}(r) = P_{3d}(r)/r$.

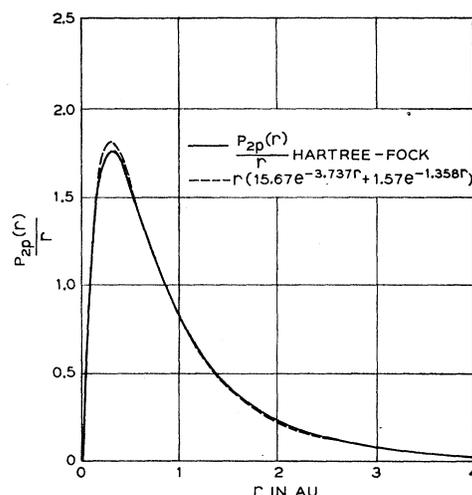[13] The numerical values of V_{core} were kindly supplied by A. J. Freeman.

FIG. 2. A comparison of Froese's numerical values of $R_{2p}(r) = P_{2p}(r)/r$ with the analytical function shown in Eq. (4.2).

Thus, (3.6) can be written as

$$\Delta = (v|h|v) - (\zeta|h|\zeta), \qquad (3.7)$$

where v and ζ are the molecular orbitals belonging to e and t_2, respectively. The explicit forms of V_d^{Coul} and V_d^{ex} are

$$V_d^{\text{Coul}} = \sum_{\gamma=\xi\xi\eta\eta\zeta uv} \int d\tau_2\ r_{12}^{-1} |\varphi_\gamma(2)|^2, \qquad (3.8)$$

$$V_d^{\text{ex}} = -\sum_{\gamma=\xi\eta} \int d\tau_2\ r_{12}^{-1} \varphi_\gamma^*(2)\varphi_\gamma(1)P_{12}, \qquad (3.9)$$

where P_{12} is the permutation operator for electrons 1 and 2.

In (3.3) V_L is the contribution from the six fluoride ions, which can be decomposed as follows,

$$V_L = V_L^{\text{point}} + V_L^K + V_L^E. \qquad (3.10)$$

In (3.10), V_L^{point} is the point-charge potential given by

$$V_L^{\text{point}} = \sum_{i=1}^{6} 1/|\mathbf{r}-\mathbf{R}_i|, \qquad (3.11)$$

which comes from a single negative point charge assumed at the position, $\mathbf{R}_i$, of the six fluorine nuclei. We have separated out of the Hamiltonian the point-charge contribution because historically this has been discussed as an approximation of the crystalline field potential. As mentioned previously, V_L^K in (3.10) is Kleiner's additional potential due to the imperfect screening of the ligand nuclear charge by ligand electrons, and it is expressed as

$$V_L^K = \sum_{i=1}^{6} -8/|\mathbf{r}-\mathbf{R}_i|$$
$$+2\int d\tau_2\ r_{12}^{-1} \sum_{k=2s,2pz,2px,2py} |\varphi_{ik}(2)|^2. \qquad (3.12)$$
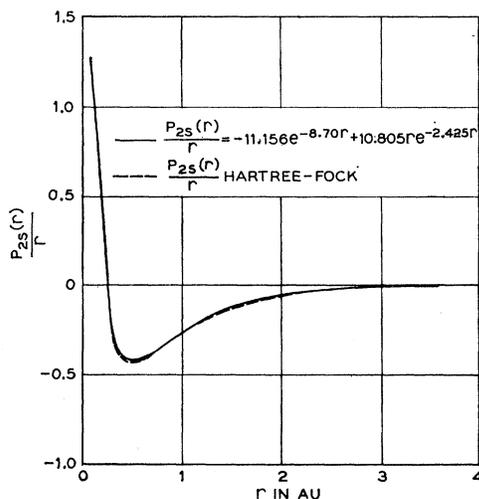
FIG. 3. A comparison of Froese's numerical values of $R_{2s}(r)$ $=P_{2s}(r)/r$ with the analytical function shown in Eq. (4.4).

$V_L{}^E$ is the exchange-interaction operator introduced by Tanabe and Sugano with the explicit form,

$$V_L{}^E = -\sum_{i=1}^{6} \int d\tau_2\, r_{12}{}^{-1} \sum_{k=2s,2pz,2px,2py} \varphi_{ik}{}^*(2)\varphi_{ik}(1)P_{12}.$$
$$(3.13)$$

We shall see later that this term makes important contributions.

The Hamiltonian h' in (3.2) gives only a small contribution when the overlap integral S and the covalency γ are small. In the following calculation, this term will be neglected. This means that our calculation is the first step of a self-consistent field (SCF) calculation where $S=0$ and $\gamma=0$ are assumed in the Hamiltonian. A SCF calculation would then substitute our calculated values of S and γ into the Hamiltonian and repeat the procedure until self-consistency was obtained.

IV. ORBITAL FUNCTIONS

As long as V_{crys} in the Hamiltonian (3.1) is assumed to be a constant, the eigenfunction satisfying the Hartree-Fock equation (2.1) is a molecular orbital of the [NiF$_6$]$^{4-}$ molecule. Furthermore, in predominantly ionic crystals such as KNiF$_3$ it is a good starting approximation to assume that the molecular orbital Ψ is a linear combination of free ion orbitals. Thus, we use the molecular orbitals given in (2.1–5) of part I in which the atomic orbitals are the Hartree-Fock solutions of free Ni^{2+} and F$^-$ ions.[14]

[14] An equivalent approach to this problem was described by F. Keffer, T. Oguchi, W. O'Sullivan, and J. Yamashita, Phys. Rev. 115, 1553 (1959). However, their evaluation of the matrix elements was only qualitative. On the other hand, A. Mukerjee and T. P. Das [Phys. Rev. 111, 1479 (1958)], by claiming that the observed F^{19} hfs could be explained by the overlap term arising from the orthogonalization, i.e., $\lambda=S$, did not allow the ligand electrons enough freedom to describe the F^{19} hfs subsequently measured. In an extension of the purely ionic model, W. Marshall and R. Stuart [Phys. Rev. 123, 2048 (1961)] claimed to explain many transition ion properties in crystals by expanding the metal ion radial function. This approach is discussed below.

The normalized radial part of the Ni^{2+} $3d$ function, taken from Watson's tables,[7] is

$$R_{3d}(r) = r^2(3.4096e^{-2.315r}+45.261e^{-4.523r}$$
$$+129.48e^{-8.502r}+24.071e^{-15.01r}). \quad (4.1)$$

This function is plotted in Fig. 1.

Froese's numerical values[15] of F$^-$ radial functions from her Hartree-Fock calculation were used for our F$^-$ functions. The numerical values of $R_{2p}(r)$ were fitted to a two-term analytical function

$$R_{2p}(r) = r(15.671r^{-3.7374r}+1.5742e^{-1.3584r}), \quad (4.2)$$

which is compared with the numerical values in Fig. 2. The coincidence of the two functions is not perfect but the error introduced is negligible. The complete F$^-$ $2p$ functions are

$$\varphi_{2p\sigma} = Y(10)R_{2p},$$
$$\varphi_{2p\pi^{\pm}} = Y(1\pm1)R_{2p}. \quad (4.3)$$

For the $2s$ function we used the Slater function orthogonalized to the $1s$-core function:

$$R_{2s}(r) = (-11.156e^{-8.70r}+10.805re^{-2.425r}). \quad (4.4)$$

The agreement with Froese's numerical values is excellent as shown in Fig. 3. The complete $2s$ function is

$$\varphi_{2s} = (4\pi)^{-1/2}R_{2s}. \quad (4.5)$$

The $1s$ function has been shrunk into the fluorine nucleus. However, the $1s$-Slater function was used at times[8] and it is compared in Fig. 4 with Froese's values.

Since the radial functions are all drawn to the same scale, it is possible to compare them. It can be seen that $R_{2p}(r)$ falls off more slowly than the others. To compare the amplitude along a particular line, such as the inter-
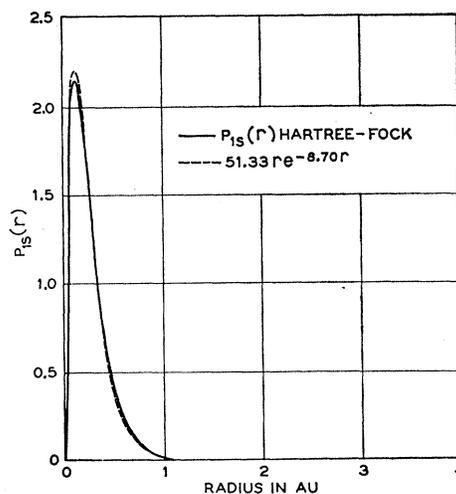

FIG. 4. A comparison of the Slater $1s$ function with Froese's Hartree-Fock calculations.

[15] C. Froese, Proc. Cambridge Phil. Soc. 53, 206 (1957).

nuclear radius, it must be remembered that the angular parts of the different orbitals have different values.

V. EVALUATION OF MATRIX ELEMENTS

Four types of matrix elements will be considered, namely: the overlap integrals between nickel and fluorines of the form $(\varphi|\chi)$; the nickel diagonal terms $(\varphi|h_0|\varphi)$; the fluorine diagonal terms $(\chi|h_0|\chi)$; and finally the off-diagonal terms, also called resonance integrals, of the form $(\varphi|h_0|\chi)$. The matrix elements of the molecular orbitals were expressed in terms of atomic orbitals. Details of this analysis are shown in the Appendices. The integrals expressed in terms of atomic orbitals were evaluated numerically by the following four means.

Two-center integrals were: (1) mainly computed on the IBM 7090 using Switendick and Corbato's program[16]; (2) in a few cases evaluated analytically. (3) Some two-center integrals which could not be handled adequately by Switendick and Corbato's program were evaluated by an auxiliary IBM 7090 computation. Non-negligible three-center integrals were (4) determined by a direct summation conducted on the IBM 7090.

$(\varphi|\chi)$

The overlap integrals are listed in Table I. The atomic overlaps were calculated by Switendick and Corbato's program on the IBM 7090 and confirmed by a separate machine program. These are related in Appendix I to the molecular overlaps which are the last three listed in the table. It is clear that the molecular overlaps are independent of the subscript γ indicating the component of a degenerate set of molecular orbitals.

$(\varphi|h_0|\varphi)$

By using the orbital energy ϵ_d of Ni^{2+} $3d$ electrons,

$$\epsilon_d = (\varphi|-\tfrac{1}{2}\Delta+V_M|\varphi), \quad (5.1)$$

we have

$$(\varphi|h_0|\varphi) = \epsilon_d + (\varphi|V_L|\varphi), \quad (5.2)$$

where V_L is separated into three terms as shown in (3.10). Detailed methods of calculating $(\varphi|V_L|\varphi)$ are

TABLE I. The overlap integrals.

$(d\sigma|s)$	0.04701_4
$(d\sigma|p\sigma)$	0.06391_8
$(d\pi^+|p\pi^+)$	0.03778_4
$(\varphi_{e\gamma}|\chi_{\gamma s})$	0.08143_1
$(\varphi_{e\gamma}|\chi_{\gamma\sigma})$	0.11071
$(\varphi_{t\gamma}|\chi_{\gamma\pi})$	0.07556_8

[16] A. C. Switendick and F. J. Corbató, Quarterly Progress Report, October 15, 1959, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts (unpublished).

TABLE II. The $(\varphi|V_L|\varphi)$ integrals.

I_0	0.26384_6
I	0.00379_3
$(\varphi_{e\gamma}|V_L^{\text{point}}|\varphi_{e\gamma})$	1.58687
$(\varphi_{t\gamma}|V_L^{\text{point}}|\varphi_{t\gamma})$	1.58055
$(d\sigma,s\|d\sigma,s)$	0.27063
$(d\sigma,p\sigma\|d\sigma,p\sigma)$	0.28602
$(d\sigma,p\pi^\pm\|d\sigma,p\pi^\pm)$	0.26136
$(d\pi^\pm,s\|d\pi^\pm,s)$	0.26605
$(d\pi^\pm,p\sigma\|d\pi^\pm,p\sigma)$	0.28048
$(d\pi^\pm,p\pi^+\|d\pi^\pm,p\pi^+)$	0.25786
$(d\pi^+,p\pi^-\|d\pi^-,p\pi^+)$	0.00073
$(d\delta^\pm,s\|d\delta^\pm,s)$	0.25810
$(d\delta^\pm,p\sigma\|d\delta^\pm,p\sigma)$	0.27111
$(d\delta^\pm,p\pi^+\|d\delta^\pm,p\pi^+)$	0.25111
$(\varphi_{e\gamma}|V_L^{\text{Coul}}|\varphi_{e\gamma})$	12.6648
$(\varphi_{t\gamma}|V_L^{\text{Coul}}|\varphi_{t\gamma})$	12.6237
$(d\sigma,s\|s,d\sigma)$	0.17577×10^{-2}
$(d\sigma,p\sigma\|p\sigma,d\sigma)$	0.52749×10^{-2}
$(d\sigma,p\pi^\pm\|p\pi^\pm,d\sigma)$	0.01921×10^{-2}
$(d\pi^\pm,s\|s,d\pi^\pm)$	0.01233×10^{-2}
$(d\pi^\pm,p\sigma\|p\sigma,d\pi^\pm)$	0.14436×10^{-2}
$(d\pi^+,p\pi^+\|p\pi^+,d\pi^+)$	0.07668×10^{-2}
$(d\pi^+,p\pi^-\|p\pi^-,d\pi^+)$	0.00858×10^{-2}
$(d\delta^\pm,s\|s,d\delta^\pm)$	0.00082×10^{-2}
$(d\delta^\pm,p\sigma\|p\sigma,d\delta^\pm)$	0.04545×10^{-2}
$(d\delta^+,p\pi^+\|p\pi^+,d\delta^+)$	0.00870×10^{-2}
$(d\delta^+,p\pi^-\|p\pi^-,d\delta^+)$	0.00211×10^{-2}
$(\varphi_{e\gamma}|V_L^{\text{ex}}|\varphi_{e\gamma})$	0.02396
$(\varphi_{t\gamma}|V_L^{\text{ex}}|\varphi_{t\gamma})$	0.01082
$(\varphi_{e\gamma}|V_L|\varphi_{e\gamma})$	1.5327
$(\varphi_{t\gamma}|V_L|\varphi_{t\gamma})$	1.5490
Difference	-0.0163

given in Appendix II. Numerical values of the integrals are given in Table II. The orbital energy ϵ_d is -1.4125 in atomic units in Watson's calculation,[7] and we use this value since we are using Watson's Hartree-Fock functions.

$(\chi|h_0|\chi)$

We arrange $(\chi|h_0|\chi)$ as follows:

$$(\chi|h_0|\chi) = (\chi|-\Delta/2+V_L|\chi) + (\chi|V_M|\chi). \quad (5.3)$$

Neglecting the differential overlap between the fluorine orbitals at different sites as mentioned in Appendix IV, Eq. (5.3) can be rewritten as follows,

$$(\chi|h_0|\chi) = \epsilon + (\chi|V_L|\chi)' + (\chi|V_M|\chi), \quad (5.4)$$

where

$$(\chi|V_L|\chi)' = (\chi|V_L|\chi) - (\varphi_i|V_{i,L}|\varphi_i), \quad (5.5)$$

and ϵ is the orbital energy of the fluorine $2s$ or $2p$ electron when χ is composed of the $2s$ or $2p$ orbital: we use the Hartree-Fock energies calculated by Froese[15] which

TABLE III. The $(\chi|V_M|\chi)$ integrals.

$(\chi_{vs}\|V_{\text{core}}\|\chi_{vs})$	-2.6385
$(\chi_{v\sigma}\|V_{\text{core}}\|\chi_{v\sigma})$	-2.7934
$(\chi_{vs}\|V_{\text{core}}\|\chi_{v\sigma})$	-0.4226
$(\chi_{\zeta\pi}\|V_{\text{core}}\|\chi_{\zeta\pi})$	-2.5590
$(d\sigma,s\|\|d\sigma,p\sigma)$	0.04533
$(d\pi^{\pm},s\|\|d\pi^{\pm},p\sigma)$	0.04292_5
$(d\delta^{\pm},s\|\|d\delta^{\pm},p\sigma)$	0.03950
$(\chi_{vs}\|V_d^{\text{Coul}}\|\chi_{vs})$	1.84308
$(\chi_{v\sigma}\|V_d^{\text{Coul}}\|\chi_{v\sigma})$	1.94079
$(\chi_{vs}\|V_d^{\text{Coul}}\|\chi_{v\sigma})$	0.29261
$(\chi_{\zeta\pi}\|V_d^{\text{Coul}}\|\chi_{\zeta\pi})$	1.78790
$(d\pi^{\pm},s\|\|p\sigma,d\pi^{\pm})$	0.00036_8
$(d\delta^{\pm},s\|\|p\sigma,d\delta^{\pm})$	0.00005_2
$(\chi_{vs}\|V_d^{\text{ex}}\|\chi_{vs})$	0.00013_2
$(\chi_{v\sigma}\|V_d^{\text{ex}}\|\chi_{v\sigma})$	0.00189_8
$(\chi_{vs}\|V_d^{\text{ex}}\|\chi_{v\sigma})$	0.00042_0
$(\chi_{\zeta\pi}\|V_d^{\text{ex}}\|\chi_{\zeta\pi})$	0.00009_7
$(\chi_{vs}\|V_M\|\chi_{vs})$	-0.7955
$(\chi_{v\sigma}\|V_M\|\chi_{v\sigma})$	-0.8545
$(\chi_{vs}\|V_M\|\chi_{v\sigma})$	-0.1304
$(\chi_{\zeta\pi}\|V_M\|\chi_{\zeta\pi})$	-0.7712

are $\epsilon_{2s}=-1.0765$ and $\epsilon_{2p}=-0.1815$. φ_i is the fluorine orbital at site i. The $(\chi|V_L|\chi)'$ term represents the effect of five fluorines on a remaining fluorine. The four identical fluorine-fluorine interactions in this term were calculated exactly by using Switendick and Corbato's program on the IBM 7090. The interaction with the more distance fluorine was approximated as a point-charge interaction as shown in Appendix IV. Numerical values of $(\chi|V_L|\chi)'$ are given in Table IV.

Neglecting again the differential overlap between φ_i and $\varphi_j (i \neq j)$, methods of evaluating the $(\chi|V_M|\chi)$ term are given in Appendix III. Numerical values of the integrals appearing in this term are given in Table III. It should be borne in mind that, in contrast to $(\varphi|h|\varphi)$, $(\chi|h|\chi)$ is not the orbital energy of the fluorine electron in the crystal as V_M in h involves

TABLE IV. The $(\chi|V_L|\chi)'$ integrals, where $(\chi|V_L|\chi)' \equiv (\chi|V_L|\chi) - (\varphi_i|V_{i,L}|\varphi_i)$.

$(2\rho)^{-1}$	0.13193
$(\varphi_{3,s}\|V_{1,L}\|\varphi_{3,s})$	0.18603
$(\varphi_{3,z}\|V_{1,L}\|\varphi_{3,z})$	0.18532
$(\varphi_{3,s}\|V_{1,L}\|\varphi_{3,z})$	0.01406
$(\varphi_{3,y}\|V_{1,L}\|\varphi_{3,y})$	0.18333
$(\varphi_{3,y}\|V_{2,L}\|\varphi_{3,y})$	0.18532
$(\chi_{vs}\|V_L\|\chi_{vs})'$	0.87605
$(\chi_{v\sigma}\|V_L\|\chi_{v\sigma})'$	0.87322
$(\chi_{vs}\|V_L\|\chi_{v\sigma})'$	0.05624
$(\chi_{\zeta\pi}\|V_L\|\chi_{\zeta\pi})'$	0.86924

V_d^{Coul} and V_d^{ex} coming from only seven d electrons of Ni^{2+} as mentioned in Sec. III.

$$(\varphi|h_0|\chi)$$

The use of the relation,

$$(\varphi|-\tfrac{1}{2}\Delta+V_M|\chi)=\epsilon_d(\varphi|\chi), \qquad (5.6)$$

leads to the expression,

$$(\varphi|h_0|\chi)=\epsilon_d(\varphi|\chi)+(\varphi|V_L|\chi). \qquad (5.7)$$

As shown in Appendix V, the $(\varphi|V_L|\chi)$ term is divided into two-center and three-center integrals, the latter of which are important and cannot be neglected. The three-center integrals were neglected in Tanabe and Sugano's[4] work. Details of the evaluation of both these two- and three-center integrals are given in Appendix V, and the numerical results are listed in Table V.

TABLE V. The $(\varphi|V_L|\chi)$ integrals. $(\varphi|V_L|\chi)=(\varphi|V_L|\chi)'+(\varphi|V_L|\chi)''$, where $(\varphi|V_L|\chi)'$ is the two-center integral and $(\varphi|V_L|\chi)''$ the three-center integral.

$(\varphi_v\|V_L^{\text{point}}\|\chi_{vs})'$	0.058109
$(\varphi_v\|V_L^{\text{point}}\|\chi_{v\sigma})'$	0.070939
$(\varphi_{\zeta}\|V_L^{\text{point}}\|\chi_{\zeta\pi})'$	0.035267
$(d\sigma,s\|\|s,s)$	0.030302
$(d\sigma,p\sigma\|\|s,p\sigma)$	0.030326
$(d\sigma,p\pi^{\pm}\|\|s,p\pi^{\pm})$	0.027970
$(d\sigma,s\|\|p\sigma,s)$	0.038090
$(d\sigma,p\sigma\|\|p\sigma,p\sigma)$	0.039937
$(d\sigma,p\pi^{\pm}\|\|p\sigma,p\pi^{\pm})$	0.034763
$(d\pi^{\pm},s\|\|p\pi^{\pm},s)$	0.016874
$(d\pi^{\pm},p\sigma\|\|p\pi^{\pm},p\sigma)$	0.016871
$(d\pi^{\pm},p\pi^{\pm}\|\|p\pi^{\pm},p\pi^{\pm})$	0.016155
$(\varphi_v\|V_L^{\text{Coul}}\|\chi_{vs})'$	0.40380
$(\varphi_v\|V_L^{\text{Coul}}\|\chi_{v\sigma})'$	0.51112
$(\varphi_{\zeta}\|V_L^{\text{Coul}}\|\chi_{\zeta\pi})'$	0.26422
$(d\sigma,p\sigma\|\|p\sigma,s)$	0.010867
$(d\sigma,p\pi^{\pm}\|\|p\pi^{\pm},s)$	0.003749
$(d\sigma,s\|\|s,p\sigma)$	0.006166
$(d\sigma,p\pi^{\pm}\|\|p\pi^{\pm},p\sigma)$	0.001062
$(d\pi^{\pm},s\|\|s,p\pi^{\pm})$	0.001910
$(d\pi^{\pm},p\sigma\|\|p\sigma,p\pi^{\pm})$	0.001499
$(d\pi^{\pm},p\pi^{\pm}\|\|p\pi^{\pm},p\pi^{\pm})$	0.016155
$(d\pi^{\pm},p\pi^{\mp}\|\|p\pi^{\mp},p\pi^{\pm})$	0.000783
$(\varphi_v\|V_L^{\text{ex}}\|\chi_{vs})'$	0.08429
$(\varphi_v\|V_L^{\text{ex}}\|\chi_{v\sigma})'$	0.08352
$(\varphi_{\zeta}\|V_L^{\text{ex}}\|\chi_{\zeta\pi})'$	0.04069
$(\varphi_v\|V_L\|\chi_{vs})'$	-0.08725
$(\varphi_v\|V_L\|\chi_{v\sigma})'$	-0.06899
$(\varphi_{\zeta}\|V_L\|\chi_{\zeta\pi})'$	-0.02334
$(\varphi_v\|V_L\|\chi_{vs})''$	0.08626
$(\varphi_v\|V_L\|\chi_{v\sigma})''$	0.12681
$(\varphi_{\zeta}\|V_L\|\chi_{\zeta\pi})''$	0.08578
$(\varphi_v\|V_L\|\chi_{vs})$	-0.00099
$(\varphi_v\|V_L\|\chi_{v\sigma})$	0.05782
$(\varphi_{\zeta}\|V_L\|\chi_{\zeta\pi})$	0.06244

TABLE VI. Numerical values of $(\varphi|h_0|\varphi)$, $(\varphi|h_0|\chi)$ and $(\chi|h_0|\chi)$ in atomic units of 27.2 eV.

Orbital	$(\varphi\|h_0\|\varphi)$	$(\varphi\|h_0\|\chi)$	$(\chi\|h_0\|\chi)$
$e_g\begin{Bmatrix}s\\\sigma\end{Bmatrix}$	0.1202	$\begin{cases}-0.1160\\-0.0986\end{cases}$	$\begin{matrix}-0.9959\\-0.1628\end{matrix}$
$t_{2g}\ \pi$	0.1365	-0.0443	-0.0835

For summary the calculated values of $(\varphi|h_0|\varphi)$, $(\varphi|h_0|\chi)$ and $(\chi|h_0|\chi)$ are listed in Table VI.

VI. COVALENCY

Now it is possible to determine the covalency parameters, γ, by using (2.13), (2.14), and (2.15). The calculated results are given in Table VII together with the experimental values.[8] The agreement with the experimental values is good, particularly for the experimental value of $N^{-\frac{1}{2}}\lambda_s=0.116$ which ignores the $1s-2s$ cross-term.

In Table VII we see that the covalency admixture of the $2s$ orbital, γ_s, is only about one-third as large as the $2s$ overlap, S_s. It is particularly important to note that the reason for the small value of γ_s is the large negative value of $(\chi_s|h_0|\chi_s)$ which mainly arises from the large negative value of the $2s$ atomic orbital energy of F^-. In contrast to this small $2s$ covalency, the covalencies for the $2p\sigma$ and $2p\pi$ orbitals are more than twice the overlap integrals, S_σ and S_π, respectively.

It is interesting to compare γ_σ with γ_π via (2.13) and (2.15). We see that $-(\varphi|h_0|\chi)+S(\chi|h_0|\chi)=0.0986-0.0180=0.0806$ for σ. This is more than twice as large as the numerator for the π orbitals which is 0.0380. However, since $-(\chi|h_0|\chi)$ in the denominator of the expression for γ is larger for σ than for π by ~0.08, the final value of γ_σ is only ~1.6 times γ_π. Therefore, we may argue that the origin of the relatively large π covalency is partly the lowering of $2p\sigma$ orbital energy relative to the $2p\pi$ energy in the molecule by the attractive potential of the central metal ion. In the semiclassical model this is the crystal field splitting of the F^- ion and it has been mentioned in a previous report.[17] The large value of $\gamma_\pi=0.246$ confirms the previous conclusions from experiments[18,19] that the π bonding is large.

TABLE VII. Calculated values of γ and λ and comparison with the experimental values.

Orbital	γ	λ	$N^{-\frac{1}{2}}\lambda$ Calc	$N^{-\frac{1}{2}}\lambda$ Exp[a]
s	0.031	0.113	0.109	0.116
σ	0.285	0.396	0.383	0.337
π	0.173	0.249	0.246	...

$\mu_\sigma(\text{calc})=0.9616$ $\mu_s(\text{calc})=0.2744$

[a] See Eq. (4.3) of Part I.

[17] R. G. Shulman and S. Sugano, J. Chem. Phys. **36**, 3496 (1962).
[18] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535, 549 (1956).
[19] R. G. Shulman and K. Knox, Phys. Rev. Letters **4**, 603 (1960).

We wish to emphasize that although the π admixture into the molecular orbital is almost as large as the σ admixture still the bonding *energy* is given by $-\gamma(\varphi|h_0|\chi)$ which is 6960 cm^{-1} for σ and 1670 cm^{-1} for π. Therefore, we may say that the π bonding is important wherever the *wave functions* themselves are important but it is not as important as the σ bond when the *energy* is involved.

VII. CUBIC FIELD-SPLITTING PARAMETER

Let us discuss the separate contributions to Δ shown in (2.11). In Table VIII the contributions to Δ from the nickel diagonal terms on the first line of (2.11) are listed. We see that the point-charge approximation gives a very small contribution, 1390 cm^{-1}, while Kleiner's correction makes Δ negative. Furthermore,

TABLE VIII. The various contributions to Δ.

Origin	Term	Contribution to Δ in cm^{-1}
Nickel diagonal	point-charge (V_L^{point})	$+1390$
	Kleiner's correction (V_L^K)	-2080
	Exchange (V_L^E)	-2880 $\quad\Big\}-2670$
	renormalization	$+900$
	$(\lambda_e S_e-\lambda_t S_t)(\varphi_e\|h_0\|\varphi_e)$	
Non-orthogonality	$-S_s\mu_s(\varphi_e\|h_0\|\chi_s)$	$+2060$
	$-S_\sigma\mu_\sigma(\varphi_e\|h_0\|\chi_\sigma)$	$+2390$ $\quad\Big\}+3730$
	$+S_\pi(\varphi_t\|h_0\|\chi_\pi)$	-720
Covalency	$-\gamma_s\mu_s(\varphi_e\|h_0\|\chi_s)$	$+790$
	$-\gamma_\sigma\mu_\sigma(\varphi_e\|h_0\|\chi_\sigma)$	$+6170$ $\quad\Big\}+5290$
	$+\gamma_\pi(\varphi_t\|h_0\|\chi_\pi)$	-1670
	Total calculated	6350
	experimental	7250

although the individual exchange terms are small as shown in Table II, they make a larger negative contribution to Δ than the total Coulomb contribution. Thus, the semiclassical model $(S=0, \gamma=0)$ which includes only the contribution from the nickel diagonal term predicts a negative value of Δ and disagrees with experiment. To a first approximation this conclusion is independent of the specific $3d$ wave function adopted because if a more expanded wave function were used, the point-charge contribution would increase but so would the negative contributions from Kleiner's correction and the exchange interaction.

After the contributions from the nickel diagonal term we have listed the contributions of the nonorthogonality to Δ. In this approximation, which could be called the quantum mechanical purely ionic model, the assumption is that $\gamma=0$ but $S\neq0$. The metal ion orbitals are orthogonalized to the ligand orbitals in this approach which was followed by Tanabe and Sugano.[4] In this approximation, where $\lambda=S$ the renormalization term is reduced to about 300 cm^{-1}. The contributions of the nonorthogonality term is $+3730$ cm^{-1} while the contributions of V_L^K and V_L^E total -4960 cm^{-1}. These two

terms cancel to within 1200 cm⁻¹ which is a small number when compared with Δ. Within this accuracy therefore we have confirmed Phillips's[5] claim that the contribution from the nonorthogonality approximately cancels those from $V_L{}^K$ and $V_L{}^E$. Within this purely ionic model the calculated value of Δ is ~ 500 cm⁻¹ which does not agree with the observed value of 7250 cm⁻¹. Furthermore, while an expansion (Marshall and Stuart[14]) of the metal wave function would increase S and the positive contribution of the nonorthogonality term it would at about the same rate increase the negative contributions of the nickel diagonal term. Therefore, by merely expanding the metal ion function one could not hope to explain the observed Δ under the assumption of $\lambda = S$. However, good agreement with the observed value is obtained when the calculated values of the covalency parameters are included in the calculation as shown by the last terms in Table VIII. Furthermore, it is noteworthy that with the exception of the small point-charge contribution the off-diagonal terms are the only contributions to Δ with the correct sign.

VIII. OTHER PARAMETERS IN THE CRYSTALLINE FIELD THEORY

In the previous discussion we have not explicitly touched upon the normalization factors, $N_e^{-1/2}$ and $N_t^{-1/2}$. These factors are more than unity when $\gamma = 0$ but less than unity when $\gamma > S$. They are just unity when $\gamma = S$. Assuming that γ and S are small, we have

$$N_e^{-1/2} = 1 - \tfrac{1}{2}(\gamma_s{}^2 + \gamma_\sigma{}^2 - S_s{}^2 - S_\sigma{}^2),$$
$$N_t^{-1/2} = 1 - \tfrac{1}{2}(\gamma_\pi{}^2 - S_\pi{}^2). \tag{8.1}$$

Inserting the calculated values of γ and S

$$N_e^{-1/2} = 0.968,$$
$$N_t^{-1/2} = 0.988. \tag{8.2}$$

These reduced normalization factors are important in explaining the small reduction of the Racah parameter, B, which is reduced by $\sim 7\%$ from the free-ion value as determined in part II. The exact calculation of B is tedious, but a crude estimate was made by substituting our calculated molecular orbitals into the Coulomb and exchange integrals which determine the term splitting and Racah parameters. It was seen that neglecting the normalization our calculated molecular orbitals gave a negligible reduction of B. On the other hand, the normalization factors are important. Since B is proportional to N^{-2} (or the fourth power of the normalization constant) the calculated reduction of the normalization factors as shown in (8.2) is large enough to account for the observed $\sim 7\%$ reduction in B. Since all the reduction of B could be ascribed to the normalization factors, the use of Koide and Pryce's[20] covalency parameter ϵ is justified and it is given as

$$(1-\epsilon)^{1/2} = (N_e/N_t)^{-1/2}, \tag{8.2}$$

²⁰ S. Koide and M. H. L. Pryce, Phil. Mag. 3, 607 (1958).

which leads to

$$\epsilon = (\gamma_\sigma{}^2 + \gamma_s{}^2 - \gamma_\pi{}^2) - (S_\sigma{}^2 + S_s{}^2 - S_\pi{}^2). \tag{8.4}$$

In our problem, substituting numerical values, we obtain

$$\epsilon = 0.039. \tag{8.5}$$

It is interesting to compare (8.5) with Zahner and Drickamer's[21] conclusion for $MnCl_2$ and $MnBr_2$ that ϵ can be no larger than 0.04 in these crystals. Pappalardo[22] also has found values of ϵ in the range 0.03–0.05 for Mn^{2+} in crystals. It also is interesting to note that the B value has been found to decrease with increasing isotropic pressure[21,23,24] and that this fact can easily be explained, as seen in Eq. (8.1), by assuming the covalency γ increases more than the overlap S.

In order to explain the first observations[25] of ligand hfs in iridium hexachloride complexes the molecular orbital model was proposed by Stevens.[26] Among his many important contributions to this problem he considered how covalency would reduce the orbital angular momentum. It has been shown by Geschwind[27] for our case of Ni^{+2} in O_h symmetry that the electronic g factor should be

$$g = 2.0023 - (8\lambda_{crys}k_{\sigma\pi}{}^2/10Dq) \tag{8.6}$$

in which λ_{crys} is the coupling constant of the spin-orbit operator $\lambda_{crys}\mathbf{L}\cdot\mathbf{S}$ in the crystal and $k_{\sigma\pi}$ is the orbital reduction factor

$$k_{\sigma\pi} = (\Psi_e|\mathbf{L}|\Psi_t)/(\varphi_e|\mathbf{L}|\varphi_t), \tag{8.7}$$

which can be expressed as

$$k_{\sigma\pi} = N_t^{-1/2}N_e^{-1/2}(1 - \lambda_e S_e - \lambda_t S_t)$$
$$= 1 - (\lambda_e{}^2 + \lambda_t{}^2)/2. \tag{8.8}$$

In deriving (8.8) we have assumed, after Tinkham,[18] cancellation of the last two terms in his exact expression. Substituting numerical values we find

$$k_{\sigma\pi} \approx 0.88. \tag{8.9}$$

Substituting in (8.6) and solving for λ_{crys}, we obtain

$$\lambda_{crys} = -320 \text{ cm}^{-1} \tag{8.10}$$

which agrees very well with the value of $\lambda = -324$ cm⁻¹ observed in the free-Ni^{2+} ion. In other words, this calculation shows that to within experimental accuracy

²¹ J. C. Zahner and H. G. Drickamer, J. Chem. Phys. 35, 1485 (1961).
²² R. Pappalardo, J. Chem. Phys. 31, 1050 (1959); 33, 613 (1960).
²³ D. R. Stephens and H. G. Drickamer, J. Chem. Phys. 34, 937 (1961).
²⁴ A. L. Schawlow, A. H. Piksis, and S. Sugano, Phys. Rev. 122, 1469 (1961).
²⁵ J. H. E. Griffith, J. Owen, and I. M. Ward, Proc. Roy. Soc. (London) A219, 526 (1953).
²⁶ K. W. H. Stevens, Proc. Roy. Soc. (London) A219, 542 (1953).
²⁷ S. Geschwind (private communication).

$\lambda_{\text{crys}} = \lambda_{\text{free ion}}$. The observed reduction in $\lambda_{\text{crys}} k_{\sigma\pi}{}^2$ from the free-ion value is completely explained by the effects of covalency upon the orbital reduction parameter $k_{\sigma\pi}$. We also note here that

$$k_{\pi\pi} = (\Psi_t | \mathbf{L} | \Psi_t)/(\varphi_t | \mathbf{L} | \varphi_t) \qquad (8.11)$$

is given as[26]

$$k_{\pi\pi} = 1 - \lambda_t{}^2/2$$
$$= 0.97. \qquad (8.12)$$

IX. CONCLUDING DISCUSSION

As previously mentioned we have succeeded in calculating $10Dq$ and the covalency in $KNiF_3$. Before discussing these results further we first summarize the approximations adopted in the present calculation. They are as follows:

(1) We have assumed V_{crys} to be a constant, in other words, we have treated a specific molecule $[NiF_6]^{4-}$ placed in a potential well, instead of treating the crystal as a whole. This approximation should be valid in the determination of Δ for the experimental and theoretical reasons mentioned at the beginning of Sec. III. However, in calculating the covalency the approximation might be a little worse, since the expression for the covalency involves the value of $(\chi | h | \chi)$ which is sensitive to the possible deviation from the potential well model. However, the final agreement with the measured covalency supports the applicability of this approximation.

(2) The most characteristic approximation in our calculation is to neglect h' in the Hamiltonian. This is equivalent to doing the first step of the SCF calculation where in the Hamiltonian $\gamma = 0$ and $S = 0$. This approximation cannot easily be justified for the calculation of Δ even in ionic crystals where γ and S are very small, since Δ is essentially a small quantity of the order ϵ^2 as mentioned previously. It would be an important future problem to examine why our approximation has given such good agreement with experiment.

(3) We have neglected some three-center integrals which seem to be unimportant. As long as h' is ignored, the only many-center integrals are the three-center integrals appearing in $(\varphi | h_0 | \chi)$ and $(\chi | h_0 | \chi)$. The three-center integrals in $(\varphi | h_0 | \chi)$ are important and have been calculated more or less accurately. The three-center integrals in $(\chi | h_0 | \chi)$ should be small. In particular, the value of Δ does not involve $(\chi | h_0 | \chi)$ so that the calculation of Δ is independent of this approximation.

(4) We have assumed that γ and S are small and have neglected higher-order small quanties. This approximation is justified in so-called ionic crystals such as $KNiF_3$.

With these possible sources of error in the calculation, it is immediately clear that further calculations intending to improve the agreement with experiment are not warranted at this time. These extended calculations might follow the SCF approach, or vary the metal ion radial functions, or the ligand radial functions (or mix

in metal ion or ligand excited states, which are equivalent to radial expansion). Closer agreement with experimental values would not justify the physical existence of these terms so long as the errors implicit in the calculation are as large as they appear to be. Furthermore, we have shown[8] that expanding the metal ion radial functions (Marshall and Stuart[14]) cannot explain the observed F^{19} hfs. Here we see that this assumption is unnecessary to explain the Racah parameters while an expanded radial function in the crystal is inconsistent with our finding from the spin-orbit interaction that $\langle 1/r^3 \rangle_{\text{crys}} = \langle 1/r^3 \rangle_{\text{free-ion}}$. In summary, we have shown that in $KNiF_3$ the concept of expanded d-electron radial functions is unnecessary to explain some of our observations and inadequate to explain the remainder.

The extensive numerical agreement of the molecular orbital calculations with the experimental measurements leads to the conclusion that molecular orbitals provide an accurate physical model of the crystal. We feel that the main value of our calculation lies in the physical understanding we now have of the crystal, not in any particular agreement between a calculated number and a measurement.

In order to discuss the important physical phenomena in this crystal let us turn to the energy level diagram shown in Fig. 5. The left-hand column shows the effects of the crystal field upon the d-electron orbital energies. In this approximation, we display $\epsilon + (\varphi_\gamma | V_L | \varphi_\gamma)$ where ϵ is the orbital energy of the d orbitals. Notice that in this approximation the t_{2g} levels are higher in energy than the e_g. The reasons for this have been discussed above in Sec. VII. In the next column the contributions
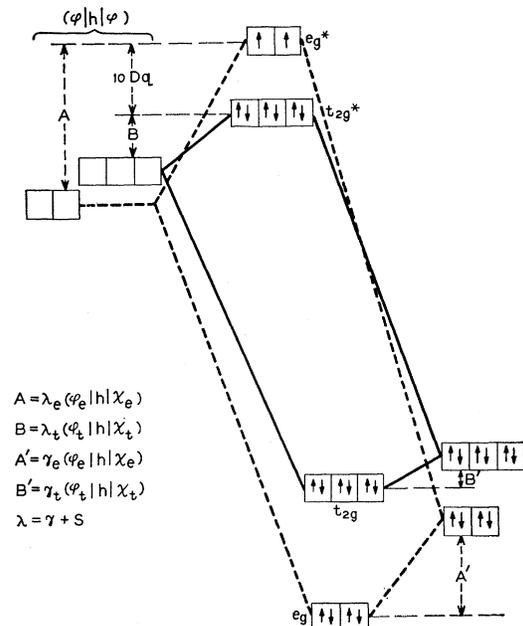

$A = \lambda_e (\varphi_e | h | \chi_e)$
$B = \lambda_t (\varphi_t | h | \chi_t)$
$A' = \gamma_e (\varphi_e | h | \chi_e)$
$B' = \gamma_t (\varphi_t | h | \chi_t)$
$\lambda = \gamma + S$

FIG. 5. Energy-level diagram for the molecular orbitals formed between Ni^{2+} d electrons and the F^- ligands.

of the covalency, in our perturbation treatment, are presented. Energies for the antibonding orbitals are increased above the $(\varphi_\gamma | h_0 | \varphi_\gamma)$ levels by $-\lambda_\gamma(\varphi_\gamma | h_0 | \chi_\gamma)$ in accordance with Eq. (2.4). Here the strength of the σ bond dominates and the antibonding e_g^* orbitals are raised above the t_{2g}^*. The energy difference is $10Dq$ as indicated in the figure. The lowering of the bonding orbitals from the F$^-$ orbital energies is shown to scale. Substituting the approximate relation

$$\lambda \approx \frac{-(\varphi | h_0 | \chi)}{(\varphi | h_0 | \varphi) - (\chi | h_0 | \chi)}, \qquad (9.1)$$

the increase of the antibonding orbital energy is approximately

$$\frac{(\varphi | h_0 | \chi)^2}{(\varphi | h_0 | \varphi) - (\chi | h_0 | \chi)}. \qquad (9.2)$$

At this point, we can stop and relate Eq. (9.2) to chemical bonding in general. Pauling's[28] two considerations for the strength of a chemical bond were first the overlap of the wave functions corresponding to the numerator of (9.2) and second, the energy difference between the atomic orbitals corresponding to the denominator. From (9.1) we can see a possible explanation of one surprising aspect of covalency as measured by ligand hfs. The fluorines[19] in K$_2$NaCrF$_6$ have approximately the same value of λ_π as the chlorines[25] in (IrCl$_6$)$^{-2}$. All chemical arguments say that the "covalency" should be larger in the Ir^{+4} complex than in the Cr^{+3}; i.e., the larger charge on the metal ion, $5d$ electrons instead of $3d$ and chlorine instead of fluorine. But by covalency in this general chemical usage one means the energy associated with the covalency. From (2.4)–(2.7) it is clear that when the values of λ are the same for two complexes the bond energies might still be different. In fact, we are led to the conclusion that both the numerator and the denominator of (9.1) are larger for (IrCl$_6$)$^{-2}$ than for (CrF$_6$)$^{-3}$. Since it is considerably easier to calculate the diagonal terms in the denominator than the off-diagonal terms in the numerator it should not be very difficult to estimate the validity of these conclusions.

Another interesting anomaly in covalency and crystal field splitting, i.e., the large value of $10Dq$ in the cyanides, is now understandable. Previously in discussing $10Dq$ in terms of a point-charge model it had been necessary to introduce the effects of covalency in an *ad hoc* fashion to explain the large values of $10Dq$ in the essentially non-ionic cyanides. However, now we see that even in the extremely ionic fluorides $10Dq$ arises from the covalency terms. However whether the large value of $10Dq$ in the cyanides arises from a small amount of π bonding or a relatively large amount of σ bonding is still unanswered.

[28] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, N. Y., 1939).

In conclusion, we have shown that the LCAO-MO introduced by Van Vleck[29] and extended by Stevens,[26] and Tinkham[18] can explain the NMR, optical, and ESR experiments in KNiF$_3$.

ACKNOWLEDGMENTS

APPENDIX

I. Overlap Integrals

The overlap integrals between φ's and χ's are given in terms of those between atomic orbitals as follows:

$$\begin{aligned}(\varphi_{e\gamma} | \chi_{\gamma s \text{ or } \sigma}) &= \sqrt{3}(\varphi_u | \varphi_{3s \text{ or } z}) \\ &= \sqrt{3}(d\sigma | s \text{ or } p\sigma), \qquad (A1)\end{aligned}$$

$$\begin{aligned}(\varphi_{t\gamma} | \chi_{\gamma\pi}) &= 2(\varphi_\xi | \varphi_{3,y}) \\ &= 2(d\pi^+ | p\pi^+). \qquad (A2)\end{aligned}$$

II. $(\varphi | V_L | \varphi)$ Integrals

In the following calculations, we use the relations:

$$(\varphi_{e\gamma} | V_L | \varphi_{e\gamma}) = 3 \sum_{\gamma=u,v} (\varphi_\gamma | V_{3,L} | \varphi_\gamma), \qquad (A3)$$

$$(\varphi_{t\gamma} | V_L | \varphi_{t\gamma}) = 2 \sum_{\gamma=\xi,\eta,\zeta} (\varphi_\gamma | V_{3,L} | \varphi_\gamma). \qquad (A4)$$

(a) $\quad (\varphi | V_L{}^{\text{point}} | \varphi), \quad V_L{}^{\text{point}} = \sum_{i=1}^{6} 1/|\mathbf{r} - \mathbf{R}_i|.$

In our problem it is convenient to calculate the spherically symmetric and cubic parts of these integrals separately without using Switendick and Corbato's machine program; the main contributions to these integrals come from the spherically symmetric parts which are canceled by each other in the expression for the crystalline field splitting. The analytical expressions for $(\varphi | V_L{}^{\text{point}} | \varphi)$ are well known as follows:

$$(\varphi_{e\gamma} | V_L{}^{\text{point}} | \varphi_{e\gamma}) = 6I_0 + I, \qquad (A5)$$

$$(\varphi_{t\gamma} | V_L{}^{\text{point}} | \varphi_{t\gamma}) = 6I_0 - \tfrac{2}{3}I, \qquad (A6)$$

[29] J. H. Van Vleck, J. Chem. Phys. 3, 807 (1935).

where

$$I_0 = \int_0^\rho dr\, P_{3d}^2(r)/\rho + \int_\rho^\infty dr\, P_{3d}^2(r)/r, \quad \text{(A7)}$$

$$I = \int_0^\rho dr\, r^4 P_{3d}^2(r)/\rho^5 + \rho^4 \int_\rho^\infty dr\, P_{3d}^2(r)/r^5, \quad \text{(A8)}$$

where $P_{3d}(r) = rR_{3d}(r)$.

(b) $(\varphi | V_L^{\text{Coul}} | \varphi)$,

$$V_L^{\text{Coul}} = 2 \sum_{i=1}^6 \int d\tau_2\, r_{12}^{-1} \sum_{k=2s,2px,y,z} | \varphi_{i,k}^{(2)} |^2.$$

By using (A3) and (A4), it is easy to see that

$$(\varphi_{e\gamma} | V_L^{\text{Coul}} | \varphi_{e\gamma}) = 6 \sum_{\gamma=u,v} \sum_{k=2s,2px,y,z} (\varphi_\gamma \varphi_k \| \varphi_\gamma \varphi_k), \quad \text{(A9)}$$

with

$$(u,s\|u,s) = (d\sigma,s\|d\sigma,s),$$
$$(u,z\|u,z) = (d\sigma,p\sigma\|d\sigma,p\sigma),$$
$$(u,x\|u,x) = (u,y\|u,y),$$
$$= (d\sigma,p\pi^\pm\|d\sigma,p\pi^\pm), \quad \text{(A10)}$$
$$(v,s\|v,s) = (d\delta^\pm,s\|d\delta^\pm,s),$$
$$(v,z\|v,z) = (d\delta^\pm,p\sigma\|d\delta^\pm,p\sigma),$$
$$(v,x\|v,x) = (v,y\|v,y),$$
$$= (d\delta^\pm,p\pi^+\|d\delta^\pm,p\pi^+), \quad \text{(A11)}$$

and

$$(\varphi_{t\gamma} | V_L^{\text{Coul}} | \varphi_{t\gamma})$$
$$= 4 \sum_{\gamma=\xi,\eta,\zeta} \sum_{k=2s,2px,y,z} (\varphi_\gamma \varphi_k \| \varphi_\gamma \varphi_k), \quad \text{(A12)}$$

with

$$(\zeta,k\|\zeta,k) = (v,k\|v,k),$$
$$(\xi,k'\|\xi,k') = (\eta,k'\|\eta,k'), \quad (k' \neq x, y)$$
$$(\xi,x\|\xi,x) = (\eta,y\|\eta,y),$$
$$(\xi,y\|\xi,y) = (\eta,x\|\eta,x), \quad \text{(A13)}$$
$$(\xi,s\|\xi,s) = (d\pi^\pm,s\|d\pi^\pm,s),$$
$$(\xi,z\|\xi,z) = (d\pi^\pm,p\sigma\|d\pi^\pm,p\sigma),$$
$$(\xi,x\|\xi,x) = (d\pi^\pm,p\pi^+\|d\pi^\pm,p\pi^+)$$
$$\qquad - \tfrac{1}{2}(d\pi^+,p\pi^-\|d\pi^-,p\pi^+),$$
$$(\xi,y\|\xi,y) = (d\pi^\pm,p\pi^+\|d\pi^\pm,p\pi^+)$$
$$\qquad + \tfrac{1}{2}(d\pi^+,p\pi^-\|d\pi^-,p\pi^+). \quad \text{(A14)}$$

Notice the following abbreviations:

$$(\varphi_a\varphi_b\|\varphi_c\varphi_d)$$
$$\equiv (a,b\|c,d)$$
$$\equiv \int\int d\tau_1 d\tau_2\, r_{12}^{-1} \varphi_a(1)^* \varphi_b(2)^* \varphi_c(1) \varphi_d(2), \quad \text{(A15)}$$

$$\varphi_k \equiv \varphi_{3,k} \quad \text{for} \quad k = s, x, y, z,$$

which are used throughout this paper.

(c) $(\varphi | V_L^{\text{ex}} | \varphi)$, $V_L^{\text{ex}} = -V_L^E$:

$$(\varphi_{e\gamma} | V_L^{\text{ex}} | \varphi_{e\gamma}) = 3 \sum_{\gamma=u,v} \sum_{k=2s,2px,y,z} (\varphi_\gamma \varphi_k \| \varphi_k \varphi_\gamma), \quad \text{(A16)}$$

with

$$(u,s\|s,u) = (d\sigma,s\|s,d\sigma),$$
$$(u,z\|z,u) = (d\sigma,p\sigma\|p\sigma,d\sigma),$$
$$(u,x\|x,u) = (u,y\|y,u)$$
$$= (d\sigma,p\pi^\pm\|p\pi^\pm,d\sigma), \quad \text{(A17)}$$
$$(v,s\|s,v) = (d\delta^\pm,s\|s,d\delta^\pm),$$
$$(v,z\|z,v) = (d\delta^\pm,p\sigma\|p\sigma,d\delta^\pm),$$
$$(v,x\|x,v) = (v,y\|y,v)$$
$$= \tfrac{1}{2}[(d\delta^+,p\pi^+\|p\pi^+,d\delta^+)$$
$$\qquad + (d\delta^+,p\pi^-\|p\pi^-,d\delta^+)], \quad \text{(A18)}$$

and

$$(\varphi_{t\gamma} | V_L^{\text{ex}} | \varphi_{t\gamma}) = 2 \sum_{\gamma=\xi,\eta,\zeta} \sum_{k=2s,2px,y,z} (\varphi_\gamma \varphi_k \| \varphi_k \varphi_\gamma), \quad \text{(A19)}$$

with

$$(\zeta,k\|k,\zeta) = (v,k\|k,v),$$
$$(\xi,k'\|k',\xi) = (\eta,k'\|k',\eta), \quad \text{for} \quad k' \neq x, y,$$
$$(\xi,x\|x,\xi) = (\eta,y\|y,\eta),$$
$$(\xi,y\|y,\xi) = (\eta,x\|x,\eta), \quad \text{(A20)}$$
$$(\xi,s\|s,\xi) = (d\pi^\pm,s\|s,d\pi^\pm),$$
$$(\xi,z\|z,\xi) = (d\pi^\pm,p\sigma\|p\sigma,d\pi^\pm),$$
$$(\xi,x\|x,\xi) = \tfrac{1}{2}(d\pi^+,p\pi^-\|p\pi^-,d\pi^+),$$
$$(\xi,y\|y,\xi) = (d\pi^+,p\pi^+\|p\pi^+,d\pi^+)$$
$$\qquad + \tfrac{1}{2}(d\pi^+,p\pi^-\|p\pi^-,d\pi^+). \quad \text{(A21)}$$

III. $(\chi | V_M | \chi)$ Integrals

As mentioned in the text,

$$V_M = V_{\text{core}} + V_d^{\text{Coul}} + V_d^{\text{ex}}, \quad \text{(A22)}$$

where

$$V_{\text{core}} = (a + be^{-\alpha r})/r, \quad \text{(A23)}$$

and, in general,

$$V_d^{\text{coul}} \equiv \sum_\gamma V_\gamma^{\text{coul}} = \sum_\gamma \int d\tau_2\, r_{12}^{-1} | \varphi_\gamma(2) |^2, \quad \text{(A24)}$$

$$V_d^{\text{ex}} \equiv \sum_\gamma V_\gamma^{\text{ex}} = \sum_\gamma{}' \int d\tau_2\, r_{12}^{-1} \varphi_\gamma(2)^* \varphi_\gamma(1) P_{12}. \quad \text{(A25)}$$

In (A24) the summation runs over all valence electrons γ and in (A25) the summation extends over all the valence electrons with spins parallel to the spin of the χ electron. In our specific treatment of KNiF$_3$, $\sum_\gamma$ means $\sum_{\gamma=\xi,\xi,\eta,\eta,\zeta,u,v}$ and $\sum_\gamma{}'$ means $\sum_{\gamma=\xi,\eta}$. Here, we will treat V_γ^{Coul} and V_γ^{ex} with any γ as a general rule. It should be noticed that three-center integrals are

completely neglected in the following expressions of $(\chi|V_M|\chi)$.

(a) $(\chi|V_{core}|\chi)$.

Since V_{core} is spherically symmetric, we have

$$(\chi_{\gamma k}|V_{core}|\chi_{\gamma k'})=(\varphi_{3,k}|V_{core}|\varphi_{3,k'}), \quad (A26)$$

$$(\chi_{\gamma \pi}|V_{core}|\chi_{\gamma \pi})=(\varphi_{3,px}|V_{core}|\varphi_{3,px}), \quad (A27)$$

which can be calculated analytically. In (A26), k and k' are s or pz.

(b) $(\chi|V_\gamma^{Coul}|\chi)$.

We need this type of integral with $\chi=\chi_{vs \text{ or } z}$ and $\chi=\chi_{\zeta\pi}$. By using symmetry considerations, we obtain

$$(\chi_{vk}|V_\xi^{Coul}|\chi_{vk'})=(\chi_{vk}|V_\eta^{Coul}|\chi_{vk'})$$
$$=\tfrac{1}{2}[(\xi,k\|\xi,k')+(\zeta,k\|\zeta,k')], \quad (A28)$$

$$(\chi_{vk}|V_\zeta^{Coul}|\chi_{vk'})=(\xi,k\|\xi,k'), \quad (A29)$$

$$(\chi_{vk}|V_u^{Coul}|\chi_{vk'})=\tfrac{1}{4}[(u,k\|u,k')+3(v,k\|v,k')], \quad (A30)$$

$$(\chi_{vk}|V_v^{Coul}|\chi_{vk'})=\tfrac{1}{4}[3(u,k\|u,k')+(v,k\|v,k')], \quad (A31)$$

where $k,k'=s$ or z, and

$$(\chi_{\zeta\pi}|V_\xi^{Coul}|\chi_{\zeta\pi})=(\chi_{\zeta\pi}|V_\eta^{Coul}|\chi_{\zeta\pi})$$
$$=\tfrac{1}{2}[(\xi,x\|\xi,x)+(\zeta,x\|\zeta,x)], \quad (A32)$$

$$(\chi_{\zeta\pi}|V_\zeta^{Coul}|\chi_{\zeta\pi})=(\xi,y\|\xi,y), \quad (A33)$$

$$(\chi_{\zeta\pi}|V_u^{Coul}|\chi_{\zeta\pi})=\tfrac{1}{4}[(u,y\|u,y)+3(v,y\|v,y)$$
$$-2\sqrt{3}(u,y\|v,y)], \quad (A34)$$

$$(\chi_{\zeta\pi}|V_v^{Coul}|\chi_{\zeta\pi})=\tfrac{1}{4}[3(u,y\|u,y)+(v,y\|v,y)$$
$$+2\sqrt{3}(u,y\|v,y)]. \quad (A35)$$

Almost all integrals in (A28)–(A35) have already been given in (A10), (A11), (A13), and (A14). Cross integrals $(\gamma,s\|\gamma,z)$ are simply obtained by substituting for z or $p\sigma$ the suitable s's in $(\gamma,s\|\gamma,s)=(dm,s\|dm,s)$. The only new type of integral appearing in (A34) and (A35) is given as follows:

$$(u,y\|v,y)=-(u,x\|v,x)$$
$$=(1/\sqrt{2})(d\sigma,p\pi^+\|d\delta^+,p\pi^-). \quad (A36)$$

(c) $(\chi|V_\gamma^{ex}|\chi)$.

Also in this case, the χ's are restricted to those with components v and ζ. Then, integrals for any γ are expressed as follows:

$$(\chi_{vk}|V_\xi^{ex}|\chi_{vk'})=(\chi_{vk}|V_\eta^{ex}|\chi_{vk'})$$
$$=\tfrac{1}{2}[(\xi,k\|k',\xi)+(\zeta,k\|k',\zeta)], \quad (A37)$$

$$(\chi_{vk}|V_\zeta^{ex}|\chi_{vk})=(\xi,k\|k',\xi), \quad (A38)$$

$$(\chi_{vk}|V_u^{ex}|\chi_{vk})=\tfrac{1}{4}[(u,k\|k',u)+3(v,k\|k',v)], \quad (A39)$$

$$(\chi_{vk}|V_v^{ex}|\chi_{vk})=\tfrac{1}{4}[3(u,k\|k',u)+(v,k\|k',v)], \quad (A40)$$

where $k,k'=s$ or z, and

$$(\chi_{\zeta\pi}|V_\xi^{ex}|\chi_{\zeta\pi})=(\chi_{\zeta\pi}|V_\eta^{ex}|\chi_{\zeta\pi})$$
$$=\tfrac{1}{2}[(\xi,x\|x,\xi)+(\zeta,x\|x,\zeta)], \quad (A41)$$

$$(\chi_{\zeta\pi}|V_\zeta^{ex}|\chi_{\zeta\pi})=(\xi,y\|y,\xi), \quad (A42)$$

$$(\chi_{\zeta\pi}|V_u^{ex}|\chi_{\zeta\pi})=\tfrac{1}{4}[(u,y\|y,u)+3(v,y\|y,v)$$
$$-2\sqrt{3}(u,y\|y,v)], \quad (A43)$$

$$(\chi_{\zeta\pi}|V_v^{ex}|\chi_{\zeta\pi})=\tfrac{1}{4}[3(u,y\|y,u)+(v,y\|y,v)$$
$$+2\sqrt{3}(u,y\|y,v)]. \quad (A44)$$

Almost all the integrals in (A37)–(A44) have already appeared in (A17), (A18), (A20), and (A21). The cross integrals $(\gamma,s\|z,\gamma)$ are simply given by substituting z or $p\sigma$ for the suitable s's in $(\gamma,s\|s,\gamma)=(dm,s\|s,dm)$. The only new type of integral appearing in (A43) and (A44) is expressed as follows:

$$(u,y\|y,v)=-(u,x\|x,v)$$
$$=(1/\sqrt{2})(d\sigma,p\pi^+\|p\pi^-,d\delta^+). \quad (A45)$$

IV. $(\chi|V_L|\chi)$ Integrals

To the approximation in which we neglect the differential overlap between the fluorine orbitals at different sites, the $(\chi|V_L|\chi)$ integrals are expressed, in general, as follows;

$$(\chi|V_L|\chi)=(\varphi_i|V_{i,L}|\varphi_i)+(\varphi_i|\sum_{j\neq i}' V_{j,L}|\varphi_i), \quad (A46)$$

where φ_i is a fluorine orbital at the ith site. The first term in (A46) is combined with the kinetic-energy matrix element, $(\varphi_i|-\tfrac{1}{2}\Delta|\varphi_i)$, to give the orbital energy of the fluorine electron, and the second term is given for χ with the component, vs or vz, as

$$(\varphi_{3,k}|V_{6,L}|\varphi_{3,k'})+4(\varphi_{3,k}|V_{1,L}|\varphi_{3,k'})$$
$$\text{with} \quad k,k'=s \text{ or } z, \quad (A47)$$

and for $\chi_{\zeta\pi}$ as

$$(\varphi_{3,y}|V_{6,L}|\varphi_{3,y})+2[(\varphi_{3,y}|V_{1,L}|\varphi_{3,y})$$
$$+(\varphi_{3,y}|V_{2,L}|\varphi_{3,y})]. \quad (A48)$$

The first terms in (A47) and (A48) may be well approximated by $(2\rho)^{-1}$ except for the $s-z$ cross term which is assumed to be zero in our calculation. The remaining integrals are the Coulomb, exchange, and nuclear attraction integrals appearing in a homonuclear diatomic molecule with nuclear distance $\sqrt{2}\rho$. One must be careful of the components z and y which do not refer to the molecular axis.

V. $(\varphi|V_L|\chi)$ Integrals

For this calculation, it is convenient to use the relations

$$(\varphi_{e\gamma}|V_L|\chi_{e\gamma})=3\sum_{\gamma=u,v}(\varphi_\gamma|V_{3,L}|\chi_\gamma), \quad (A49)$$

$$(\varphi_{t\gamma}|V_L|\chi_{t\gamma})=2\sum_{\gamma=\xi,\eta,\zeta}(\varphi_\gamma|V_{3,L}|\chi_\gamma), \quad (A50)$$

which are similar to (A3) and (A4). These relations lead to the following equations for $\gamma = v$ and ζ,

$$(\varphi_v | V_L | \chi_{vk}) = \sqrt{3}[(\varphi_u | V_{3,L} | \varphi_{3,k})$$
$$+ (\varphi_u | \sum_{i \neq 3}' V_{i,L} | \varphi_{3,k})] \quad (k = s \text{ or } z), \quad (A51)$$

$$(\varphi_\zeta | V_L | \chi_{\zeta\pi}) = 2[(\varphi_\xi | V_{3,L} | \varphi_{3,y})$$
$$+ (\varphi_\xi | \sum_{i \neq 3}' V_{i,L} | \varphi_{3,y})], \quad (A52)$$

where the first and second terms are two- and three-center integrals, respectively.

(a) The two-center integrals.

The contribution from $V_{3,L}^{\text{point}}$ has the form of a split nuclear attraction integral. The explicit forms are as follows:

$$(\varphi_u | V_{3,L}^{\text{point}} | \varphi_{3,k}) = (d\sigma | 1/r' | k), \quad (A53)$$

$$(\varphi_\xi | V_{3,L}^{\text{point}} | \varphi_{3,y}) = (d\pi^\pm | 1/r' | p\pi^\pm), \quad (A54)$$

where r' is the electron coordinate measured from the fluorine site at which orbitals k and $p\pi^\pm$ are located.

The matrix elements of $V_{3,L}^{\text{Coul}}$ are obtained as follows:

$$(\varphi_u | V_{3,L}^{\text{Coul}} | \varphi_{3,k}) = 2[(d\sigma, s || k, s) + (d\sigma, p\sigma || k, p\sigma)$$
$$+ 2(d\sigma, p\pi^\pm || k, p\pi^\pm)], \quad (A55)$$

$$(\varphi_\xi | V_{3,L}^{\text{Coul}} | \varphi_{3,y}) = 2[(d\pi^\pm, s || p\pi^\pm, s) + (d\pi^\pm, p\sigma || p\pi^\pm, p\sigma)$$
$$+ 2(d\pi^\pm, p\pi^\pm || p\pi^\pm, p\pi^\pm)]. \quad (A56)$$

The matrix elements of $V_{3,L}^{\text{ex}}$ are given as follows:

$$(\varphi_u | V_{3,L}^{\text{ex}} | \varphi_{3,k}) = (d\sigma, s || s, k) + (d\sigma, p\sigma || p\sigma, k)$$
$$+ 2(d\sigma, p\pi^\pm || p\pi^\pm, k), \quad (A57)$$

$$(\varphi_\xi | V_{3,L}^{\text{ex}} | \varphi_{3,y}) = (d\pi^\pm, s || s, p\pi^\pm) + (d\pi^\pm, p\sigma || p\sigma, p\pi^\pm)$$
$$+ (d\pi^\pm, p\pi^\pm || p\pi^\pm, p\pi^\pm)$$
$$+ (d\pi^\pm, p\pi^\mp || p\pi^\mp, p\pi^\pm). \quad (A58)$$

(b) The three-center integrals.

In our calculation of the three-center integrals, $V_{i,L}$ is assumed to be the point-charge potential. The three-center integrals are computed approximately, replacing the integrals by the sum in which a fine cube mesh has the volume $(0.0625)^3$. The summation in fact extends over the region, $0 < x < \rho$, $0 < y < \rho$ and $-\rho/2 < z < 2\rho$, and is finally multiplied by 4. Difficulties associated with the singular points of the potential, $\sum' V_{i,L}$, at $x = \rho$, $y = 0$ and $x = 0, y = \rho$ are eliminated by cutting off a small cube involving these singular points. This is justified by the fact that no appreciable change in the value of the integral is seen when the size of the small cube is varied.

In order to check this, the overlap integrals were calculated this way. The comparisons with the exact calculated values are:

	Approx.	Exact	Error %	
$(\varphi_u | \varphi_{3,s})$	0.01209	0.01175	2.9	
$(\varphi_u | \varphi_{3,z})$	0.01727	0.01598	8.1	(A59)
$(\varphi_\xi | \varphi_{3,y})$	0.00967	0.00945	2.3	

The region over which the summation was performed was determined after examining the contribution from several regions separately.

Numerical values of the three-center integrals are

$$I_s \equiv (\varphi_v | V_L | \chi_{vs})_{3\text{-cent}} = \sqrt{3}(\varphi_u | \sum' V_{i,L} | \varphi_{3,s})$$
$$= 0.08626,$$

$$I_\sigma \equiv (\varphi_v | V_L | \chi_{vz})_{3\text{-cent}} = \sqrt{3}(\varphi_u | \sum' V_{i,L} | \varphi_{3,z})$$
$$= 0.12681, \quad (A60)$$

$$I_\pi \equiv (\varphi_\zeta | V_L | \chi_{\zeta\pi})_{3\text{-cent}} = 2(\varphi_\xi | \sum' V_{i,L} | \varphi_{3,y})$$
$$= 0.08578.$$

It should be noted that the ratio between the three-center integral and the overlap integral is found to be almost the same for s, σ, and π, e.g., $I_s/S_s = 1.06$, $I_\sigma/S_\sigma = 1.14$ and $I_\pi/S_\pi = 1.13$. This means that the following relation approximately holds:

$$(\varphi_\gamma | V_L | \chi_{\gamma k})_{3\text{-cent}} \approx V_L^{\text{eff}}(\varphi_\gamma | \chi_{\gamma k}), \quad (A61)$$

where V_L^{eff} is a constant being independent of γ and k, and it is ~ 1.1 in our case. Thus, a very interesting fact appears, when we see the values of $\sum' V_{i,L}$ at several points:

$$\sum' V_{i,L}(x=y=0, z=0) = 1.32,$$
$$\sum' V_{i,L}(x=y=0, z=\rho) = 0.88, \quad (A62)$$
$$\sum' V_{i,L}(x=y=0, z=\rho/2) = 1.12,$$

namely, that V_L^{eff} is very close to the value of $\sum' V_{i,L}$ at the midpoint between the nickel and fluorine site 3.