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Approximate Self-Consistent-Field Study of the $(NiF_6)^{4-}$ Cluster

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An approximate Hartree-Fock self-consistent-field (SCF) calculation has been carried out for the $(NiF_6)^{4-}$ cluster. Exponential-type orbitals with four independent radial functions were employed for the nickel $3d$ electrons, two radial functions for the fluorine $1s$ and $2s$ electrons, and one for the fluorine $2p$ electrons. A core potential was used to represent the metal ($1s$-$3p$) electrons. All one-electron integrals and all one- and two-center two-electron integrals were evaluated. A closed-shell SCF program was used with orbital occupation numbers adjusted to approximate the open shell. The results of comparisons at different stages in the convergence of the SCF iteration show large differences in $10Dq$ and the degree of delocalization. This implies that some of the earlier simplifications of the SCF treatment are not valid; that is, significant ligand ($2s$-$2p_\sigma$) mixing is found and the metal $3d$ functions make an important contribution to the bonding orbitals.

I. INTRODUCTION

Although crystal and ligand field theory have been highly successful in fitting experimental data for transition-metal complexes when used in a semiempirical framework,[1] attempts to study such system from a fundamental theoretical viewpoint have been less satisfactory. Each new calculation has revealed that parts of previously used theoretical models are inadequate. As a result, a generally accepted description is not yet available.

A number of recent efforts[2-8] have concentrated on a common subject, the $(NiF_6)^{4-}$ cluster of crystalline $KNiF_3$, because of the detailed experimental results that exist for this system.[9,10] The pioneering calculation of Sugano and Shulman[2] was soon followed by that of Watson and Freeman.[3] The disagreements between these two studies, both of which involved severe approximations, stimulated a series of papers that attempted to analyze some of the possible shortcomings.[4-7] All of the papers followed closely the work of Sugano and Shulman in that only an approximate self-consistent-field (SCF) calculation or its Heitler-London analog was attempted, that a minimum basis set was used, that the inner-shell Ni electrons were replaced by a core potential, and that only two-center two-electron integrals and some three-center one-electron integrals were included. More recently, Ellis, Freeman, and Ros[11] and Gladney and Veillard[11] have carried out limited basis set SCF calculations involving all the electrons and free of additional approximations. Since the former used a one-center (Ni or F) expansion, whereas the latter employed Gaussian functions, it is important to have an exponential orbital SCF calculation for comparison.

In this paper we report the first step in such a treatment of the $(NiF_6)^{4-}$ cluster of $KNiF_3$, with primary emphasis on the analysis of the approximations introduced in earlier studies. A basis set consisting of four d orbitals on Ni and the minimum set for the ligands is used; the $1s^22s^22p^63s^23p^6$ core electrons are replaced by an effective potential. Because of the magnitude of the work required to evaluate the integrals over these exponential orbitals, the calculation includes all one- and two-electron one- and two-center integrals, and one-electron three-center integrals, but neglects, all two-electron three- and four-center integrals. Although this approximation is a limitation on the relation between the present work and that of

Ellis, Freeman, and Ros[11] and Gladney and Veillard,[11] the results are of interest for our understanding of bonding in transition-metal complexes. In particular, a comparison of different approximations made in the Sugano-Shulman and related type models is presented. This is important because of the variability of the results obtained by others and the very successful calculation reported most recently by Offenhartz.[8]

II. FORMULATION

The single-determinant Hartree-Fock LCAO molecular orbital method[12] was employed, with the molecular orbitals ψ_i expressed in terms of atomic orbitals χ_k on the central nickel atom and on the ligand fluorine atoms. The resulting equations for the orbital energies ϵ_i and expansion coefficients c_{ik} are

$$\textstyle\sum_k c_{ik}[F_{kl} - \epsilon_i S_{kl}] = 0 \quad , \tag{1}$$

where

$$\psi_i = \textstyle\sum_k c_{ik}\chi_k \tag{2}$$

and

$$\begin{aligned} F_{kl} &= H_{kl} + 2J_{kl} - K_{kl} \quad , & H_{kl} &= (\chi_k | h | \chi_l) \quad , \\ J_{kl} &= \textstyle\sum_j (\chi_k | J_j | \chi_l) \quad , & K_{kl} &= \textstyle\sum_j (\chi_k | K_j | \chi_l) \quad , \\ S_{kl} &= (\chi_k | \chi_l) \quad , \end{aligned} \tag{3}$$

with (atomic units are used in all equations)

$$\begin{aligned} h(\mu) &= -\tfrac{1}{2}\nabla_\mu^2 - \textstyle\sum_a (Z_a / r_{a\mu}) \ , \\ J_j(\mu) &= \int \psi_j^*(\nu)(1/r_{\mu\nu})\psi_j(\nu)\, d\tau_\nu \quad , \\ K_j(\mu) &= \int \psi_j^*(\nu)(P_{\mu\nu}/r_{\mu\nu})\psi_j(\nu)\, d\tau_\nu \quad . \end{aligned} \tag{4}$$

Here the subscripts μ, ν designate electrons and a the nuclei; the permutation operator $P_{\mu\nu}$ interchanges the coordinates of electrons μ and ν. The expression used for F_{kl} corresponds to a system of doubly occupied orbitals; the modification introduced for the present open-shell problem is described below.

A. Core Potential

The $(NiF_6)^{4-}$ complex is composed of 86 electrons of which 26 are from Ni^{2+} and 10 from F^-. Eighteen of the Ni^{2+} electrons are in closed shells (1*s* through 3*p*) whereas the remaining eight are in an unfilled 3*d* shell. It was assumed that the 1*s*-3*p* electrons constitute a core whose effect is to shield the Ni^{2+} nucleus. This reduces the total number of molecular orbitals to be considered and replaces a large number of two-electron integrals by a smaller number of more easily computed one-electron integrals.

With a core potential V_c the Hartree-Fock equations involve only the 3*d* molecular orbitals of nickel and the ligand 1*s*, 2*s*, and 2*p* orbitals. The matrix elements H_{kl} of Eq. (3) are modified by the redefinition

$$H_{kl} = (\chi_k | h + V_c | \chi_l) \quad , \tag{5}$$

where the core potential given by Sugano and Shulman,[2]

$$V_c = 31 \exp(-4.73r)/r \tag{6}$$

is used. This limits the orbital sums in Eqs. (1)-(4) in the obvious manner.

The validity of the core potential is subject to question. Since the radial dependence of the nickel 3*s* and 3*p* functions is similar to that of the 3*d* functions, the functions 3*s*, 3*p*, and 3*d* may have comparable overlaps with the functions on the ligand atoms. Consequently, one cannot expect that keeping the 3*s* and 3*p* functions constant is exact. Nevertheless, the closed-shell character of the 3*s* and 3*p* orbitals makes their neglect a reasonable approximation.

B. Orbitals and Symmetry

The $(NiF_6)^{4-}$ complex with which we are concerned has the structure shown in Fig. 1, with the six fluorine ions equally distant from the nickel ion at the origin. This cluster is invariant under the transformations of the octahedral group. In the LCAO formalism we choose for $\{\chi_k\}$ [Eq. (2)] the basis functions of the irreducible representations of the symmetry group of the molecule; they are given in Table I. Table II lists the atomic orbital basis functions included in the calculation and Table III gives the free-ion orbital energies. Each F^- ion has a set of analytic functions for the 1*s*, 2*s*, and 2*p* orbitals. They were obtained from Sugano and Shulman's fit to the Hartree-Fock calculation of Froese.[13] The 3*d* functions of Ni^{2+} are from a Hartree-Fock calculation by Watson.[14]

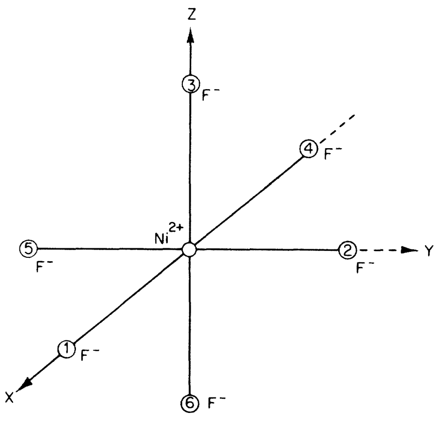

FIG. 1. Geometry of $(NiF_6)^{4-}$ complex; coordinate system used in the text is indicated.

TABLE I. Metal and ligand symmetry orbitals.

Representation	Metal orbitals	Ligand[a]
$A_{1g}(\sigma)$		$(1/\sqrt{6})(\phi_{1k}+\phi_{2k}+\phi_{3k}$ $+\phi_{4k}+\phi_{6k})$
$E_g(\sigma)$	$3d(3z^2-r^2)$	$(1/\sqrt{12})(2\phi_{3k}+2\phi_{6k}-\phi_{1k}$ $-\phi_{2k}-\phi_{3k}-\phi_{4k})$
	$3d(x^2-y^2)$	$\frac{1}{2}(\phi_{1k}-\phi_{2k}+\phi_{4k}-\phi_{5k})$
$T_{1u}(\sigma,\pi)$		$(1/\sqrt{2})(\phi_{1k}-\phi_{4k})$, $\frac{1}{2}(\phi_{2x}+\phi_{3x}+\phi_{5x}+\phi_{6x})$ $(1/\sqrt{2})(\phi_{2k}-\phi_{5k})$, $(\phi_{1y}+\phi_{3y}+\phi_{4y}+\phi_{6y})$ $(1/\sqrt{2})(\phi_{3k}-\phi_{6k})$, $\frac{1}{2}(\phi_{1z}+\phi_{2z}+\phi_{4z}+\phi_{5z})$
$T_{2u}(\pi)$		$\frac{1}{2}(\phi_{2x}-\phi_{3x}+\phi_{5x}-\phi_{6x})$ $\frac{1}{2}(\phi_{1y}-\phi_{3y}+\phi_{4y}-\phi_{6y})$ $\frac{1}{2}(\phi_{1z}-\phi_{2z}+\phi_{4z}-\phi_{5z})$
$T_{1g}(\pi)$		$\frac{1}{2}(\phi_{1z}-\phi_{3x}-\phi_{4z}+\phi_{6x})$ $\frac{1}{2}(\phi_{2z}-\phi_{3y}-\phi_{5z}+\phi_{6y})$ $\frac{1}{2}(\phi_{1y}-\phi_{2x}-\phi_{4y}+\phi_{5x})$
$T_{2g}(\pi)$	$3d(xy)$	$\frac{1}{2}(\phi_{1y}-\phi_{4y}+\phi_{2x}-\phi_{5x})$
	$3d(xz)$	$\frac{1}{2}(\phi_{1z}-\phi_{4z}+\phi_{3x}-\phi_{6x})$
	$3d(yz)$	$\frac{1}{2}(\phi_{3y}-\phi_{6y}+\phi_{2z}-\phi_{5z})$

[a] The ϕ_{ik} represent ligand orbitals on ligand i with $k=1s$, $2s$, or $2p_\sigma$; σ is always directed towards the origin. The ϕ_{ix}, ϕ_{iy}, ϕ_{iz} refer to $2p_\pi$ ligand orbitals. All the atomic functions are normalized.

TABLE II. Normalized basis functions.

Ligand	
$1s=\left(\frac{\zeta_1^3}{\pi}\right)^{1/2} e^{-\zeta_1 r}$	$\zeta_1=8.70$
$2s=\left(\frac{\zeta_2^5}{3\pi}\right) re^{-\zeta_2 r}$	$\zeta_2=2.425$
	$\zeta_3=1.358$
$2p_x=A\left(\frac{\zeta_3^5}{\pi}\right) xe^{-\zeta_3 r}+B\left(\frac{\zeta_4^5}{\pi}\right)^{1/2} xe^{-\zeta_4 r}$	$\zeta_4=3.737$
$2p_y=A\left(\frac{\zeta_3^5}{\pi}\right) ye^{-\zeta_3 r}+B\left(\frac{\zeta_4^5}{\pi}\right)^{1/2} ye^{-\zeta_4 r}$	$A=0.634\,352\,25$ $B=0.502\,711\,7$
$2p_z=A\left(\frac{\zeta_3^5}{\pi}\right) ze^{-\zeta_3 r}+B\left(\frac{\zeta_4^5}{\pi}\right)^{1/2} ze^{-\zeta_4 r}$	
Metal[a]	
$3d(3z^2-r^2)=\left(\frac{\zeta^7}{18\pi}\right)^{1/2}(3z^2-r^2)e^{-\zeta r}$	$\zeta_5=2.3154$
$3d(x^2-y^2)=\left(\frac{\zeta^7}{6\pi}\right)^{1/2}(x^2-y^2)e^{-\zeta r}$	$\zeta_6=4.5232$ $\zeta_7=8.5025$ $\zeta_8=15.0077$
$3d(xy)=\left(\frac{2\zeta^7}{3\pi}\right)^{1/2} xy\, e^{-\zeta r}$	
$3d(xz)=\left(\frac{2\zeta^7}{3\pi}\right)^{1/2} xz\, e^{-\zeta r}$	
$3d(yz)=\left(\frac{2\zeta^7}{3\pi}\right)^{1/2} yz\, e^{-\zeta r}$	

[a] Metal d orbitals were represented by a linear combination of four orbitals with $\zeta=\zeta_5$, ζ_6, ζ_7, and ζ_8, respectively.

Watson's functions consist of a linear combination of four $3d$ radial functions, each with a different exponential parameter. We consider each radial function as a separate basis orbital so as to obtain an expanded set that can respond to the ligand environment.

C. Open-Shell Approximation

To obtain the Hartree-Fock equation for the present system, we compare the total energy expression for a closed shell,

$$E=2\sum_i H_i+\sum_{ij}(2J_{ij}-K_{ij}) \ , \tag{7}$$

with that for a system having one open shell,[15]

$$E=2\sum_i H_i+\sum_{ij}(2J_{ij}-K_{ij})+f\Big[2\sum_m H_m +f\sum_{m,n}(a2J_{mn}-bK_{mn})+\sum_{i,m}(2J_{im}-K_{im})\Big] \ , \tag{8}$$

where i, j refer to orbitals with electrons in closed shells and m, n refer to orbitals with electrons in the open shell or subshell. The factor f is the fractional occupancy of the open shell; that is, f is the number of open-shell electrons divided by the number for filled orbitals; and a and b depend on the spin alignment of the electrons.

The expression for the energy given in Eq. (8) is deceptively simple since the corresponding Hartree-Fock operator is considerably more complex than in the closed-shell formulation and requires different operators for the filled and unfilled orbitals. To avoid this difficulty, average spin states for the complex were introduced and the calculations were done employing a program for closed-shell systems.[16] In this program, the fractional occupation f was properly specified, but the coefficients a and b corresponded to the doubly occupied orbital values. Thus, the effective ground and first excited states considered for $(NiF_6)^{4-}$ are represented as ground state $(^3A_{2g})$

$$E_g\!:\ \tfrac{1}{2}(\downarrow\uparrow)\tfrac{1}{2}(\downarrow\uparrow), \quad T_{2g}\!:\ \downarrow\uparrow\ \downarrow\uparrow\ \downarrow\uparrow$$

and excited state $(^3T_{2g})$

$$E_g\!:\ \downarrow\uparrow\tfrac{1}{2}(\downarrow\uparrow), \quad T_{2g}\!:\ \downarrow\uparrow\ \downarrow\uparrow\tfrac{1}{2}(\downarrow\uparrow) \ .$$

D. Integral Evaluation

A large number of one- and two-electron integrals must be computed in order to perform the Hartree-Fock SCF iteration. The one- and two-center one-electron integrals (kinetic energy, overlap, nuclear attraction, and core potential) were evaluated with a diatomic molecular integral program prepared

TABLE III. Orbital energies of free-ion functions.

Ni^{2+}: $3d=-1.4125$ a.u.	F^-: $2p=-0.1815$ a.u.
	: $2s=-1.0765$ a.u.

by Nesbet and Stevens. All three-center nuclear attractions were calculated with a general four-center integral program,[17] based on the Gaussian transform analysis of Shavitt and Karplus.[18] The three-center core integrals are of the form

$$I=(F_i|e^{-\alpha r_{1C}}/r_{1C}|F_j)_{i\neq j} \ , \tag{9}$$

where r_{1C} is the distance from the electron to the Ni^{2+} nucleus, and F_i and F_j represent ligand basis functions. These integrals can be expressed as a linear combination of (i) a three-center nuclear attraction integral, (ii) a three-center two-electron Coulomb integral, and (iii) a three-center "overlap" integral. The integrals required for (i) and (ii) were computed. Since the overlap term (iii) of the form $(F_i|e^{-\alpha r_C}|F_j)$ is expected to be considerably smaller than either of the other terms, this term was neglected. The one- and two-center two-electron integrals were also evaluated with the diatomic-molecule integral program. Because the computer time required for an accurate evaluation of all three-center and four-center two-electron integrals was prohibitively large, they were neglected.

III. RESULTS AND DISCUSSION

The basic question concerning the transition-metal complexes is, what are the essentials for a satisfactory description of their electronic structure. In an attempt to provide some information for answering this question, we compare the results of a number of approximations to the complete Hartree-Fock treatment (with neglect of the multicenter two-electron integrals) of the $(NiF_6)^{4-}$ complex in the shielded core approximation. Because of the simplifications in the present model, it is to be expected only that the relation between different results is meaningful; the individual values and their comparison with experiment are of lesser significance.

In addition to the complete SCF study (designated SCF) described in Sec. II, a second SCF calculation was made restricting the input data to integrals over one and two atomic centers (SCF_2). For both cases the results of a pure ionic calculation and those from a single step in the SCF iteration were obtained. The "ionic" results are designated $I(0)$ and $I_2(0)$; the results of the single step as $I(1)$ and $I_2(1)$.

A. 10Dq Values

Table IV presents the results obtained for the crystal-field splitting (10Dq), which in the present case is equal to the energy difference between the ground and excited states defined in Sec. II; that is,

$$10Dq=E(^3T_{2g})-E(^3A_{2g}) \ ,$$

where the Hartree-Fock energy was obtained for both states with the approximations described above. The most important point evident from the table is that the results from each approximation differ significantly from all others [except for $I(0)$ and $I_2(0)$, which are essentially identical]. That the pure ionic model [$I(0)$] has a negative 10Dq and is in agreement with the results of earlier workers, although the present $I(0)$ calculation is somewhat more flexible than the classical ionic cluster; it demonstrates once again that considering the ligand electrons without introducing covalency leads to an unbalanced model. The large difference between $I(1)$ and SCF is somewhat more surprising and shows that the use of an ionic Hamiltonian without carrying out the iteration to a converged SCF solution is not justified. It is also of interest that there are large differences between including and neglecting the three-center one-electron integrals. This suggests that the omitted multicenter two-electron integrals are also of importance. Finally, the difference between the 10Dq results for the case in which the SCF calculations were made for both states (SCF) and those for the case in which ground-state orbitals were used for both states (SCF*) suggests that a non-negligible correction is introduced by the change in the orbitals on excitation.

TABLE IV. Crystal field splitting (10Dq).[a]

	No 3-center integrals (cm)	Including 3-center integrals (cm)
$I(0)$	−3 572	−3 566
$I(1)$	14 266	107 103
SCF	27 434	17 119
SCF*	31 385	20 850
Expt	7250	

[a] For definitions, see text.

One might have expected that the Sugano and Shulman calculation and some of the related schemes would correspond to the $I(1)$ model. However, the 10Dq value obtained by them is 6365 cm^{-1}, so that some of their additional assumptions cannot be valid.

B. Form of Wave Function

From the above variation in 10Dq as a function of approximation, it is evident that significant delocalization occurs in the present treatment of the $(NiF_6)^{4-}$ complex. To make this conclusion explicit, we present in Table V the results for the three highest E_g orbitals and the two T_{2g} orbitals obtained with the SCF and $I(1)$ calculation for the ground state of the complex. It is clear from the table that the $I(1)$ and SCF orbital energies and coefficients are very different. Moreover, the

TABLE V. Ground-state molecular orbitals for $(NiF_6)^{4-}$.

E_g	Orbital 1		Orbital 2		Orbital 3		T_{2g}	Orbital 4		Orbital 5	
	SCF	$I(1)$	SCF	$I(1)$	SCF	$I(1)$		SCF	$I(1)$	SCF	$I(1)$
Energy	−1.9813	−2.1565	−0.4254	−1.6791	1.7973	−0.8324	Energy	−0.7363	−2.2095	0.9926	−1.0462
Coef. of $d(1)$	1.2042	−1.0472	−0.3837	−0.4117	−0.1455	−0.5078	Coef. of $d(1)$	0.6551	−0.1168	−0.1763	0.5815
$d(2)$	0.8035	−0.5666	0.1845	0.6333	0.6859	0.3498	$d(2)$	−0.3822	−0.3290	−0.4537	−0.4204
$d(3)$	−0.3655	0.4967	−0.0999	0.3927	0.3356	−0.0147	$d(3)$	0.2034	−0.5551	−0.3943	0.0692
$d(4)$	0.0881	−0.0101	0.0129	0.2089	0.1785	0.0623	$d(4)$	−0.0340	−0.1797	−0.1524	−0.0673
$1s$	−0.1666	0.1638	0.1522	−0.0956	−0.0138	0.1312	$2p_\pi$	−0.9739	0.0873	−0.1917	−0.9903
$2s$	0.7928	−0.7612	−0.6394	0.4332	0.0717	−0.5299					
$2p_\sigma$	0.5455	−0.4721	0.7235	0.1174	0.1906	0.7924					

mixing between metal and ligand orbitals is large, as is the s-p mixing on the ligands themselves. Also, the variation in the d-orbital coefficients shows that the flexibility introduced by having an extended basis set is important. The changes in going from the ground to the excited state are much smaller than the SCF, $I(1)$ differences shown in the table, but apparently are sufficient to produce significant changes in $10Dq$ (see above). For both $I(1)$ and SCF, leaving out the three-center integrals resulted in a set of coefficients and orbital energies that are very far from the tabulated values.

The atomic populations[19] obtained from the SCF orbitals correspond to Ni and F ions that have approximately one-half of a negative charge each; that is, there is significant electron transfer from the F^- ions to the Ni^{2+}. The p_σ orbitals of F^- make the largest contributions, though $2s$ and $2p_\pi$ are also involved. The transfer of electrons from the F^- to Ni^{2+} is smaller in the SCF_2 calculation that did not include the three-center integrals [i.e., the net charge on the Ni in the $(NiF_6)^{4-}$ cluster is + 1 by a population analysis]. This suggests that inclusion of these integrals, while excluding the multicenter electron repulsion integrals, may lead to a somewhat unbalanced charge distribution.

C. Hyperfine Interaction

The assumption of constant covalency for electrons of either spin leads to the following expression for the ligand spin density $f_k(k=s,\sigma)$ due to the E_g electrons[3]

$$f_k=\tfrac{1}{3}C_{4k}^2(k=s \text{ or } \sigma) \ .$$

The values obtained with the different approximations are given in Table VI. Again the large variation in the results is of primary interest.

A number of the papers on $(NiF_6)^{4-}$ have discussed the origin of the ligand spin density. Some workers have argued that Heitler-London–type charge transfer must be included; others have stated that the difference between the covalency of the (+) and (−) spin electrons must be taken into account. However, it is not evident from the available results that either effect is important, though one or the other may be. Clearly, if one starts with a localized model (i.e., pure ionic system), charge transfer of the Heitler-London-type must be introduced to obtain ligand spin density. Most of the resulting charge transfer is, however, accounted for in a restricted Hartree-Fock treatment of the type carried out in the present paper, so that care must be taken in making the comparison.[20] What is not included is the spin polarization that could be introduced by configuration interaction or by an

TABLE VI. Ligand spin densities.

	s	σ
SCF_3	0.001 78	0.0121
SCF_2	0.014 6	0.0318
$I_3(1)$	0.093 6	0.2093
$I_2(1)$	0.062 8	0.1973
Expt (Ref. 2)	0.004 48	0.0378

unrestricted Hartree-Fock model. Additional calculations that take account of all contributions are clearly required to determine their relative importance.

Note added in proof. For a recent calculation with an extensive Gaussian-type basis set in the restricted and unrestricted Hartree-Fock approximation, see J. W. Moscowitz, C. Hollister, C. J. Hornback, and H. Basch, J. Chem. Phys. 53, 2570 (1970).

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APPENDIX: ACCURACY OF THE CALCULATION

Since the present calculation was considered to be a large-scale effort when it was completed, some attempt was made to determine the computational errors involved.

Round-off error. During each iteration of the SCF calculation approximately 400 000 integrals are multiplied by elements of a previously determined density matrix and formed into a 50×50 matrix. Matrix multiplications by other computed matrices then partition this matrix according to the symmetry of the system. The secular equation is then solved and a new density matrix is obtained from multiplication and addition of the eigenvectors. The numbers processed may be positive or negative and range over several orders of magnitude.

The round-off error in the calculation was estimated by comparing the results obtained using single- and double-precision arithmetic (i.e., keeping 8 and 16 significant figures). Table VII shows that the total energy varied in the seventh significant figure or the third decimal place. This error is sufficiently small to validate $10Dq$. A similar accuracy was found in the coefficients of the eigenvectors.

TABLE VII. Total energy comparison.[a]

	Double precision	Single precision
SCF_3 – ground state	– 1022.413 94	– 1022.412 70
SCF_3 – excited state	– 1022.335 36	– 1022.333 90
	Truncation	Addend
SCF_3 – ground state	– 1022.397 96	– 1022.426 65

[a] Truncation and addend were evaluated with double-precision arithmetic.

Inherent error. The numerical values of the integrals define a model of the physical system represented by the theoretical formulation. The comparison of single- and double-precision calculations indicated the validity of the results for this model. A second problem is the propagation of errors inherent in the values of the integrals.

All one- and two-center integrals are determined accurately through seven significant figures. The three-center integrals cannot be considered reliable through more than five significant figures. Therefore, two additional SCF calculations were made with modified values of the integrals. The computed integrals had eight significant figures. In one calculation we kept the first five figures, but set all the binary bits corresponding to the last three figures equal to zero (truncation); in the second calculation, we set these same bits equal to 1 (addend). It was hoped that these two extremes would give an upper bound to the error. The results given in Table VII show that the integral changes affect the second decimal place of the total energy. This might seem to invalidate the determination of $10Dq$. However, the test modified all the integrals beyond the fifth figure. Many integrals, including the largest kinetic-energy and nuclear-attraction integrals, have seven-figure accuracy. This distinction between the number of significant figures and number of accurate decimal places suggests that $10Dq$ should be meaningful. The orbital coefficients appear consistent through at least three significant figures, and this is enough to justify the quantities we have derived from them.

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Surface Relaxation and Quasiparticle Interactions in Conduction-Electron Spin Resonance*

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A modified Bloch equation for the conduction-electron magnetization density is developed starting from the Landau-Silin kinetic equation, and a boundary condition describing surface relaxation is formulated. These basic results include the effects of the drift magnetization current density and predict relaxation of the magnetization density to the instantaneous local value of the applied microwave field. The conditions of validity of this and previous theories are critically discussed, and it is shown that in the collision-dominated regime, for example, the modified Bloch equation is valid only under classical-skin-effect conditions. A way of obtaining useful results for anomalous-skin-effect conditions is then outlined. Formulas for the surface impedance and for the amplitude of the microwave field transmitted through a thin metallic slab are derived.

I. INTRODUCTION

The observation of spin-wave excitations in sodium and potassium metals by Schultz and Dunifer[1] has stimulated considerable theoretical interest[2,3] in conduction-electron spin resonance (CESR). Many, but not all, of the interesting features of the data[1] are explained by Platzman and Wolff's adaptation of the Landau-Silin Fermi-liquid theory.[4] Also, a conventional theoretical interpretation of certain anomalous features of the CESR experiments of Walsh, Rupp, and Schmidt[5] on potassium is lacking, although Overhauser and de Graaf[5] have suggested that the anomalous behavior may be due to charge density waves. Thus, it appears that, while current theories of CESR have had their successes, they merit closer examination, particularly in the limit of low temperatures and very pure metals.

The origin of many of our present ideas concerning CESR is Dyson's famous paper.[6] In it, he points out that each electron spin diffuses into and out of the skin depth many times before it relaxes, and argues that this is the reason such narrow lines are observed in CESR. He also puts forward a quantitative theory of the surface impedance. In another important development, Azbel', Gerasimenko, and Lifshitz[7] showed that electron spins could be excited by a microwave field in the skin depth on one side of a thin metallic slab, and could then, after diffusing across the slab, emit radiation out the far side. A comprehensive review of both theoretical and experimental developments has been given by Walsh.[8]

In this paper, a theory of CESR is developed which has as its basis the Landau-Silin theory of a Fermi liquid. It is shown that, in a linear theory, long-wavelength oscillations of the magnetization density are governed by a modified Bloch equation similar to that suggested by Torrey.[9] Relaxation of the conduction-electron spins at a surface is described by an appropriate boundary condition on the magnetization density, and solutions of the modified Bloch equation consistent with the boundary condition are obtained for cases of practical