THEORETICAL DETERMINATIONS OF CHARGE AND SPIN DENSITIES
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To cite this version:
A. Freeman, D. Ellis. THEORETICAL DETERMINATIONS OF CHARGE AND SPIN DENSITIES. Journal de Physique Colloques, 1974, 35 (C6), pp.C6-3-C6-20. <10.1051/jphyscol:1974602>. <jpa-00215702>

HAL Id: jpa-00215702
https://hal.archives-ouvertes.fr/jpa-00215702
Submitted on 1 Jan 1974
Résumé. — Nous avons examiné les récents développements théoriques relatifs à la détermination des densités de charge et de spin des atomes, des molécules et des solides cristallisés. Dans le but d’illustrer l’état d’avancement de la théorie dans les approximations relativiste et non relativiste, nous présentons les résultats pour quelques exemples choisis parmi les travaux récents dans chacun des domaines précités. Des comparaisons avec des résultats expérimentaux tels que déplacements isomériques, éclatements quadrupolaires et facteurs de structure magnétique obtenus par diffraction de neutrons sont faites, quand il paraît opportun, afin d’indiquer la fiabilité des résultats théoriques obtenus.

Abstract. — Recent developments in the theoretical determinations of charge and spin densities in atoms, molecules and crystalline solids are reviewed. Results for selected examples of recent work in each of these areas are presented in order to illustrate the present state of the theory for both the nonrelativistic and relativistic regimes. Comparisons with such experimental data as isomer shifts, quadrupole splittings and neutron magnetic form factors are given when appropriate in order to indicate the reliability of the results obtained.

1. Introduction. — With the discovery of the Mössbauer effect, it was widely recognized that the measurement of isomer shifts had great potential for becoming an important tool for the study of both nuclear and electronic properties of atoms in various environments [1]. The isomer shift provides a measure of the product of the difference of mean square radii of two nuclear isomers and the difference in electron density in the region of the nucleus, between two isomeric atoms in different chemical environments. Whereas these quantities are impossible to measure by themselves, isomer shift measurements coupled with independent information about either the isomeric radii or the electronic densities provides knowledge of the other. Thus, in principle, a measurement of the isomer shift between two ions in different environments and an accurate calculation of the electronic charge densities would allow one to deduce the change in nuclear isomeric radii. Unfortunately, the enormous difficulties involved in determining theoretically either electron or nuclear densities has left the promised potential largely unfulfilled. Recent progress in the theoretical determination of electronic charge (and spin) densities has revived hope for achieving some of the hoped-for results.

The theoretical determination of electron densities at the nucleus is a special case of the more general problem of obtaining quantum mechanically accurate electron charge and spin densities in condensed matter systems. Many of the most widely used methods originated, both for practical and historical reasons, as descriptions of free atom behavior and were later extended (with some modifications) to the treatment of molecules and solids. In this paper we follow this same procedure, and discuss the solution of the Schrödinger (or Dirac) equation in the context of free atom phenomena and later treat the molecular and solid state systems as derived from this overview.

The basic problem is to obtain the stationary eigenfunctions of the many-electron Hamiltonian (time-dependent theory will not be considered here) in order to evaluate the expectation values of physical observables, such as the electron-nuclear interaction, of concern to us in this paper. The Hamiltonian for this interacting electron system is

\[ H = \sum_{i,j=1}^{N} K_i - \frac{2Z_i}{r_{ij}} + \sum_{i<j} \frac{2Z_i Z_j}{r_{ij}} + \sum_{i,j} \frac{2}{r_{ij}} \]  

where \( K_i = p_i^2 \) for non-relativistic kinematics and \( K_i = C a_i p_i \) for relativistic kinematics in Rydberg units.
Eq. (1) gives, respectively, the kinetic energy of the \( N \) electrons, the nuclear attraction between the \( i \)th nucleus and the \( j \)th electron, the nuclear repulsion terms between the \( Z_a \) and \( Z_b \) nuclei separated by a (fixed) distance \( r_{ab} \) and the electrostatic repulsion term between \( i \)th and \( j \)th electrons a distance \( r_{ij} \) apart.

Unfortunately, Schrödinger's equation (or equivalently the Dirac equation) has yet to be solved exactly for systems involving more than one electron. It was recognized, even in the early days of quantum mechanics that one has, of necessity, to resort to the use of approximate wave functions which are often expanded in terms of some basis set of functions. Because of computational difficulties, an incomplete set which spans but a limited subspace of Hilbert space is chosen. The variation principle is then used to determine the best solution according to the criterion that the lower the total energy, the better the approximate wave function. In practice, the determination of the functions is limited by the fact that the energy is insensitive to further variation of the functional parameters. In addition, a small improvement in the solution, i.e., in its total energy, does not necessarily improve the prediction of some other physical observable.

Since the direct solution of the many-electron Hamiltonian, eq. (1), is obviously not possible for a many-electron system, we will make an approximation which separates the variables to yield an effective single particle Hamiltonian. In the Hartree-Fock method the state function of the system is approximated by a single Slater determinant of one-electron orbitals which allows for electron correlations between electrons of the same spin. The minimization of the total energy of the system subject to the variation of the one-electron orbitals yields a set of coupled integral-differential equations known as the Hartree-Fock equations (or Dirac-Fock equations for its relativistic counterpart) which still contain Coulomb and exchange interaction terms between the electrons. Even with this approximation, the problem is still a complex one and its exact solution is beyond our present capabilities. Thus, one makes the additional approximation of averaging the exchange term \([\text{from the } (r_{ij})^{-1} \text{ operator of eq. (1)}]\) which appears in the Hartree-Fock equations. This averaging procedure is necessary in order to obtain an effective single-electron local potential. The average of the nonlocal exchange term is to use Slater's \( p^{1/3} \) approximation [2] for the free electron gas (i.e., replace the exchange term by its Thomas-Fermi-Dirac equivalent); namely

\[
V_{ex}(r) = -6 \alpha \left[ \frac{3}{8\pi} \rho(r) \right]^{1/3} = \alpha C[\rho(r)]^{1/3}
\]

where \( \rho(r) \) is the electronic density at the spatial position, \( r \), arising from superposition of the charge density of the central atom and neighbouring shells of atoms.

In this paper then, we shall be mainly concerned with the one-electron approximation which represents one of the most successful schemes for approximating solutions of the many-electron Schrödinger (or Dirac) equation. But basic to the scheme is the assumption that one has available one-electron wave functions, called orbitals, whose description depends only on the coordinates of a single particle. Recently, the Hartree-Fock-Slater (HFS) or the relativistic counterpart the Dirac-Fock-Slater (DFS) method has enjoyed widespread use and application to a number of problems ranging from free atom through molecular cluster and solid state (energy band) calculations. We discuss some of these developments, particularly as they relate to isomer shift measurements. Unfortunately, space limitations preclude a full and detailed description of all the work which has been done in this field. This report then must be viewed as a more personal view of some recent developments in which the authors have participated; its justification is that such a presentation may make the pedagogical presentation more coherent (albeit more restricted) and more understandable to the reader. A full report and more extensive references are given elsewhere [3].

2. Relativistic effects on free ion charge densities and isomer shifts. — In the face of the greater difficulties inherent in the state of nuclear theory, some progress has been made in the field of isomer shifts by assuming, as a first crude approximation, that the electronic charge difference between several ions in different chemical environments may be ascribed to a change in ionicity [4]. Thus, Hartree-Fock calculations have been performed, on various charge states of an atom [5] and the resultant electron charge densities at the nucleus are then used to estimate relative isomer shifts. Implicit in this procedure is the assumption that the difference in nuclear radii is the same for the various cases. Using these calibrations, comparison with experimental isomer shifts then provides estimates of other effects due to the chemical environment, such as ligand bonding and electron correlation. Free atom results are useful (as a first crude approximation) particularly for complex materials such as are found in the archaeological and painting studies reported elsewhere in this volume-materials for which \textit{ab initio} calculations of the molecular cluster and solid state types to be described later are clearly impossible.

The isomer shift \( \Delta_{AB} \) between a source B and an absorber A is given by the well known expression [6, 1, 7]:

\[
\Delta_{AB} = \frac{2}{3} \frac{\pi e}{E_{\gamma}} Z e^2 \left( |\psi_A(0)|^2 - |\psi_B(0)|^2 \right) < \delta < R^2 > \equiv \alpha \rho_{AB}(0)
\]

where \( E_{\gamma} \) is the \( \gamma \) ray energy, \( Z \) is the nuclear charge,
e \mid \psi_{A}(0) \mid^2 \text{ and } e \mid \psi_{B}(0) \mid^2 \text{ are the electron charge densities at the nuclei of the source and the absorber respectively, and } \delta < R^2 \text{ is the fractional change in nuclear charge radius between isomers. For a given pair of isomers, } \delta < R^2 \text{ is constant, and }

\mid \psi_{A}(0) \mid^2 - \mid \psi_{B}(0) \mid^2

measures the change in electronic charge densities as the ions are placed in different compounds. Implicit in this formulation are the assumptions that the electron density is constant over the nuclear volume and that the change in electronic state (\psi_{A} \text{ to } \psi_{B}) \text{ does not affect the nuclear densities. Thus, the calculated values of } \Delta_{AB} \text{ for various charge states of the same isomers yield the dependence of isomer shift on changes in atomic electron density; the differences between measured and calculated } \Delta_{AB} \text{ allow one to deduce the additional effects of the chemical environment. In the second form of eq. (3), the isomer shift has been written as a simple proportionality to the change in density

\rho_{AB}(0) = \left[ \mid \psi_{A}(0) \mid^2 - \mid \psi_{B}(0) \mid^2 \right];

the proportionality constant } a, \text{ which contains all the nuclear constants, is called the isomer shift calibration constant.}

Recent efforts at relating measured relative isomer shifts have centered on the calculation of free ion atomic electron charge densities using numerical H-F and D-F theory, with exact exchange, to describe the ionic systems. Here we cite but two of these (unpublished) results to indicate the magnitude of the relativistic effects (and the accuracy of one-electron relativistic corrections [8]) and to demonstrate the need to go beyond the free ion approximation to describe the role of the chemical environment even for the highly ionic systems.

Figure 1 compares the [9] H-F and [10] D-F free ion results for } \rho_{AB}(0) \text{ between the } +2 \text{ and } +3 \text{ states of the rare-earth ions. In each case, the authors calculated the ionic ground states: for the Hartree-Fock problem, this was the single-configuration Hund's rule ground state in Russell-Saunders coupling. In the relativistic treatment, the single particle wave functions are eigenfunctions of the total angular momentum, but not of the separate spin and orbital angular momenta; thus the Dirac-Fock calculations are performed in j-j coupling. However, in these calculations, the total wave function is not a single j-j configuration but rather a linear combination of j-j configurations of total angular momentum } J = L \pm S; \text{ thus, the multi-configuration Dirac-Fock wavefunction formally approximates as closely as possible the } (L-S) \text{ Hartree-Fock wave function. The importance of including all relevant j-j configurations has been discussed elsewhere [11] as has the appropriateness of the } L-S \text{ coupling model even for fairly heavy ions, where relativistic corrections are important.}

The surprising aspect of the results shown in figure 1 is the relative constancy of the H-F values over the whole range of the rare-earths. The D-F results differ in a dramatic way from the H-F values showing a large (factor of 2 to 3.5) increase in } \rho_{AB}(0) \text{ in going from } Ce \text{ to } Yb. The one-electron relativistic correction factor } S'(Z) \text{ multiplying the H-F results is seen to overestimate the magnitude of the relativistic correction but gives a linear dependence on atomic number, } Z, \text{ with almost the same slope as the D-F results.}

A systematic study of relativistic electron densities and isomer shifts in 4d and 5d ions has been made by Mallow, Freeman and Desclaux [12]. Both multi-configuration D-F (for both point and finite nuclei) and H-F calculations of the changes in } \rho(0) \text{ were performed (with } \delta < R^2 \text{ assumed constant) for each set of ions; they have thus obtained relative values of } \Delta_{AB} \text{ due to atomic effects. They then compared all values with experimental shifts in order to separate the nonrelativistic and relativistic atomic contribution to the isomer shift from those contributions due to the chemical environment. We cite here just one aspect of their results, shown in figure 2, namely the strong dependence of isomer shift on charge state. This is well-known for Hartree-Fock states; not unexpectedly, the Dirac-Fock isomer shifts exhibit the same strong dependence. The relativistic corrections depend strongly on the different ionicity and different nuclear charge; while it varies for different ion pairs of the same } Z, \text{ this variation does not appear to exhibit any systematic behavior. However, there is a systematic dependence in the particular model used, viz., the finite nucleus relativistic corrections are considerably lower than the point nucleus corrections since the finite nucleus density shifts are lower.}

Comparison with experiment (cf. Fig. 2) shows a large systematic variation between the theoretical and measured values for Ru and Ir ions with increasing charge states (ionocities). It is thus very apparent that bonding effects (covalency) start to play a concomitant
large role with increasing charge state and that the free ion approach becomes a poorer and poorer approximation to reality.

3. Molecular cluster approach. — The past decade has seen the steady development of molecular orbital (MO) theories, which have proceeded from the development of techniques to describe optical transitions and ionization energies, to attempts to predict wave function-dependent properties. Semi-empirical models have been refined considerably, and when applied carefully, have given much insight into bonding and charge-transfer mechanisms responsible for many solid-state effects. For the Mössbauer isomer shift (IS) and quadrupole splitting (QS) the underlying premise is that a cluster of near-neighbor atoms provides the dominant electronic environment for the nuclear $\gamma$-ray transition; and that more distant atoms can be ignored, or treated by a simple molecular field approximation.

Following efforts to treat the perturbing effect of the environment by orthogonalization schemes (the overlap distortion approximation), first-principles MO methods have gradually become sufficiently accurate to test the assumptions inherent to a cluster model. One would expect the cluster model to work best for insulating solids, and that external boundary conditions would become crucially important for metallic systems. In the following sections we discuss some examples of this development, and assess the prospects for future improvements.

3.1 Semi-empirical models. — We shall not discuss the many beautiful qualitative interpretations of Mössbauer IS data, and their correlations with QS, hyperfine fields, empirical ionicities, etc. We refer the reader to the paper by Sawatzky in this volume for a review, which shows how useful this approach has been in systematizing a vast number of experimental results. In this section we limit ourselves to theories which attempt to make quantitative or semi-quantitative predictions rather than a posteriori explanations.

The Hückel MO theory (and its descendant, the Wolfsberg-Helmholz approximation) as developed and refined by Hoffman and others [13], remains as the most successful semi-empirical scheme. Appealing in its simplicity, relying upon experimental atomic data and overlaps between a minimal basis of free-atom orbitals, it has produced an astonishing amount of semi-quantitative data and qualitative interpretations. In its most popular form, one assumes a Hamiltonian matrix

$$\mathbf{H}_{ij} = K S_{ij} (h_{ii} + h_{jj})$$

where $K$ is a constant, $S_{ij}$ are two-center overlap integrals and $h_{ii}$ are experimentally determined ionization potentials or electron affinities. The secular equation

$$(\mathbf{H} - \mathbf{E} \mathbf{S}) \mathbf{C} = 0$$

is solved to obtain MO energies $E_n$ and wave functions $\psi_n = \sum_j q_j C_{jn}$ which are linear combinations of free-atom orbitals. The entire process can be iterated to self-consistency by adjusting atomic orbital occupation numbers to alter the input Hamiltonian matrix. This procedure, which is based upon a Mulliken population analysis [14] of the MO's, may be termed a self-consistent-charge model.

As an early example of the application of this method, we may cite the work of Basch, Viste, and Gray [15] on transition metal complexes. Treating the octahedral (FeF$_6$)$^{3-}$ complex, they obtained a 4s population of 0.32. Danon has used this result to obtain a calibration of the isomer shift [16]. Although the assumption that partial occupancy of the Fe$^{3+}$ free-ion, 4s level determines the observed IS is an oversimplification, the results are rather plausible and in fair agreement with other estimates.

Recently, the Hückel method has been successfully applied by Trautwein [17] in an effort to obtain a consistent picture of iron in a variety of biologically significant compounds. By empirically adjusting the model to fit both IS and QS data, a satisfactory result can be obtained. Treating the case of iron oxides and iron impurities in solid noble gases and compounds such as MgO by a more elaborate method including some configuration interaction, Trautwein et al. [18] have obtained further encouraging results. Recently, these results have been used, in concert with relativistic

![Fig. 2. — Some comparisons between calculated D-F and experimental IS results for Ru and Ir in different charge states.](image-url)
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atomic calculations, to obtain a new estimate of the IS calibration constant [19].

In outline, their method consists of:

(i) An extended-Hückel SCF calculation was carried out for doubly occupied valence orbitals.

(ii) An empirical valence-electron configuration interaction calculation was made to produce many-electron states with proper \(L, S\) quantum numbers.

(iii) Core orbitals were orthogonalized to the valence functions and the total density \(\rho(0)\) was obtained.

(iv) To take into account the relativistic increase in \(|\psi_d(0)|^2\), each orbital was corrected separately, making use of fully relativistic mixed-configuration Dirac-Fock free atom calculations. This procedure represents an improvement over the traditional \(S'(Z)\) correction factor.

By considering a number of different systems, the authors found an average value for the relative change in nuclear charge radius \(\delta R/R = (-5.96 \pm 0.6) \times 10^{-4}\).

Semi-empirical MO calculations on heavy-atom clusters are few in number, and of uncertain reliability. We mention the attempt of Unland and Letcher [20] to apply the method of localized and equivalent orbitals in a study of \(^{119}\)Sn.

3.2 OVERLAP DISTORTION APPROXIMATION. — By overlap distortion we indicate an entire class of approximations where the solid is considered as an assembly of free atoms or ions, upon which certain overlap constraints are placed. It was immediately recognized that direct overlap of wave functions from a distant site onto the Mössbauer nucleus was too small to have significant effect in most cases. In a single determinant model for the many-electron (solid) wave function, a very general procedure for constructing a properly normalized charge density was given by Löwdin [21]. This density can be written as

\[
\rho(r) = \sum_{i,j} q_i^* S_{ij}^{-1} \varphi_j
\]  

(6)

where the sum runs over all occupied atomic (ionic) orbitals \(\varphi_i\), and \(S_{ij}^{-1}\) is an element of the inverse to the atomic (ionic) overlap matrix. The charge density can be thought of as the sum of contributions from Löwdin-Orthogonalized atomic orbitals,

\[
\rho(r) = \sum_i |\chi_i|^2
\]  

(7)

where

\[
\chi_i = \sum_j S_{ij}^{-1/2} \varphi_j.
\]  

(8)

However, the expression (6) is independent of any particular orthogonalization procedure.

Early efforts to calculate \(\rho\) using orthogonalized atomic orbitals (OAO) constructed by arbitrary procedures met with mixed success. The pioneering work of Simanek et al. on iron salts concentrated on the distortion of the valence Fe-4s orbital [22]. However, it was emphasized by Freeman and Watson [23] and others that cross-terms in eq. (6) connecting iron core and ligand valence orbitals would have a sizeable effect on hyperfine fields and, by inference, also on the charge density at the iron nuclei. More recent OAO studies on iron compounds by Sharma have explored features of the overlap distortion model, often obtaining IS and QS results consistent with experiment [24].

The isomer shifts of \(^{129}\)I in alkali halide lattices were calculated using OAO's by Flygare and Hafemeister [25]. For heavy atoms one must consider changes in valence-orbital «tails» due to indirect relativistic (shielding) effects. Relativistic atomic calculations were subsequently used to show that two-center overlaps were reduced by \(\sim 10 \%\), and that for iodine, OAO estimates of the isomer shift could be changed by \(\sim 20 \%\) [26].

The overlap distortion scheme has also been applied in efforts to determine nuclear quadrupole moments. The system Al\(_2\)O\(_3\) was studied by Sawatzky and Hupkes [27] and by Sharma [24a]. Differences in the measured electric field gradient (EFG) of ferrous versus ferric compounds were similarly explained by Sharma [24b, c]. However, an unambiguous interpretation of EFG data is difficult in these models because of the presence of the Sternheimer shielding factors. The inner shielding is determined by perturbed free ion calculations; changes due to the crystalline environment are difficult to estimate [28, 29]. The outer shielding factor is supposed to take into account all fields external to the ion; however, the orthogonalization procedure has similar effects. Apparently a form of consistent molecular cluster approach needs to be developed.

Walch and Ellis made a systematic study of overlap distortion for \(^{57}\)Fe embedded in an argon lattice [30]. Charge density changes at the nucleus, \(\Delta \rho(0)\) were calculated as a function of lattice spacing. Both Hartree-Fock (HF) and Hartree-Fock-Slater (HFS) wave functions were studied, and the expected monotonic increase of \(\Delta \rho(0)\) with lattice compression was found, as shown in figure 3. However, by making HFS variational molecular orbital calculations on an FeAr\(_2\) cluster, they were able to show that relaxation effects were very important, vide infra.

In a recent study of properties of FeCl\(_4\) anions, Ellis and Averill investigated the overlap distortion model for both HF free-atom and free-ion (Fe\(^{3+}\), Cl\(^-\)) wavefunctions [31]. As might be expected, free-atom and ionic models give very different \(\Delta \rho(0)\) and slopes \(\partial \Delta \rho/\partial R\) near the equilibrium bond length (see Fig. 4). Since the effective atomic configuration is doubtless somewhere between these two extremes for (FeCl\(_4\))\(^{-1}\), the predictive power of the OAO scheme seems rather dubious. Results of more rigorous first-principles molecular calculations are discussed in the following section.
3.3 First-principles calculations. — Despite the large number of first-principles MO calculations performed in recent years, very few studies of charge and spin densities have been made. Most published results are limited to energy levels, and occasionally, a Mulliken population analysis. The population analysis has been very useful and popular for restricted (minimal basis) variational calculations. However, as more accurate wave functions are achieved by expanding the MO basis sets, the utility of the Mulliken analysis is lost. The only alternative remaining is the direct numerical calculation of the density from the occupied MO eigenfunctions.

For transition metal complexes such as (FeF₃)³⁻ both HF and HFS one-electron methods are feasible. If the complex is assumed to be representative of the environment in, say, the KFeF₃ crystal one can obtain variational MO's with reasonable precision. For more complex geometries and for systems containing rare-earth and heavy metal atoms, only the HFS method is computationally feasible. It is important to note that neither HF nor HFS theories can be expected to produce highly accurate charge and spin densities. The work of Benesch and Smith [32] and Naon and Corlille [33] among others, shows that correlation effects on charge and momentum densities in atoms are important. Das and coworkers [34] have found similar important effects on spin densities and hyperfine fields. Thus the main hope of one-electron theories is to provide quantitative estimates of charge density differences Δρ between rather similar systems. With these caveats in mind, we proceed to discuss recent attempts to obtain Δρ(0) by variational methods.

3.3.1 Hartree-Fock-Slater approach. — The matrix isolation experiments of Barrett and collaborators [35] are of particular interest to theorists, since the interpretation of results in terms of free atom (ion) models seems most justifiable. The HFS molecular cluster model was employed by Walch and Ellis [30], using a Discrete Variational Method (DVM), to study the isomer shift of an FeAr₁₁ cluster embedded in an argon matrix. The DVM is characterized by the use of a basis set to expand the molecular eigenfunctions (Slater-type orbitals were used in the present case), and matrix elements of the complete Hamiltonian are calculated by a numerical integration (sampling) procedure. No approximations in the form of the potential are made [30].

The theoretical results show that potential distortion (relaxation) effects are important even at the large Ar lattice spacings (R₁₁-Ar = 7 a. u.). The calculated Δρ(0) is found to have sign opposite to that predicted by the overlap distortion model discussed previously, with an effective iron configuration somewhere between the neutral atom and Fe⁺⁺ (see Fig. 3). Since the HFS model was not iterated to self-consistency, the absolute value of Δρ(0) is probably uncertain by ~ 30 %.

As a second example we briefly discuss the results
of Byrom et al. [36] on the IS and magnetic form factors of yttrium iron garnet (YIG). In YIG one finds two distinct Fe sites: a slightly irregular octahedron \((\text{FeO}_6)^{8-}\), and a slightly irregular tetrahedron \((\text{FeO}_4)^{5-}\). The neutron scattering form factors of the two sites have recently been shown to be different [37], and the difference in isomer shifts is well known [38]. Since in both cases one is nominally dealing with the \(\text{Fe}^{3+}\) ion, the measured differences can be ascribed to covalency. From a computational point of view, a maximum cancellation of errors (including correlation errors) can be anticipated in treating the two clusters in the MO approximation, so YIG forms an excellent test case. A series of non-self-consistent HFS-DVM calculations were made; it was found essential to include the potential field of a large number of surrounding ions to obtain stable meaningful results. While the results must be called preliminary, Byrom et al. find striking agreement with the experimental IS results (if \(a\), the calibration constant, is taken to be 0.33), and a good qualitative description of the neutron form factor differences, arising from greater covalency in the tetrahedral cluster.

Ellis and Averill studied the optical spectra, charge densities, isomer shift, and quadrupole splitting of \(\text{FeCl}_4\) anions in the HFS model [31]. In order to avoid restrictions in basis set completeness, they obtained HFS fully self-consistent wavefunctions using the multiple-scattering MS-Xa numerical technique of Johnson and Smith [39].

The MS-Xa method can be briefly described as follows:

(i) The molecular space is divided into spherical atomic regions, an interstitial region, and an exterior region bounded by a sphere around the entire molecule. The HFS Hamiltonian is approximated by generating spherically symmetric potentials in atomic and exterior regions; a constant potential is chosen for the interstitial region. In this muffin-tin potential approximation, different values for the exchange constant may be taken for each region.

(ii) In each spherical region radial Schrödinger equations are solved, and eigenfunctions are obtained in a partial wave expansion. The amplitude of each partial wave is obtained from matching conditions on the spherical boundaries as in the KKR or Green’s Function method of energy band theory.

(iii) The charge density is spherically averaged in each spherical region, and used to calculate a new potential for a self-consistent iterative procedure.

These calculations yielded \(\Delta \rho(0)\) values greater than those predicted by the overlap distortion model near the equilibrium bond length, and outside reasonable values estimated by other workers. Their results are shown in figure 4. This discrepancy was traced to the muffin-tin spherical potential approximation made within the MS-Xa scheme. While this potential approximation is probably also responsible for the poor oscillator strengths found, atomic properties like the \(<r^{-3}>\) quadrupole matrix element appear to be satisfactory.

Larson et al. [40] investigated the MS-Xa scheme further, by calculating properties of a number of \((\text{MF}_6)^{8-}\) transition metal complexes, with a spin-unrestricted procedure. They found that \(\Delta \rho(0)\) depended strongly upon the muffin-tin radii chosen for spherical averaging and that reasonable results could be obtained by adjusting these parameters.

Baerends et al. [41] have developed HFS-SCF numerical methods, using the discrete variational scheme, which do not make such potential approximations. Byrom et al. [42] have developed similar methods which are being applied to IS studies of Eu chalcogenides and Fe impurities in intermetallic compounds.

We have not mentioned relativistic effects on MO calculations; these have generally been included only by multiplication of nonrelativistic \(\Delta \rho(0)\) values by the scale factor \(\alpha'(\varepsilon)\) as given by Shirley [8]. Recently Rosin and Ellis [43] have presented a fully-relativistic Dirac-Slater method for molecules which should prove very interesting for rare-earth and actinide compounds, because of the indirect relativistic effects on metal-ligand overlaps pointed out by Hafemeister.

3.3.2 Hartree-Fock approach. — While the HFS scheme can clearly be extended to heavy atom systems currently beyond the reach of HF methods, there remain some questions about its accuracy, quite aside from problems of computational precision. Thus it will be extremely valuable to compare HF and HFS predictions for charge and spin densities for a variety of 3d-transition metal compounds. The results of atomic comparisons suggest, at the least, that empirical scaling relations can be found [44]. At present an insufficient number of MO calculations have been performed to make these comparisons very useful [45].

Duff performed HF-SCF calculations on the \((\text{FeF}_6)^{3-}\) cluster appropriate to KFeF$_3$ using Gaussian basis sets [46]. Using free-ion \(\text{Fe}^{2+}\) values for the ferrous charge density, he attempted a new calibration of the iron isomer shift, and sought to analyze the considerable differences between published estimates of the calibration constant. This spin-unrestricted all-electron cluster calculation points the way for further studies; however, one should note that effects of the crystalline environment on such anion clusters may be rather large. Further, the assumption made that free \(\text{Fe}^{2+}\) accurately represents the ferrous density introduces considerable uncertainty.

Recently, Post et al. [47] have done a set of HF-MO calculations for two low spin states, \(\text{K}_4\text{Fe(CN)}_6\), and \(\text{K}_4\text{Fe(CN)}_6\), and two high spin states of iron. As in the work of Duff, Gaussians were used as basis functions and the calculations were carried to self-consistency. Their results are shown in figure 5 as a plot of \(\rho(0)\) in (a.u.)\(^{-3}\) units vs. IS in mm/s. A least squares fit for the calibration constant \(a\) yields \(a = 0.31\); if \(\text{K}_4\text{Fe(CN)}_6\) is not included then the results for the other three
FIG. 5. — Charge density \( p(0) \) in \((\text{a.u.})^{-3}\) vs. IS for some Fe cluster calculations (after Post et al. [47]).

compounds gives a better straight line whose slope yields \( \alpha = 0.27 \). One important feature of these calculations is that since the same methods were used for all compounds one expects a certain cancellation of errors to occur.

4. Energy band determinations of charge and spin densities in crystalline solids. — In a crystalline solid, the periodic arrangement of the constituent atoms leads to a situation in which the potential energy acting on an electron as it moves through the lattice is also periodic in space. The energy band method has been developed to exploit this essential simplification due to the periodicity symmetry of the lattice and also explains its great success and concomitant popularity [48]. It is clear that the energy band method has become an increasingly powerful and sophisticated tool for studying theoretically the multitudinous properties of solids. Although relatively little work has been done on the determination of charge (and spin) densities in solids, developments have been so rapid in the last few years that it is important to the work of this conference, with its emphasis on perspectives, to discuss the present status and future expectations in this field. It is important in this context to recall that the manifold successes we have come to expect of energy band theory are all the more remarkable when only some 15-20 years ago very little confidence or physical meaning was attributed to \textit{ab initio} energy band structure. In the last few years, the emphasis has shifted from band structure determinations of the simpler systems (metals and compounds with simple crystallographic structure) to those of more complex structures. More importantly, the focus of these efforts has been towards obtaining \textit{wave functions} and, from these, expectation values of operators in order to compare predictions of calculated observables with experiment and to assess the relative magnitude and importance of many-body effects.

4.1 The energy band method. — The energy band method for calculating electronic eigenstates in crystals is based on a number of simplifying assumptions and approximations which reduce the many-body problem involving the interaction between all the particles in the system, electrons and nuclei, to a one-electron or independent electron model. (The reason for these approximations is clear: the many-body problem for the crystal entails the solution of Schrödinger's equation for \( 10^{23} \) nuclei and electrons and is a completely hopeless task.) It is important to keep these approximations in mind as they are not completely justifiable and may affect seriously some of the physical results obtained [49].

The first of these is the zero order Born-Oppenheimer approximation which essentially amounts to neglecting the electron-phonon interaction and reduces the problem to that of an interacting electron system in the field of fixed nuclear potentials. Actually electron-phonon interactions in metals can cause an enhancement of the measured electron mass and the measured oscillator strength for optical transitions (by a factor of up to 2.5 for some polyvalent metals). The neglect of the electron-phonon interactions does not appear to be so bad for alkali metals as it is for polyvalent metals and in general it does not appear to seriously affect Fermi surface dimensions even though it modifies the density of states obtained from specific-heat measurements. The difficulties inherent in obtaining direct solutions of the many-electron Hamiltonian (cf. eq. (1)) were discussed in Sec. 1, as were the approximations made in arriving at the Hartree-Fock and the Hartree-Fock-Slater methods.

With these approximations, each electron is assumed to experience, as it moves through the crystal, an average but spatially periodic potential, \( V(r) \), due to all the other electrons and nuclei in the crystal. The single particle Hamiltonian, which replaces the complicated eq. (1), is then simply given as

\[
\hat{H}_i = K_i + V(r_i) \quad (\text{all } i) \tag{9}
\]

where \( V(r_i) \) is now a local (and periodic) potential, unlike eq. (1). All the band methods thus reduce the problem into two parts: the choice of the crystal potential and the accurate solution of the Schrödinger (or, in the relativistic case, the Dirac) equation with the assumed potential. High speed computers, good mathematical analysis and programming, have made the second part of the problem relatively easy to solve and have led to considerable confidence in the numerical accuracy of the solutions obtained. The crystal potential problem still remains to introduce uncertainties into the reliability of the resulting solutions.

The solution of the band Hamiltonian, eq. (9), yields eigenvalues, \( E_{n,k} \) which, as labeled, depend not only on the particular band index \( n \) but also on the new quantum number \( k \) which measures the crystal momentum of the electron in the solid. Thus in addition to the compli-
cation of having bands of allowed (and forbidden) energies, instead of the simple discrete electronic energy levels found in atoms and molecules, we need to know (in principle) the $\psi_{n,k}$ and the $E_{n,k}$ at all points in the $k$, or reciprocal lattice, space for the Brillouin zone (BZ) for the given crystal symmetry. The BZ for the body centered-cubic lattice, for example, is shown in figure 6 with the principal symmetry directions labeled in the irreducible 1/48th of the zone.

Of the various methods developed for the calculation of energy bands in solids, the most popular and most widely applied is the Augmented Plane Wave (APW) method [50], which we now describe.

4.2 THE APW METHOD: WAVE FUNCTIONS IN SOLIDS.

The APW method has considerable intuitive appeal; the one-electron states of the crystal are expanded in atomic-like functions for regions near the atomic sites, and in plane waves for regions in the unit cell away from the atomic sites. This basis is physically reasonable and results from considering the crystal potential in the muffin-tin approximation.

In this approximation the unit cell is separated into two regions by nonoverlapping spheres surrounding each atomic site. Inside each sphere the potential is assumed spherically symmetric, and appears quite atomic-like; outside the spheres the potential is assumed constant. This is easy to avoid this last assumption and include the general potential outside the spheres. This so-called warped muffin-tin (WMT) potential [51] is easy to incorporate into the APW formalism and has been used in our calculations.

Since we are after charge and spin densities, we need to understand the nature of wave functions in solids and the complications involved in their determination. A crystal wave function is expanded in augmented plane waves as

$$\psi_{n,k}(r) = \sum_{l} A_{l}(k) \varphi_{n,l}(r)$$  \hspace{1cm} (10)

with the coefficients $A_{l}(k)$ to be determined variationally. The sum is over a set of reciprocal lattice vectors $k_l$, where we have written $k + k_l$. An APW has the following representation:

Outside the spheres

$$\varphi_{n,l}(r) = \frac{1}{\sqrt{\Omega}} e^{i r \cdot k_l}$$  \hspace{1cm} (11)

where $\Omega$ is the volume of the unit cell.

Inside the $v$th sphere

$$\varphi_{n,l}(r) = e^{i r \cdot k_{v}} \sum_{l,m} A_{l,m}(k) R_{l,E}(\rho) \ Y_{m}(\rho);$$

$$| \rho | = | r - r_{v} | < R_{v}$$  \hspace{1cm} (12)

where $R_{v}$ is the radius of the sphere, and $r_{v}$ is the vector to the center of the sphere.

The $A_{l,m}$ are chosen so that each APW basis function is continuous at the sphere boundary. This guarantees that the crystal wavefunction will be continuous; there will remain, however, a slope discontinuity since we are limited to a finite expansion. The $R_{l,E}(\rho)$ are the radial solutions to Schrödinger's equation inside the APW sphere

$$\left\{ - \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{l(l+1)}{r^2} + V(r) - E' \right\} R_{l,E}(\rho) = 0.$$  \hspace{1cm} (13)

The $R_{l,E}(\rho)$ must be regular at the origin, but unlike the atomic case there is no boundary condition at infinity and hence there exist solutions for all values of $E'$. The proper creation of the potential in this equation is of the utmost importance if physically meaningful results are to be obtained. The wave function and eigenvalue are determined by the Rayleigh-Ritz variational procedure as solutions of a standard eigenvalue problem. As discussed in references [48] and [51], the APW secular equation can be solved by finding those $E_i$ which satisfy

$$\det \left| \tilde{H}(E_i) - E_i \tilde{S} \right| = 0.$$  \hspace{1cm} (14)

This procedure is useful for finding the eigenvalues, but is not as convenient for obtaining wave functions. One problem with obtaining eigenvectors is that the normalization is over the region outside the spheres and not over the unit cell. Since we are primarily concerned with obtaining normalized wave functions, it is best to employ the linearized form of the APW method as given by Koelling [52] to solve the equation

$$\tilde{H}(E_0) \ A = E S(E_0) \ A \ S = \text{total overlap matrix}.$$  \hspace{1cm} (15)

The procedure is to pick an $E_0$ and evaluate the resulting eigenvalues $E_i$. If one of the $E_i$ is equal to $E_0$ then
the wavefunction is evaluated. If $E_0$ does not equal an $E_i$, then $E_0$ is set equal to one of the $E_i$ found, and an iteration performed. In practice this procedure converges very rapidly [53].

Having thus obtained, at least formally, APW wave functions $\psi_{n,k}(r)$ for the different bands ($n$) and at different $k$ points in the BZ, the charge density is obtained by summing over the entire volume of the BZ.

To simplify this task, one usually takes a finite (small) number of points into the summation with a weighting factor $S_{n,k}$ for the $k$th point which is given by the local (in $k$ space) density of states for band $n$. Thus,

$$\rho(r) = \sum_n \sum_k S_{n,k} |\psi_{n,k}(r)|^2$$  \hspace{1cm} \text{(16)}$$

where

$$S_{n,k} = \frac{2 \Omega_0}{(2\pi)^3} \Delta A_n^k |V_{n,k} E_n|$$  \hspace{1cm} \text{(17)}$$

and $\Omega_0$ is the volume of the unit cell and $\Delta A_n^k$ denotes the element of surface area at the $k$ point in the zone with energy $E_n$ of the $n$th band.

For calculating the isomer shift, we need to employ eq. (16) which gives the total charge density as a function of $r$. Clearly, since the isomer shift measures only the value at the nucleus, $\rho(0)$, a further simplification may be made of using a spherical harmonic expansion for $\rho(r)$ and selecting only the $s$-part (i. e., the $l = 0$ component).

4.3 SOME FEATURES OF SPIN DENSITIES, CHARGE DENSITIES AND ISOMER SHIFTS IN METALS. — Having described the theoretical energy band formalism let us look at some recent work which, although approximate in nature, is on its way towards giving a detailed understanding of the various factors involved in the determination of solid state charge (and also spin) densities and their relation to isomer shifts.

4.3.1 Projected density of states and isomer shifts. — As a first approximation, a qualitative understanding of the temperature dependence of the IS may be obtained, as was done for iron metal, from a study of the projected density of states and assuming a constancy to the $|\psi_{n,k}(r)|^2$ values which enter eq. (16). We have written eq. (16) in a somewhat unfamiliar form because, written in this way, eq. (17) shows how one may determine the total density of states, $N(E)$ (one sums the $S_{n,k}$ over all $k$ values and all $n$ bands), which is a quantity of great interest for a variety of solid state phenomena (magnetic susceptibility, specific heat, optical properties). Alternatively, one may also use eq. (17) to determine the band density of states, $N_l(E)$ (merely by suppressing the band summation), or obtaining the $l$-character of the density of states (by using a projection operator to determine the percent $l$-character of the energy bands).

Figure 7 shows the projected density of states results of Maglic and Mueller [54] on paramagnetic iron.
broken down into a conduction electron (or s-like) part and 3d electron parts (having symmetry \( T_{2g} \) or \( E_g \)).

It is seen that the conduction electron density of states shows considerable structure as a function of energy—unlike the usual view that \( N(E) \) be proportional to \( E^2 \) as expected from a free electron model. This figure may be used to understand the IS anomaly at the Curie point \( T_c \) of Fe metal observed by Preston et al. [55a].

Ingalls [55b] first invoked a non-free-electron-like \( N(E) \) which showed a depletion of s-like states due to hybridization and calculated the changes in numbers of s, p, and d electrons in going from well below \( T_c \) to above. Recently, Maglic [54b], attributed the IS anomaly to a decrease in \( n_d \) (the number of d electrons) of 0.02 from the main peak (van Hove singularity) in the density of states (Fig. 7). More recent work has shown the general validity of the Maglic and Mueller observation about the need for realistic, and at times, sharp structure to be expected from projected densities of states. As a further example of this effect, we show the density of states results of Das et al. on hcp Sc metal into its constituent s and d parts [56] in figure 8. As pointed out by

Freeman et al. [57] in their work on Pt metal, such sharp structure in the density of states for bands having \( l = 0 \) character would also result in a strong temperature dependence of the Knight shift and cause a breakdown of the usual method of analyzing such data.

As stated, the simple analysis based on structure in the density of states assumes little variation in the character of the wave function (cf. eq. (16)). We shall see that this is not correct, as is shown by more detailed investigations. In figure 9 we show the percent \( l \) character of the APW wave function inside the APW sphere in bcc Cr metal for the different bands as found by Harmon [58].

4.3.2 Wave function character and charge and spin densities in Gd metal. — What about the wave functions themselves? What do they look like and how do they vary with energy and position inside the BZ? Recent studies have given some answers to these questions and show the present state of the art in this field. The case of Gd, an hcp rare-earth metal, is very instructive to consider in this context.

The rare-earth metals are distinguished by their unique and rather unusual magnetic, electric and
optical properties [58]. Extensive studies during the last decade have provided a fairly deep understanding of their electronic structure and properties [58]. The open shell of atomic-like (highly localized) 4f electrons is responsible for their large magnetic moments and their exotic magnetically ordered structures. The conduction electron band structure of the rare-earth metals has been determined in a number of band structures studies [59]. The first band calculations [60] showed that the band structures for these metals were similar to those of the transition metals, with high d band density of states and with Fermi surfaces unlike those expected for nearly free electrons [59]. There is now sufficient evidence to indicate that the APW method, using a muffin-tin potential and the Slater exchange approximation, yields a very reasonable energy band structure for the rare earth metals.

Consider now the resulting eigenfunctions and spin densities. For comparison with the band results and because it gives some insight into the behavior expected (and found) for the wave functions in the solid we show in figure 10 the spin polarized 5d radial functions obtained from an atomic calculation for Gd. (Also shown in the figure is the spin up 6s orbital and the position of the sphere radius.) The peak in the well localized 4f density is located near \( r = 0.7 \) Bohr radii, well inside the outer maximum of the 5d function. The spin polarized radial functions in figure 10 follow the exchange polarization rules observed by Freeman and Watson [61]. Here the 5d spin up function experiences

\[
GADOLINIUM
\]

\[
E=1\text{ Ry}
\]

\[
4f
\]

\[
\text{SPHERE RADIUS}
\]

\[
(a)
\]

\[
GADOLINIUM
\]

\[
E=3\text{ Ry}
\]

\[
4f
\]

\[
\text{SPHERE RADIUS}
\]

\[
(b)
\]

\[
GADOLINIUM
\]

\[
E=7\text{ Ry}
\]

\[
4f
\]

\[
\text{SPHERE RADIUS}
\]

\[
(c)
\]

\[
\text{RADIUS (a.u.)}
\]

\[
\text{RADIUS (a.u.)}
\]

\[
\text{RADIUS (a.u.)}
\]

**FIG. 11.** — The radial density of the different \( l \) components of the wave functions at \( a) E = 0.1 \text{ Ry}, b) E = 0.3 \text{ Ry} \) and \( c) E = 0.7 \text{ Ry}. The radial functions have been normalized to \( \frac{1}{2} \) inside the Wigner-Seitz sphere. The 4f eigenvalue is \( -0.55 \text{ Ry.} \) The 4f function has also been normalized to \( \frac{1}{4} \) instead of \( 7 \) for convenience in plotting the figure.
a net exchange attraction to the spin up 4f electrons which pulls them radially inward. The 5d spin down functions have a zero exchange interaction with the 4f electrons in Gd and are not so affected. What is clear from figure 10 is that the net 5d radial spin density (spin up density minus spin down density) is negative in the outer regions (large r values) in a free atom for which the up and down spin orbitals are equally occupied.

The work of Harmon and Freeman [63] on both ferromagnetic and paramagnetic Gd metal has elucidated the behavior of the charge and spin densities in these metals. Figure 11 shows how the different l radial functions in paramagnetic Gd metal change as the energy increases. The bottom of the s-like conduction band (at \( \Gamma \), in the Brillouin zone) occurs near \( E = 0.1 \) Ry. At \( E = 0.3 \) Ry the d bands are beginning to be occupied and have a very diffuse density. Above the Fermi energy (\( E_F = 0.353 \) Ry), the bands are unoccupied, and the \( l = 2 \) function becomes more contracted—finally resembling an atomic 5d orbital near \( E = 0.7 \) Ry. These figures give a good intuitive feel as to how the radial parts of the wave functions depend on energy. The overlap of the \( l = 2 \) radial function with the 4f orbital is seen to increase much more rapidly from figure 11a to figure 11c than the overlap of the \( l = 0 \) or the \( l = 1 \) functions. The striking change of the \( l = 2 \) function with increasing energy is in contrast with the smaller but not insignificant changes occurring in the \( l = 0 \) function. The great difference between the \( l = 0 \) function and the atomic 6s function results in part from the different boundary conditions to be satisfied and from the fact that the atomic 6s function cannot fit into the Wigner-Seitz cell. [It should be mentioned that similar effects have been observed [64] for the case of hcp Sc metal; this is to be expected from the strong similarity of properties seen for Sc (and Y) and the heavy rare-earth metals.]

For the case of ferromagnetic Gd, a set of spin polarized energy band calculations were carried out by Harmon and Freeman [63]. The spin density for the crystal was obtained from the spin up and spin down charge densities which were calculated from a sum of occupied wave functions. The spherically averaged densities are shown in figure 12. The increase in the charge density near the sphere radius is from the \( l = 0 \) and \( l = 1 \) character of the wave functions, while the large shoulder (at the maximum of the atomic 5d function) comes from the \( l = 2 \) character and gives a spin density of predominantly d character. Harmon and Freeman have used the APW charge and spin densities to determine [63] the contribution to the neutron magnetic form factor of the conduction electrons in Gd measured by Moon et al. and to calculate [65] the magnon dispersion relation, \( J(Q) \), for Gd observed by inelastic neutron scattering experiments (Isomer shift calculations were not undertaken.) Since good agreement with experiment has been obtained, an increased measure of confidence in the validity of the APW approach to the charge density problem is warranted.

4.3.3 Induced magnetization density and form factor of Pd metal. — Having described results for a metal with few conduction electrons (3 each for Gd and Sc) and noted the large expansion of the radial functions (particularly for the \( l = 2 \) or d-like component) we must hasten to describe results for a metal, Pd, with an almost full band of electrons where the (APW) solid state wave functions actually show a substantial contraction relative to the free atom value. Freeman, Harmon and Watson-Yang [66] have reported the results of APW calculations on Pd metal which have yielded the first theoretical determination of a neutron magnetic form factor for a paramagnetic metal from \textit{ab initio} solid state wave functions. The essential features of the energy band structure of Pd metal include a strongly hybridized s-like and d-electron band structure typical of an fcc transition metal, a high density of states at the Fermi energy and a complex Fermi surface arising from the crossings of three bands (bands 4, 5 and 6) with the Fermi energy.

The neutron magnetic form factor of Pd metal is the Fourier transform of the total magnetization density induced by the external magnetic field (enhanced by the exchange interactions of the interacting electrons at the Fermi energy). Since the induced moment is very small, it is clearly a reasonable approximation to consider only those electrons close to the Fermi energy to be responsible for the observed magnetization. To obtain a spin density from the field induced uncompensated

\[ \rho_\uparrow - \rho_\downarrow \]
FIG. 13. — Some radial densities inside the APW sphere in Pd for the 6th band and different $k$ points in the BZ; also given are the $l$ decompositions in percent (after ref. [66]).

FIG. 14. — Individual spherically averaged normalized spin densities for the 4th, 5th and 6th bands (cf. eq. (7) of the text). The Hartree-Fock density for the free Pd$^{+2}$ ion is compared with the very contracted 5th band spin density shown as a dashed curve in the center panel (after ref. [66]).

states, Freeman et al. [66] first calculated a local density of states function for the $j$th band ($j = 4, 5, 6$) [cf. eq. (17)] by dividing the Fermi surface into surface elements $\Delta A$, and calculating the associated gradient of the energy at the representative point $k_i$. In this way they determined the total normalized spin density from eq. (16). The wave functions were calculated separately for the 4th, 5th, and 6th bands at 87, 368 and 181 different points respectively on the Fermi surface. Figure 13 shows the results of the individual spherically averaged, normalized band spin densities, $P_l(r)$, determined for each of the bands. It is clear that both the 4th and 5th bands have a localized distribution arising from the $l = 2$ (or d-like electrons); by contrast, the 6th band density is much more expanded indicating the large s and p-like character of some of its wave functions. The percentage $l$ character for some selected radial wave functions at different $k_i$ points on the
THEORETICAL DETERMINATIONS OF CHARGE AND SPIN DENSITIES

Fermi surface for the 6th band is given in figure 14 along with plots of the radial density inside the APW sphere. The figure shows the correlation between percent $l$ character and radial dependence of the radial density.

A surprising finding of the results shown in figure 13 is that the dominant 5th band contribution yields a spin density which is even more localized than the Hartree-Fock spin densities obtained by Freeman and Watson [67] for the free Pd$^{2+}$ ion. This is all the more remarkable when one recalls that the solid state potential is derived from a superposition of neutral free atom densities taken from the Hartree-Fock-Slater calculation with an assumed $4d^{10}$ configuration in which the 4d radial density is much more expanded spatially than the $4d^8$ ionic configuration. The explanation for the contraction lies in the fact that the wavefunctions at the top of a given band of electrons must satisfy the strong boundary condition that requires them to be antibonding functions, i.e., odd under reflection across the Wigner-Seitz boundary; this solid state condition forces the radial wave function to go to zero at the boundary of the cell rather than at infinity as required of free atom wave functions.

The induced magnetic form factor results are found to be in excellent agreement with the recent experiments of Cable et al. [68] and tends to confirm the validity of the energy band approach for the determination of magnetization densities in metals. (In this case the magnetization density at the Fermi energy is identical with the charge density.)

4.3.4 Wave functions in the actinide metals. — As a final example, we describe some results for the actinide metals. The atomic structure of the actinides consists of a partially filled 5f shell outside the radon core and several electrons in the atomic 6d and 7s levels. Whereas, most of the rare-earth metals (with the exception of Eu, Yb and one phase of Ce) are thought to have three valence electrons, there is some uncertainty as to the correct configuration in the actinide metals. This is particularly important for the band calculations when one considers the proper atomic charge densities to be used in making up the crystal potential. One expects the 5f electrons to contribute to the conduction processes in the metal along with the 6d and 7s electrons. (In the rare-earth metals, the 4f electrons are sharply localized in energy and do not contribute to the conduction processes.)

It is instructive to examine the relative outer radial extent of the atomic electrons in an actinide atom. In figure 15 we show the relative outer radial extent of the atomic electrons for Pu determined from relativistic HFS atomic calculations [69]. They found that localization and intra-atomic Coulomb correlations are of prime importance for understanding the behavior of the 5f electrons and hence of many of the properties of the actinides metals. For the lighter actinides, U through Pu, they found that the overlap between 5f electrons on neighboring atoms was large, their effective band width due to overlap and hybridization with the 6d-7s-p bands large compared with the Coulomb correlation energy and that an itinerant (or delocalized) description was appropriate. The band structure and Fermi surfaces resulting from this description were expected to agree with experiment when available.

By contrast, the 5f electrons in the heavier actinides, Am through Bk and beyond, were found to be more appropriately described by a localized picture. Here the 5f electrons are more localized spatially, do not overlap greatly their neighbors, the location of their states in energy is very sensitive to the choice of exchange parameter, do not hybridize significantly with the 6d-7s-p bands, and have small effective band widths relative to the large intra-atomic Coulomb correlation energy. As a result, the energy band or itinerant description is not appropriate for the 5f states in these metals. One immediate consequence of the localization of these...
electrons is the possibility of magnetic ordering in these metals just as in the rare-earths. For Am metal, and assuming a trivalent configuration as in the rare-earths, the $f^6$ localized configuration results in a $J = 0$ ground state and hence no localized magnetic moment and thus no magnetic ordering. For Cm, Bk and beyond, $J \neq 0$ and magnetic ordering of their local moments can easily occur; indeed, both Cm and Bk do exhibit magnetic ordering.

Since the question of the spatial dependence of wave functions in the actinides is also of interest to our discussion in this paper, let us examine some of the limited wave function results available to date. Let us consider some of the results obtained by Koelling and Freeman [71] for bcc-uranium metal. As mentioned above, perhaps the most significant feature to be seen from the calculations is that the $f$ states do have sizeable bandwidths and, although they are sensitive to the potential, they hybridize with a rather stable (i.e., insensitive to potential) transition metal-like set of bands. To illustrate the band-like behavior of the $f$-character electrons, figure 16 shows the radial charge density of the $f$-character ($l = 3$ part of the wave function) at several energies throughout the band structure range. Only the shapes are significant here, neither of the axes is labelled. The radial distance (on the horizontal axis) is linear with the radius of the core. As one moves up in energy, this OPW like character dies away and the charge density looks more like that from a tight-binding system. Only when one arrives at the top of the $f$ state region — or perhaps a bit above it — does one find the charge density looking like an atomic $5f$ confined to a single site. This appears to be a very convenient graphic way to appreciate the itinerant character of the $f$-states in this system.

Implicit in all this discussion is the fact that all calculations for the actinides must be done relativistically. Investigations [70, 71] have demonstrated that relativistic effects change the nonrelativistic energy band results in a number of significant ways of which the most important are: the states are split in energy by the spin-orbit interaction by an amount which is usually larger than the crystal field splittings for the $5f$ electrons; and the orbitals of lower angular momentum are shifted downward relative to the higher angular momentum states. For the wave functions, the relativistic effect is to cause the outer orbitals to expand because the relativistic contraction of the core electrons causes a greater screening of the effective nuclear charge acting on the valence electrons. Figure 17 shows a comparison of the relativistic and nonrelativistic APW $7s$-like electron in the conduction band of neptunium metal [72] for different energies in the band. The enormous spatial expansion of the relativistic radial wave function is striking.

![Figure 16](image1.png)

**FIG. 16.** — Radial charge densities of the $\kappa = 3$ component at various energies through the energy range of the band structure. As only shapes are significant here, neither of the axes is labelled. The radial distance (on the horizontal axis) is linear with $0 < R < \text{R_{core}} = 2.806\,\text{Å}$. The normalization of the charge density is determined by the requirement that the plot just fill the frame [71].

![Figure 17](image2.png)

**FIG. 17.** — Comparison of the relativistic and nonrelativistic $7s$-like radial function in Np metal [72].

### 4.4 Band-Theoretical Calculations of the Isomer Shift

Now that we have discussed some specific examples of results obtained for charge and spin density calculations from band-theoretical wave functions, we turn to the very small number of applications made so far for the isomer shift. There are several problems in assessing the accuracy of IS results from any band calculation:

(i) Convergence with respect to basis — have a sufficient number of APW's, OPW's, or tight-binding functions been used?

(ii) Convergence with respect to potential — is it self-consistent, or do other calculated properties agree with experiment?

(iii) Correlation effects — just how good is the particular one-electron model used to construct the band model?

Clearly a sizeable number of calculations, soon to be forthcoming, will be required to clarify these questions. The early HFS work of Wakoh and Yamashita [73] on the internal field and isomer shift of metallic iron and nickel marks a significant application of the APW method to the IS problem. Further refinements of that
work are being made, since self-consistency effects have been found to be sizeable [74]. The problem of ferromagnetic iron was also taken up by Duff and Das [75] who made use of an OPW method. In this work, the question of correlation corrections to the HF framework was seriously attacked for the first time. Since that time it has become clear that HF band structures must be heavily corrected, in order to describe most excited state properties; however the role of correlation in ground state (especially one-electron) properties is thought to be rather small.

In order to retain a simple theoretical model which does not require the full apparatus of self-consistent band calculations, several workers have preferred to develop a pseudopotential model, or to explore several empirical schemes. Ingallsfield made an early application of the pseudo-potential (PP) method in studying the IS of α-Sn, β-Sn, and SmMg₂. In order to keep the size of the problem manageable, only a few plane waves were used; however, the results were quite reasonable [76]. The PP approach has also been applied with some success to iron [77]. Since the PP approach ultimately becomes equivalent to the complete OPW scheme as basis functions are added, it probably is best used as an empirical procedure for fitting observed data as is the practice in treating optical properties. This approach could be very helpful in interpreting the behavior of complex systems. For example, recent PP studies by Ingalls [78] on volume and charging effects in alloy isomer shifts for d-atom impurities in d-band hosts provides a good insight for the experimental data.

First-principles APW calculations have been applied to dysprosium metal [79] and to the alloys DyZn, DyCu, and DyRh [80]. The kind of linear correlation that can be expected between calculated charge densities $\psi(0)^2$ and measured isomer shifts is shown in figure 18. Although the slope of the curve may well change somewhat after self-consistent iterations, the results should provide encouragement for much future work.

**Acknowledgements.** — We are indebted to a large number of colleagues, and collaborators at Northwestern University and Argonne National Laboratory, for helpful comments and for making available to us some of their as yet unpublished results quoted in the text.

**References**


