

"Invited talk presented at the International Conference on Hyperfine Interactions Studied in Nuclear Reactions and Decay, Uppsala, Sweden, June 10-14, 1974. To be published in Physica Scripta."

HYPERFINE INTERACTIONS AND ESCA DATA\*

D. A. Shirley

Department of Chemistry  
and Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

\* Work performed under the auspices of the U. S. Atomic Energy Commission.

2  
19

HYPERFINE INTERACTIONS AND ESCA DATA

D. A. Shirley

Department of Chemistry  
and Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

June 1974

Abstract

A comparison is made of those data obtained from ESCA and from hyperfine interactions that bear on the same problems. A formal Hamiltonian can be written in which ESCA shifts and structure are discussed as  $E_0$ ,  $M_1$ ,  $E_2$ , ... terms. Under the  $E_0$  term core-level shifts are compared with isomer shifts and diamagnetic shifts. The  $M_1$  term refers to exchange splitting (core polarization). Multiplet splitting can identify local moments with fluctuation times down to  $10^{-15}$  sec. Rare earths and the 3d group are considered. The  $E_2$  term yields a crystal-field energy transforming as  $Y_2^0$  and correlated with  $e^2qQ$  in metals. Finally the valence-band density of states in noble metals can be related to a  $Y_4$  term if nearest neighbors in metals are effectively negative, i.e., conduction electrons, rather than ion cores, are dominant.

## 1. Introduction

Hyperfine interactions and ESCA [1] are related in a number of ways. Various aspects of this relationship have been appreciated independently by several authors and have been alluded to in the literature over the last few years. In our Laboratory, for example, an interest in photoelectron spectroscopy began in 1965, when we realized that this method could be used to provide information complementary to that obtained from isomer shifts and from hyperfine field measurements. This led, respectively, to early ESCA studies of two Mössbauer elements--iodine and europium [2]--and to the observation of multiplet splitting in photoemission spectra of transition metals and their salts [3]. Similar work has been carried out in other laboratories and the results have been correlated with other properties, but no systematic discussion of the relation between ESCA data and the properties deduced from hyperfine structure studies has yet appeared. The object of this paper is to provide such a discussion.

It is customary to express the hyperfine interaction Hamiltonian in terms of a multipole expansion,

$$\mathcal{H}_{\text{hf}} = \mathcal{H}(E0) + \mathcal{H}(M1) + \mathcal{H}(E2) + \dots, \quad (1)$$

where the electric monopole (E0), magnetic dipole (M1), electric quadrupole (E2), etc., terms correspond to those moments of the atomic nucleus that are not required to vanish by symmetry. A formally similar approach can be employed to discuss shifts and splitting in binding energies of core electrons. The usefulness of this approach has the

same basis as in the hyperfine structure case. That is, both cases involve the interactions of rather localized states--the nucleus or an electronic core level--with electromagnetic fields arising from more extended charge and/or spin distributions. This is obvious in the nuclear case, but less so for electron core states. That it is in fact a fairly good approximation for core states may easily be appreciated by inspecting the results of atomic Hartree-Fock calculations [4], which show that the average radius,  $R$ , of each successive electronic shell decreases by a factor of  $\sim 3$  going inward from the valence shell. Thus, for Pb,

$$R_{6s} : R_{5s} : R_{4s} : R_{3s} : R_{2s} : R_{1s} = 1 : 0.35 : 0.16 : 0.07 : 0.03 : 0.007 \quad ,$$

for example. Given that any core level has characteristic dimensions significantly smaller than those of even the next electronic shell, a multipole-expansion approach should therefore be reasonably accurate. Of course, this does not require the core orbitals to be treated as point multipoles. Suitable radial integrals can be evaluated to account for radial variations of density, as is done in hyperfine studies of isomer shifts and hyperfine anomalies.

There is an important basic difference between the ESCA core-level and hyperfine-interaction problems. In hyperfine interactions the  $M1$  term really involves magnetic interactions per se, while the " $M1$ " term in photoemission arises from exchange interactions between core states and unpaired valence electrons. It still seems appropriate to separate the " $M1$ " term since like most magnetic hyperfine interactions

it arises from unpaired valence electrons. We note also that ferromagnetism in metals and most salts in fact arises from exchange rather than magnetic effects. Having noted these qualifications, we shall often find it convenient to write an effective Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}(EO) + \mathcal{H}("M1") + \mathcal{H}(E2) + \dots \quad (2)$$

to describe core-level binding-energy shifts for cases that are to be compared with hyperfine-structure data. The terms in Eq. (2) will be treated separately in the following sections.

## 2. The Electric Monopole (EO) Term

The  $\mathcal{H}(EO)$  term in Eq. (2) can be written in some detail as the effective total energy of a core-electron orbital. In the ground-state Hartree-Fock approximation  $\mathcal{H}(EO)$  for orbital  $i$  has the form [5]

$$\mathcal{H}_i(EO) = \epsilon_i^0 + \sum_{j \neq i}^n (2 J_{ij} - K_{ij}) + J_{ii} \quad (3)$$

where the sum is taken over  $n$  doubly-occupied orbitals. Here  $\epsilon_i^0$  is the one-electron energy while  $J$  and  $K$  are respectively the two-electron Coulomb and exchange terms. It is easy to show through a straightforward series of approximations that changes in  $\mathcal{H}_i(EO)$  are given with good accuracy by changes in the electrostatic potential energy  $V_i$  at the nucleus to which core level  $i$  belongs; i.e.,

$$\delta \mathcal{H}_i(EO) \cong -\delta E_B^i \cong \delta V_i \quad (4)$$

Here  $E_B^i$  is the binding energy of core level  $i$ . In a further approximation  $V_i$  may be represented as a sum over point charges on the host atom ( $q_i$ ) and surrounding atoms ( $q_k$ ),

$$V_i = kq_i + \sum_{k \neq i} \frac{e}{R_{ik}} q_k \quad (5)$$

Here  $k$  is a constant characteristic of a given element and  $R_{ik}$  is an internuclear distance. This result may be compared with the isomer-shift expression

$$IS = (\text{const}) |\Psi(0)|^2 \quad (6)$$

where  $|\Psi(0)|^2$  is the total electron density at the nucleus. In comparing measured values of  $\delta E_B^i \cong -\delta V_i$  with IS values for a given core level and isomeric transition in a series of compounds, correlations will often be found. They can usually be rationalized in terms of (perhaps over-) simplified models of molecular structure, and in some cases even used diagnostically. This approach seems most promising for cases in which quadrupole coupling constants are also available, as in iodine and xenon compounds. The reason for this is that  $\delta E_B^i$  is sensitive, through  $q_i$ , to the total number of  $s$  and  $p$  electrons, while IS and  $e^2qQ$  separately measure  $s$  and  $p$  occupation numbers, respectively. Since there is usually some uncertainty about the proportionality constant in Eq. (6), the measurement of  $\delta E_B^i$  provides a valuable fiducial point.

Another point of contact between binding-energy shifts and hyperfine structure arises in the diamagnetic shielding constant  $\sigma^d$ .

Basch [6] showed that the average value of this constant at nucleus  $n$  is given by

$$3mc^2 \sigma_{av}^d(n) = e^2 \sum_{m \neq n} \frac{Z_m}{R_{mn}} + 2 \sum_i \langle i | \frac{1}{r_n} | i \rangle = V' \quad (7)$$

Here the first sum is taken over nuclei and the second over occupied electronic orbitals.  $V'$  differs from  $V$  only in that a term is included in the second sum for the  $1s$  orbital. Clearly,  $\delta V' = \delta V$  to a very good approximation. After substitution of the appropriate physical constants the relationship

$$\delta \sigma_{av}^d = -0.65 \delta E_B \quad (8)$$

is easily derived, with  $\sigma_{av}^d$  in parts-per-million and  $E_B$  in eV. Better estimates of variations in the diamagnetic shielding constant can be made from core-level shifts  $\delta E_B$  than from direct calculation, in most cases. Good correlations of  $\delta E_B$  and the total nmr shielding constant  $\sigma_{av} = \sigma_{av}^d + \sigma_{av}^p$  have been reported for several series of similar compounds. Unfortunately, the paramagnetic shielding constant  $\sigma_{av}^p$  tends to vary much less predictably than  $\sigma_{av}^d$ , thereby seriously limiting the applicability of Eq. (8).

### 3. The Magnetic Dipole (M1) Term

Consider an ion with an open shell whose configuration is  $n\ell^v$  (e.g.,  $Mn^{2+} 3d^5$  or  $Gd^{3+} 4f^7$ ). Such a system has spin  $S = v/2$ , and a contribution to the hyperfine field directed along  $\vec{S}$  of

$$H_{hf}(cp) = 2SH_c(n\ell) \quad , \quad (9)$$

where  $H_c(n\ell)$  is the contact field arising through core polarization by a single  $n\ell$  electron. In  $Fe^{3+}$ , for example,  $H_c(3d)$  is about  $-110$  kOe. There are usually other contributions to the hyperfine field, but we shall not consider them here.

If a core electron is ejected from the  $n$ 's orbital of the above ion, two final states can be formed from the resulting  $n$ 's  $n\ell^V$  configuration. These states and their energies are given by Van Vleck's theorem [7] as

$$\begin{aligned} (n's \ n\ell^V; S_f = S - 1/2) \quad , \quad E = E_0 + \frac{S+1}{2\ell+1} G^{\ell}(s\ell) \\ (n's \ n\ell^V; S_f = S + 1/2) \quad , \quad E = E_0 - \frac{S}{2\ell+1} G^{\ell}(s\ell) \quad . \end{aligned} \quad (10)$$

In this approximation there are two peaks of intensity given by the multiplet ratio of 7:5 and separated by the multiplet splitting energy

$$\Delta E_{ms} = \frac{2S+1}{2\ell+1} G^{\ell}(s\ell) \quad . \quad (11)$$

Since  $H_c(n\ell)$  and  $G^{\ell}(s\ell)$  are both calculable,  $\Delta E_{ms}$  and  $H_{hf}(cp)$  are clearly related. Rather than discuss this relationship, however, we note that the most useful features of both parameters lie in their relationships to local moments in solids. Thus, in the first study of multiplet splitting, Fadley et al. [3] showed that  $\Delta E_{ms}(3s)$  in  $Mn^{2+}3d^5$  (in  $MnF_2$ ) was greater than in  $Mn^{4+}3d^3$  (in  $MnO_2$ ). They subsequently found that local moments exist in iron metal above  $T_c$ , at least on the  $10^{-15}$  sec



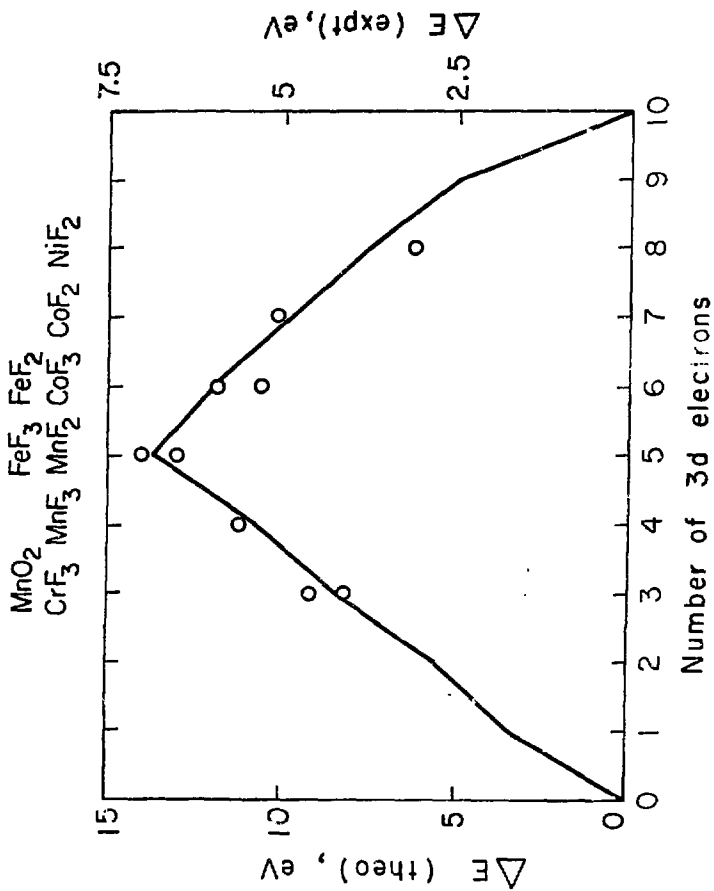
time scale of photoemission [8]. They also found, however, that the spectra deviate from the predictions of Van Vleck's theorem in two important ways:

1. The multiplet ratio is too high, being closer to 2:1 than 7:5.
2. The splitting is only about half the expected value given by Eq. (11).

Both of these discrepancies arise from electron correlation effects. Let us discuss the anomalous splitting first.

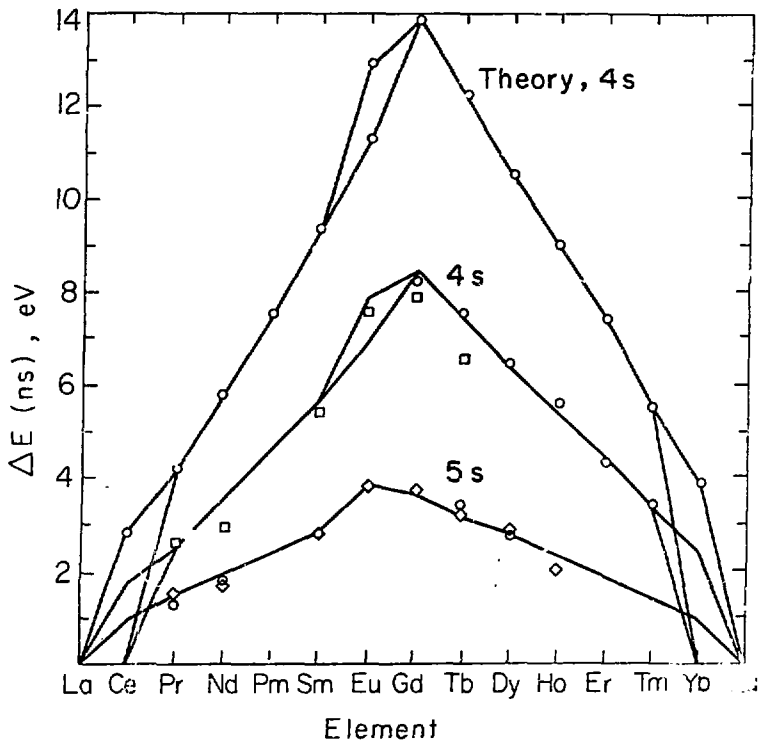
Considerable correlation is expected between the instantaneous positions of 3s and 3d electrons. None is provided for in the low spin ( $S - 1/2$ ) final state, which lies higher in energy. The lower-energy high-spin ( $S + 1/2$ ) final state has a much smaller correlation-energy error, however, because the Pauli Principle keeps 3s and 3d electrons of the same spin projection apart. Thus correlation tends to reduce  $\Delta E_{ms}$ . In fact, in the 3d ions the reduction factor is almost exactly 0.50. This is illustrated in Fig. 1 for the series  $3d^3$  through  $3d^8$ , in which are plotted selected or average experimental values of  $\Delta E_{ms}$  from several sources [3,9,10]. The constancy of this reduction factor can be attributed to pairwise additivity of 3s-3d electron-electron (or hole-hole, for  $n > 5$ ) correlation energies. Since the experimental splitting of 2.7 eV/spin is about equal to the reduction from the value predicted using Van Vleck's theorem and Mann's integrals [11], it follows that the pair-correlation energy is about 1.35 eV per 3s-3d pair.

In the rare earths the reduction factor for 4s-4f interactions is about 0.60, as shown in Fig. 2. The data for rare-earth fluorides



XBL745-3137

Fig. 1



XBL745- 3149

Fig. 2

were reported by Cohen et al. [12], while those for rare-earth metals are preliminary values from our Laboratory [13]. By actually calculating theoretical splittings, rather than plotting  $\Delta E_{ms}$  against  $S$  or  $2S + 1$ , an apparent positive deviation from linearity of the  $\Delta E_{ms}$  values for the heavy rare earths [12] is removed. This apparent deviation is, in fact, a consequence of the fact that  $G^2(4s\ 4f)$  is larger, for a given spin value  $S = n/2$ , in the heavy rare earth configuration  $4f^{14-n}$  than in the lighter element of configuration  $4f^n$ . The same is true for the  $5s$ - $4f$  case. Here, however, there is no appreciable reduction of the experimental  $\Delta E_{ms}$  values relative to the expectations of Van Vleck's theorem. The reason for this is the very small value of the intershell pairwise correlation energy; i.e., the positions of the  $5s$  and  $4f$  electrons are already radially correlated by virtue of having different radial quantum numbers. Wertheim, et al. [10] found a similar result for the  $2s$ - $3d$  correlations in the iron group.

As an illustration of the diagnostic power of multiplet splitting, Fig. 3 shows the splitting recently observed in the  $3s$  peak of paramagnetic  $\alpha$ -manganese [14]. Neutron scattering, a relatively slow technique ( $\sim 10^{-13}$  sec transit time) had shown no localized moments above  $T_N \sim 100^\circ\text{K}$ , while below  $T_K$  the atomic moments are relatively small. The substantial splitting clearly present in Fig. 3 attests to a large moment on the  $10^{-15}$  sec time scale. Comparison to  $\Delta E_{ms}$  values for manganese compounds (Fig. 4) yields a value  $2S \cong 2.4$ , or  $\mu \cong 2.4 \mu_B$  for paramagnetic  $\alpha$ -manganese.

Substantial complications exist in multiplet splitting studies.

To discuss one complication we return to the first point above: the

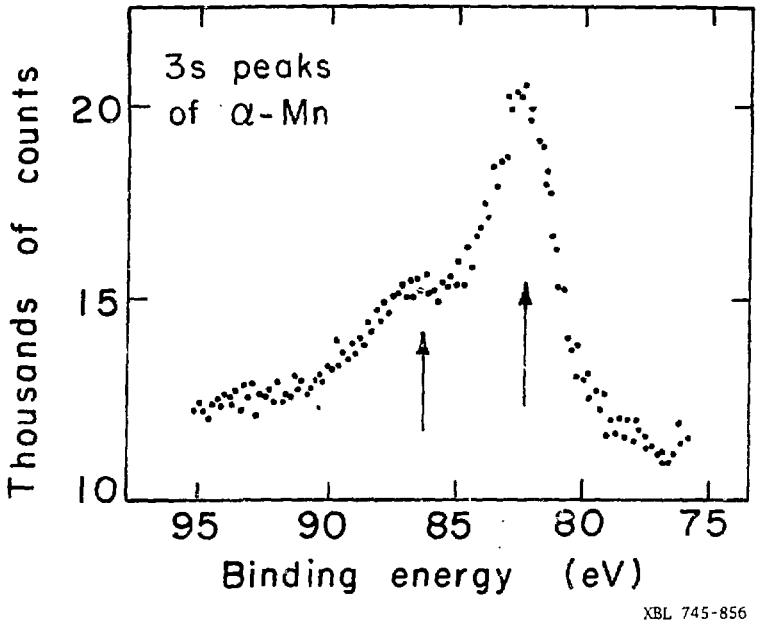
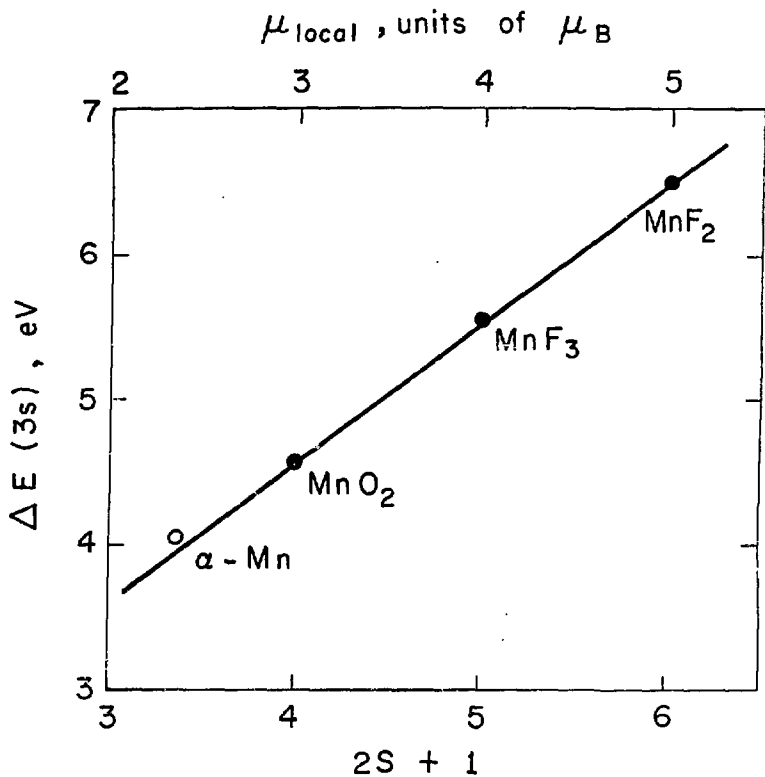


Fig. 3



XBL745 - 3 38

Fig. 4

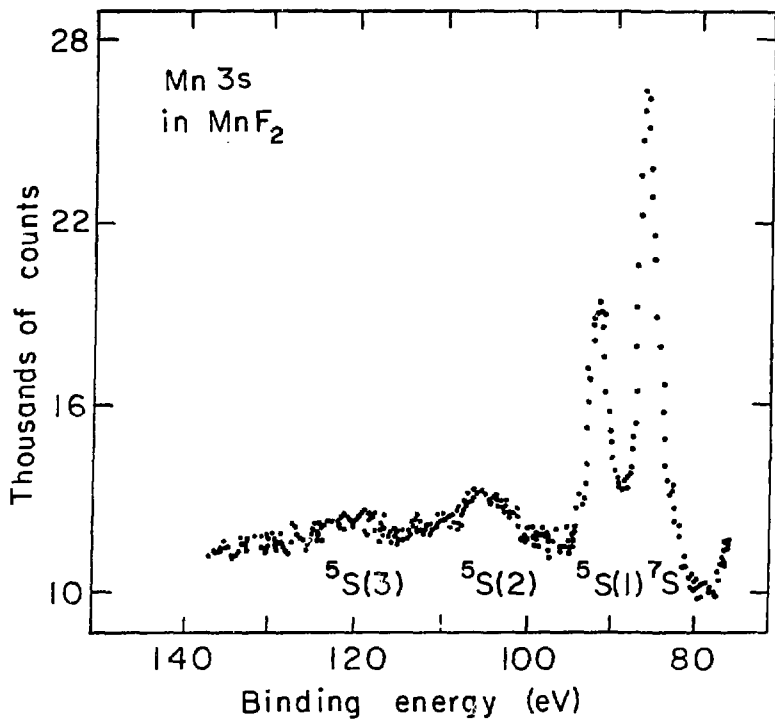
anomalous intensity ratio. The low-spin peak loses intensity to satellites through configuration interaction. These satellite peaks may be observable. Such peaks were predicted [15] in  $Mn^{2+}$  and observed [16] in  $MnF_2$  (Fig. 5).

Further complications exist. Most investigators have attributed at least part of the reduction factor in the 3d group to covalency effects in solids [3,8-10]. Whether this is correct is a moot point at present. Recently, however, Davis et al. [17] have shown theoretically that in molecules the host-atom spin-density is different in the initial and final states. Typical results for  $O_2$ , NO, and  $NF_2$  are shown in Fig. 6. On photoemission the host-atom hole is partially shielded by inward flow of electronic charge through bonding orbitals, while in  $O_2$  and NO spin density is lost. This spin-density migration probably is unimportant in ionic salts, but in covalent compounds and metals it may be an important factor.

In summary, multiplet splitting appears to possess considerable diagnostic value, especially for identifying rapidly fluctuating local moments. There are several complicating factors, but our knowledge and understanding of this effect are increasing to an encouraging extent.

#### 4. The Electric Quadrupole (E2) and Higher Terms

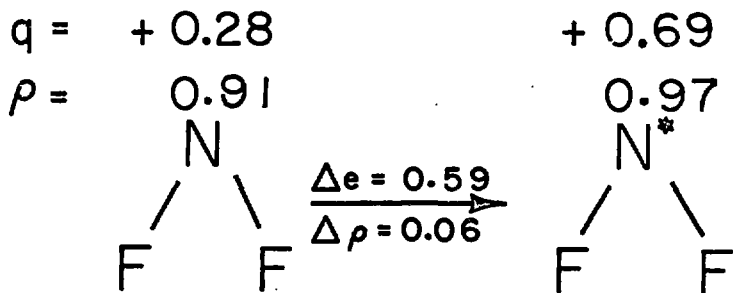
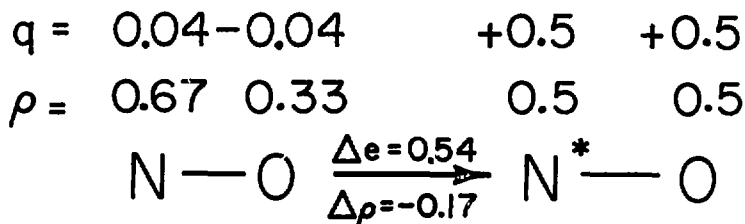
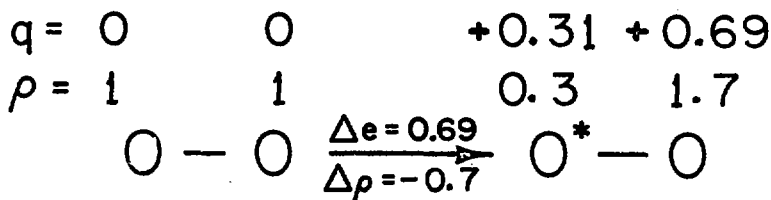
Atomic core states can be affected by crystal-field interactions. This will be apparent in photoemission spectra as deviations from free-atom expectations. In metallic cadmium, for example, the apparent spin-orbit splitting in the 4d shell is 1.0 eV rather than the atomic value of 0.7 eV [18]. The difference can be attributed to a term of  $Y_2^0$



XBL745-3136

Fig. 5





XBL745-3135

Fig. 6

symmetry in the crystal-field potential experienced by the 4d electron hole in the final state. In fact, the excess splitting in Zn, Cd, and In are strongly correlated with the magnitude of  $e^2 q_Q$ , the quadrupole coupling constant, for solute atoms in these lattices [19]. We therefore infer that both effects arise from a term of the form

$$\mathcal{H}(\text{crystal field}) = A_2^0 \sum_i (3z_i^2 - r_i^2) \quad (12)$$

Actually, the form of this Hamiltonian is deceptively simple. Rather than summing over point charges, we must in fact evaluate two-electron Coulomb and exchange integrals involving orbitals on neighboring atoms and the orbital from which photoemission occurs. One-electron-other-nucleus interactions must also be calculated between the active orbitals and other nuclei. Since the neighboring atoms are electrically neutral in metals, and the integrals are weighted as  $1/r$ , electron-electron repulsion dominates electron-nuclear attraction and the net interaction has the sign expected if the neighboring atoms had small ion cores: i.e., the "conduction electrons" rather than the "ion cores" determine the sign of the effective crystal-field potential. This is particularly clear in the fourth-order crystal field effects present in cubic symmetry. The d-band densities of states of Ag and Au can be reasonably well represented by a Hamiltonian consisting of a spin orbit term,  $\lambda \vec{l} \cdot \vec{s}$ , plus a crystal-field term of  $Y_4$  symmetry [20]. A good fit can only be obtained, however, if the neighboring ion cores have effective negative charges.

## References

1. Siegbahn, K., Nordling, C., Fahlman, A., Nordberg, R., Hamrin, K., Hedman, J., Johansson, G., Bergmark, T., Karlsson, S.-E., Lindgren, I., and Lindberg, B. J., ESCA-Atomic, Molecular, and Solid State Structure by Means of Electron Spectroscopy, Nova Acta Regiae Soc. Sci. Uppsaliensis Ser. IV, Vol. 20, 1967.
2. Fadley, C. S., Hagstrom, S. B. M., Klein, M. P., and Shirley, D. A., J. Chem. Phys. 48, 3779 (1968).
3. Fadley, C. S., Shirley, D. A., Freeman, A. J., Bagus, P. S., and Mallow, J. V., Phys. Rev. Letters 23, 1397 (1969).
4. Mann, J. B., Atomic Structure Calculations II. Hartree-Fock Wave Functions and Radial Expectation Values: Hydrogen to Lawrencium, Los Alamos Scientific Laboratory Report LA-3691 (1968).
5. Koopmans, T., Physica 1, 104 (1934).
6. Basch, H., Chem. Phys. Letters 5, 337 (1970).
7. Van Vleck, J. H., Phys. Rev. 45, 405 (1934).
8. Fadley, C. S. and Shirley, D. A., Phys. Rev. A 2, 1109 (1970).
9. Carver, J. C., Schweitzer, G. K., and Carlson, T. A., J. Chem. Phys. 57, 973 (1972).
10. Wertheim, G. K., Hüfner, S., and Guggenheim, H. J., Phys. Rev. B 7, 556 (1973).
11. Mann, J. B., Los Alamos Scientific Laboratory Report 3690 (1967).
12. Cohen, R. L., Wertheim, G. K., Rosencwaig, A., and Guggenheim, H. J., Phys. Rev. B 5, 1037 (1972).
13. McFeely, F. R., Kowalczyk, S. P., Ley, L., and Shirley, D. A., to be published.

14. McFeely, F. R., Ley, L., Kowalczyk, S. P., and Shirley, D. A., to be published.
15. Bagus, P. S., Freeman, A. J., and Sasaki, F., Phys. Rev. Letters 30, 850 (1973).
16. Kowalczyk, S. P., Ley, L., Pollak, R. A., McFeely, F. R., and Shirley, D. A., Phys. Rev. B 7, 4009 (1973).
17. Davis, D. W., Martin, R. L., Banna, M. S., and Shirley, D. A., J. Chem. Phys. 59, 4235 (1973).
18. Pollak, R. A., Kowalczyk, S. P., Ley, L., and Shirley, D. A., Phys. Rev. Letters 29, 274 (1972).
19. Haas, H. and Shirley, D. A., J. Chem. Phys. 58, 3339 (1973).
20. Ley, L., Kowalczyk, S. P., McFeely, F. R., and Shirley, D. A., to be published.

## Figure Captions

- Fig. 1. Experimental values of 3s multiplet splitting in several transition metal compounds (circles and right scale), and theoretical values from Van Vleck's theorem (line and left scale). Scales differ by reduction factor of 1/2. Data are from Refs. 3, 8, 9, and 10.
- Fig. 2. Multiplet splitting of 4s and 5s lines in rare-earth fluorides and metals. Top solid line is theoretical for 4s electrons, using Van Vleck's theorem, connecting theoretical points indicated by open circles, with branches indicating oxidation-state options (e.g.,  $\text{Eu}^{2+}$  or  $\text{Eu}^{3+}$ ). Middle line is the same theoretical line times 0.6, with experimental values from trifluorides (open circles, from Ref. 12) and preliminary results from metals (squares, from Ref. 13). Bottom points are for 5s shell (as above, from Refs. 12 and 13), while line is theoretical, with no reduction factor.
- Fig. 3. The 3s photoemission spectrum of paramagnetic  $\alpha$ -manganese at room temperature, from Ref. 14, showing resolved multiplet splitting.
- Fig. 4. Correlation plot of  $\Delta E$  (3s) versus  $2S + 1$  for manganese, after Ref. 14.
- Fig. 5. The Mn (3s) photoemission spectrum of  $\text{MnF}_2$ , showing  $^5S$  correlation peaks. After Ref. 16.
- Fig. 6. Charge ( $e$ ) and spin ( $\rho$ ) density values for  $\text{O}_2$ ,  $\text{NO}$ , and  $\text{NF}_2$  accompanying 1s photoemission from starred atoms, after Ref. 17.