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INTERPRETATION OF DATA OBTAINED FROM MÖSSBAUER, ESR, SUSCEPTIBILITY, OPTICAL AND XPS MEASUREMENTS

A. Trautwein

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Abstract.- Molecular orbital calculations are designed to calculate the electronic and magnetic structure for molecules or clusters. With the calculated electronic structure (eigenvalues $\varepsilon$ and eigenvectors $\Psi$ of the relevant electronic Hamiltonian) it is in principle possible to evaluate spectroscopic data from corresponding expectation values $\langle \Psi | \varepsilon | \Psi \rangle$, where $\Psi$ represents the initial and $\Psi_f$ the final electronic state, and $\varepsilon$ is the appropriate operator (i.e., $\varepsilon F$ for deriving electron and spin densities, $\varepsilon F$ for electric field gradients, $P$ for dipole moments and transitions, $\varepsilon g$ for magnetic moments). Including energy spacing and Boltzmann population of electronic states in the calculation lead to temperature dependent data. Experimental data obtained from Mössbauer, ESR, susceptibility, optical and XPS measurements are related to the expectation values mentioned above. The calculational procedure will be described, and comparison of calculated and measured data will be presented.

1. Introduction.- The mutual influence of electronic structure calculations and spectroscopic measurements helps the theoretician to test the reliability of the various approximations usually involved in his calculations and the experimentalist to interpret his data. Molecular orbital (MO) calculations are designed to calculate the electronic and magnetic structure of molecules or clusters. In the present communication the basic principle of the calculational procedure (section 2) is described, some common approximate methods are mentioned (section 3), molecular expectation values are defined (section 4), and calculated electric field gradients (section 5), electron charge densities at the nucleus (section 6), internal magnetic field contributions (section 7), magnetic susceptibility and g-factors (section 8), energies (section 9), dipole moments and XPS intensities (section 10) are presented for some compounds and compared with experimental data.

2. Basic Principle.- A molecular system consisting of $N$ nuclei and $n$ electrons is described by the total Hamiltonian, which includes motion and interaction of nuclei and electrons. However, we can restrict ourselves to the electronic part of $H_{\text{total}}$, this assumes that the electrons adjust themselves to new nuclear positions so rapidly, that at any instant the electron motion is just as it would be if the nuclei were at rest at the position they occupy at that same instant (Born-Oppenheimer approximation). Then the electronic system is described by the Hamiltonian (in a.u.)

$$\hat{H} = \sum_{i=1}^{n} \left( \frac{1}{2m_r} \frac{\partial^2 \Psi_i}{\partial \mathbf{r}_i^2} - \sum_{k=1}^{N} \frac{Z_k}{|\mathbf{R}_k - \mathbf{r}_i|} \right) + \sum_{i=1}^{n} \frac{1}{2m_r} \frac{\partial^2 \Psi_i}{\partial \mathbf{r}_i^2}, \quad (1)$$

where $Z_k$ and $\mathbf{R}_k$ are the charge and the position vector of nucleus $k$, and $\mathbf{r}_i$ is the position vector of electron $i$. Each of the $n$ electrons may be associated with a one-electron function $\Psi_i$, called spin orbital, which is a product of a spatial and a spin part: $\Psi_i(\mathbf{r}, \mathbf{s}) = \Psi_i(\mathbf{r}) \chi_i(\mathbf{s})$. The total $n$-electron wavefunction is now built up as an antisymmetrized product of molecular spin orbitals

$$\Psi = (n!)^{-1/2} \begin{vmatrix} \Psi_1(1) & \Psi_1(1) & \cdots & \Psi_1(n) \\ \Psi_2(1) & \Psi_2(1) & \cdots & \Psi_2(n) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_n(1) & \Psi_n(1) & \cdots & \Psi_n(n) \end{vmatrix}, \quad (2)$$

Such an array of spin orbitals, known as Slater determinant, is the simplest wavefunction which satisfies the antisymmetry principle. The electronic part of the total energy of the system is derived from eqs. (1) and (2) by

$$E = \int \Psi^* \hat{H} \Psi \, d\mathbf{r}, \quad \text{by} \quad (3)$$
According to the variational principle, the best molecular orbitals are obtained by varying the one-electron functions $\psi_i$ until $E$ achieves its minimum value. The condition for the minimum of energy leads to the differential equations, also termed Hartree-Fock (HF) equations

$$\left[ -\frac{1}{2} \nabla^2 - \frac{Z_i}{\left| \mathbf{r}_i - \mathbf{r}_j \right|} + \sum_{j \neq i} \left( \hat{J}_j - \hat{K}_j \right) \right] \psi_i = E_i \psi_i , \quad (4)$$

where $E_i$ are orbital energies, and where $\hat{J}_j$ is the Coulomb operator and $\hat{K}_j$ is the exchange operator. The orbitals $\psi_i$ obtained from the solution of these equations (4) are referred to as HF-MO's.

For molecular systems the direct solution of eq. (4) is impracticable. It is more convenient to approximate the HF-MO's by a linear combination of atomic basis orbitals $\phi_{\mu}$ (LCAO)

$$\psi_i (\mathbf{r}) = \sum_{\mu} c_{\mu i} \phi_{\mu} , \quad (5)$$

where the $\phi_{\mu}$ may be Slater type orbitals (STO's) or Gaussian type orbitals (GTO's) or linear combinations of STO's or GTO's. The coefficients $c_{\mu i}$ are now optimized so as to give minimum energy. This procedure leads to a set of equations, which are algebraic (Roothan equations)\(^1\) and for any molecular size much easier to handle than the HF equations which are differential equations:

$$\sum_{\nu} \left( F_{\mu \nu} - E_{\nu} S_{\mu \nu} \right) c_{\nu i} = 0 , \quad (6)$$

with the Fock matrix

$$F_{\mu \nu} = H_{\mu \nu} + \sum_{\lambda \delta} P_{\lambda \delta} \left( J(\mu \lambda, \delta \nu) - \frac{1}{2} K(\mu \lambda, \nu \delta) \right) , \quad (7)$$

the overlap matrix between AO's $\phi_{\mu}$ and $\phi_{\nu}$

$$S_{\mu \nu} = \int \Phi_{\mu}^{*}(\mathbf{r}) \Phi_{\nu}(\mathbf{r}) \, d^3 \mathbf{r} , \quad (8)$$

the bond order or density matrix

$$P_{\lambda \delta} = \sum_{\mu \nu} n_{\mu} c_{\mu \lambda} c_{\nu \delta} , \quad (9)$$

the one-electron energy matrix

$$H_{\mu \nu} = \int \Phi_{\mu}^{*}(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 - \frac{Z_i}{\left| \mathbf{r}_i - \mathbf{r}_j \right|} \right] \Phi_{\nu}(\mathbf{r}) , \quad (10)$$

and the four-center Coulomb and exchange integrals $J(\mu \nu, \lambda \delta)$ and $K(\mu \lambda, \nu \delta)$. The Roothan equations (6) can be transformed to a standard eigenvalue problem, which yields MO energies $E_i$ as well as LCAO-MO coefficients $c_{\mu i}$. Since the Fock matrix depends on the LCAO-MO coefficients $c_{\mu i}$, $c_{\nu j}$ through $P_{\mu \nu}$, the solutions of (6) can achieve selfconsistency by stepwise improvement of $c_{\mu i}$: with an initial guess of $c_{\mu i}$ the Fock matrix $F_{\mu \nu}$ is evaluated and the Roothan equations are solved; this leads to a new set of coefficients $c_{\nu i}$, and so on.

3. Approximations.- Eq. (6) describes closed-shell cases. A generalization of Roothan's equations for open-shell cases is given by separate representation of exchange interaction for $\alpha$ and $\beta$ spins in eq. (6).\(^2\) Calculations in which all integrals are worked out explicitly using Roothan's procedure are termed ab initio calculations. The amount of computation time required for such accurate calculations, especially for large systems, can become extremely high. Thus, for many chemical and physical problems, where qualitative or semiquantitative knowledge of the MO's is sufficient to extract the necessary information, approximations to the Roothan's equations may be considered. A number of approximate MO theories have been developed, as for example Hückel methods\(^3\)\(^-\)\(^5\) (nonextended, extended, extended and iterative), zero differential overlap methods\(^6\)\(^-\)\(^9\) (CNDO, INDO, NDDO, MTND), pseudo-potential methods\(^10\)\(^-\)\(^12\) (one-electron approximation of two-electron contributions by model potentials such as in the X$\alpha$ method).

In the present contribution the electronic structure and expectation values for molecules and clusters have been derived on the basis of the iterative extended Hückel theory (IEHT), in some cases including a limited configuration interaction calculation\(^13\); and for some smaller molecules a model potential method\(^12\) was used.

4. Expectation Values.- In order to compare experimental data with calculated values we define the expectation value of a spatial one-electron operator $\delta = \delta(\mathbf{r})$ for electron charge and spin density, $(3pq - r^2 \delta_m)$ /$r^5$ for electric field gradient, $\mathbf{r}$ for dipole moment

$$\langle \delta \rangle = \sum_{\mu \nu} n_{\mu} \int \psi_{\mu}^{*}(\mathbf{r}) \delta \, \psi_{\nu}(\mathbf{r}) \, d^3 \mathbf{r} , \quad (11)$$
where \( n_i \) is the number of electrons in MO \( \Psi_i \). Substituting the LCAO solution (5) into (11) yields

\[
<\sigma> = \sum \rho_{\mu\nu} (\Phi_{\mu}(r) \delta \Phi_{\nu}(r)) d^2r = \sum \rho_{\mu\nu} <\sigma>_{\mu\nu} \tag{12}
\]

From eq. (12) it is obvious that all molecular expectation values consist of a molecular part \( \rho_{\mu\nu} \), which is directly derived from the MO's \( \Psi_i \) (see eq. (5) and (9)), and of an atomic part \( <\sigma>_{\mu\nu} \), which can be evaluated from the basis AO's \( \phi_\mu \) and \( \phi_\nu \). In Mössbauer spectroscopy where we measure at a specific site \( k \) within a molecular system we may distinguish three different contributions to \( <\sigma>_{\mu\nu} \), depending on:

(i) whether both \( \phi_\mu \) and \( \phi_\nu \) belong to site \( k \) (direct or valence contribution)

(ii) whether only \( \phi_\mu \) belongs to site \( k \), but \( \phi_\nu \) to a ligand (overlap contribution), and

(iii) whether both, \( \phi_\mu \) and \( \phi_\nu \), belong to ligands (lattice or ligand contribution).

5. Electric Field Gradient and Quadrupole Splitting As a first example for calculating expectation values according to eq. (12) we derive electric field gradients (EFG). The corresponding tensor operator for all \( n \) electrons and \( N \) nuclei in the molecule is

\[
\hat{\mathbf{V}}_{pq} = \sum_{i=4}^{\infty} \frac{3p^4q^4 - r_i^4 \phi_i^4}{r_i^6} \tag{13}
\]

In case that core electrons of the Mössbauer isotope are excluded from the LCAO basis set in order to save computer time (i.e. for \( ^{57}\text{Fe} \): \( 1s^2...3p^6 \)), eq. (13) has to be modified by the appropriate Sternheimer shielding function \( \chi(r) \)

\[
\hat{\mathbf{V}}_{pq} = \sum_{i=4}^{\infty} \left[ 1 - \chi(r_i) \right] \frac{3p^4q^4 - r_i^4 \phi_i^4}{r_i^6} \tag{14}
\]

Case (i) and (iii) of section 4 reduces to the well-known expressions

\[
\hat{\mathbf{V}}_{\text{valence}} = \sum_i \left( 1 - \chi(r_i) \right) \frac{3p^4q^4 - r_i^4 \phi_i^4}{r_i^6} \tag{15a}
\]

and

\[
\hat{\mathbf{V}}_{\text{ligand}} = \sum_i \left( 1 - \chi(r_i) \right) \frac{3p^4q^4 - r_i^4 \phi_i^4}{r_i^6} \tag{15b}
\]

It is worth noting at this point that \( \chi \) for iron is not 0.32, which is very often used in the literature, but 0.12 if \( 3d^5 \) belongs to the core\(^{14,15} \), and 0.08 if all 3d electrons are included in the LCAO basis set\(^{15} \). For heavy Mössbauer isotopes (iodine) it might even happen that within about 2 Å \( \chi(r) \) has not yet reached its asymptotic value \( \chi_{\infty} \). \( \text{R}^+ \) and \( \chi_{\infty} \)-values for several elements and ions have been evaluated under various approximations in our group\(^{15} \). The evaluation of the overlap contribution to the EFG, case (ii) in section 4, requires the knowledge of \( \chi(r) \). Figure 1 shows the Sternheimer shielding function for \( \text{Fe}^{2+} \) with (without) \( 3d^6 \) electrons. For the present calculations, of course, the \( \chi(r) \) curve represented by the broken line has to be considered, because the 3d electrons are already included in our LCAO basis set. The contribution (ii) is finally derived from a numerical integration procedure\(^{16} \). In Table 1 we list the various contributions to \( V_{zz} \) for ferrocene, \( \text{Fe}(\text{C}_5\text{H}_5)_2 \), and the iron-pentacyanide-derivative, \([\text{Fe(CN)}_5\text{N}_3]^{3-}\), and compare \( V_{zz} (\eta=0) \) with \( \Delta E_Q^{(\text{exp.})} \).

Table 1: Various contributions to the EFG component \( V_{zz} \) (in \( \text{mm}^{-1} \)) for \( \text{Fe(CN)}_5\text{N}_3 \) and \([\text{Fe(CN)}_5\text{N}_3]^{3-}\); for \( \text{Fe}(\text{C}_5\text{H}_5)_2 \) the asymmetry parameter \( \eta \) is zero, for \([\text{Fe(CN)}_5\text{N}_3]^{3-}\) \( \eta \) takes the values 0.14

<table>
<thead>
<tr>
<th>EFG contributions</th>
<th>( \text{Fe(CN)}_5\text{N}_3 )</th>
<th>([\text{Fe(CN)}_5\text{N}_3]^{3-})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Valence</strong></td>
<td>4.29</td>
<td>-1.55</td>
</tr>
<tr>
<td>From Field</td>
<td>4.17</td>
<td>0.12</td>
</tr>
<tr>
<td>From Ligand</td>
<td>4.20</td>
<td>-1.51</td>
</tr>
<tr>
<td><strong>Overlap</strong></td>
<td>4.21</td>
<td>0.12</td>
</tr>
<tr>
<td>From Field</td>
<td>4.17</td>
<td>0.12</td>
</tr>
<tr>
<td>From Ligand</td>
<td>4.21</td>
<td>0.12</td>
</tr>
<tr>
<td><strong>Ligand</strong></td>
<td>4.21</td>
<td>0.12</td>
</tr>
<tr>
<td>From Field</td>
<td>4.17</td>
<td>0.12</td>
</tr>
<tr>
<td>From Ligand</td>
<td>4.21</td>
<td>0.12</td>
</tr>
<tr>
<td>Total</td>
<td>4.20</td>
<td>0.12</td>
</tr>
</tbody>
</table>

\( \Delta E_Q^{(\text{exp.})} \) = 2.33±0.42 \( ^{10} \) 0.47\% \( ^{10} \)

\( ^{10} \) Due to experimental uncertainties the calculated errors for the total fit in ref. 10.


\( ^{17} \) Wooster, W., Physic., U., Am. 5, 161 (1963).
Further examples for EFG calculations as described above, which are included in this volume, are on garnets (see G. Amthauer et al.), and on Fe(alkyl-dithiocarbamate)\textsubscript{2}Cl, I(see V.R. Marathe et al.).

Also in this volume Lauer et al. present a contribution, which describes the evaluation of Sternheimer factors and functions of various elements and ions.

6. Electron Density at the Mössbauer Nucleus and Isomer Shift.- From eq. (12) we derive the electron charge density at the nuclear site of a Mössbauer isotope as

\[ \rho(0) = \sum_{\mu} p_{\mu} \phi_{\mu}(0) \phi_{\mu}(0). \]  

(16)

It turns out that the overlap and ligand contributions to \( \rho(0) \), case (ii) and (iii) in section 4, are in most cases negligible because of the relatively steep decay of the ligand wavefunctions. However, considerable influence upon \( \rho(0) \) comes from \( p_{\mu} \) and \( |\phi_{\mu}(0)|^2 \), case (i). Taking \( ^{57}\text{Fe} \) again as an example, we consider \( \mu = 1s, 2s, 3s, 4s \). (Relativistic contributions from p-electrons are minor, additionally they are absolutely negligible with respect to differences in \( \rho(0) \) between two compounds\textsuperscript{17}. Rewriting eq. (16) approximately by

\[ \rho(0) \approx 2 \sum_{\mu \neq 1s} \left| \phi_{\mu}(0) \right|^2 \sum_{\mu \neq 1s} \left( 2 - 3p_{\mu} \right) \left| \phi_{\mu}(0) \right|^2 + p_{1s} \left| \phi_{1s}(0) \right|^4 \]  

we distinguish three contributions to \( \rho(0) \): (i) \( \left| \phi_{1s}(0) \right|^2 \) values, given in Table 2 for Fe 3d\textsuperscript{5} and 3d\textsuperscript{6} configuration, indicate the amount of potential shielding of nuclear potential, and its influence upon \( \rho(0) \) by adding one 3d electron to Fe 3d\textsuperscript{5} (potential contribution to \( \rho(0) \)). (ii) The deviation of the elements \( p_{\mu} \) \( \mu = 1s, 2s, 3s \) from 2 describes the amount of interaction of core orbitals with ligand orbitals (overlap distortion contribution to \( \rho(0) \)). Due to the extremely large number for \( \left| \phi_{1s}(0) \right|^2 \) even very small deviations of \( p_{1s,1s} \) from 2 may have influence upon \( \rho(0) \) to a considerable extend. (iii) The bond order matrix element \( p_{4s,4s} \) is a measure of the valence contribution to \( \rho(0) \).

Table 2: Relativistic electron charge densities \( \left| \phi_{\mu}(0) \right|^2 \) in \( a_0^3 \) for Fe 3d\textsuperscript{5} and Fe 3d\textsuperscript{6} configuration. Taken from ref. 18

<table>
<thead>
<tr>
<th>orbital ( \mu )</th>
<th>Fe 3d\textsuperscript{5} ( a_0^3 )</th>
<th>Fe 3d\textsuperscript{6} ( a_0^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>6798.7</td>
<td>6798.9</td>
</tr>
<tr>
<td>2s</td>
<td>644.1</td>
<td>644.1</td>
</tr>
<tr>
<td>3s</td>
<td>90.1</td>
<td>88.4</td>
</tr>
</tbody>
</table>

Post et al.\textsuperscript{19} have derived \( \rho(0) \) values for octahedral FeF\textsubscript{6}- and Fe(CN)\textsubscript{6}-clusters from ab initio MO calculations. Fig. 2 shows the linear proportionality between their calculated \( \rho(0) \) values and experimental isomer shift (\( \delta \)) data according to the relation

\[ \Delta \delta = \alpha \Delta \rho(0), \]  

(18)

with a mean shape of \( \alpha = -0.24 \pm 0.02 \text{ s}_0^{-1} \).

Fig. 2: Calculated relativistic electron charge densities versus measured isomer shifts. Taken from ref. 19

In MO calculations with limited basis set (i.e. without Fe 1s, 2s, 3s) the overlap distortion contribution to \( \rho(0) \) is evaluated from a separate reorthonormalization procedure\textsuperscript{17,18}. For FeP\textsubscript{2} which was represented in the IEHT-MO calculations by a \( \text{[FeP]}_4^- \) cluster, we calculated pressure dependent charge densities \( \rho(0) \), the various contributions of which are shown in Fig. 3 together with the calculated change of Fe 3d and 4s population with pressure\textsuperscript{20}. In Fig. 4 we finally compare pressure dependent isomer shifts with total charge
densities \( \varphi (0) \). The linear dependence according to eq. (18) is well represented in Fig. 4; \( \alpha \) takes a value of \(-0.22 \pm 0.02\) a\( \text{O} \) mms\(^{-1}\).

The overlap contributions to \( \varphi (o) \) from Fe 1s, 2s and 3s orbitals, c) the total overlap contribution \( \varphi_{\text{ov}}(o) \), the potential contribution \( \varphi_{\text{p}}(o) \), the valence contribution \( \varphi_{\text{val}}(o) \), and the total electron charge density \( \varphi (o) \). All \( \varphi (o) \) values in a\( \text{O} \). Taken from ref. 20.

Fig. 3: Calculated (IEHT-MO) pressure dependences for FeF\(_2\) of a) Fe 3d and Fe 4s population, b) the overlap contributions to \( \varphi (o) \) from Fe 1s, 2s and 3s orbitals, c) the total overlap contribution \( \varphi_{\text{ov}}(o) \), the potential contribution \( \varphi_{\text{p}}(o) \), the valence contribution \( \varphi_{\text{val}}(o) \), and the total electron charge density \( \varphi (o) \). All \( \varphi (o) \) values in a\( \text{O} \). Taken from ref. 20.

Fig. 4: Linear dependence between experimental pressure-dependent isomer shifts and calculated relativistic electron charge densities of FeF\(_2\). Taken from ref. 20. Experimental isomer shifts at 300 K relative to metallic iron are taken from ref. 21.

7. Internal Magnetic Field.- The various contributions to the internal field, \( H_{\text{Int}} \), measured at a Mössbauer nucleus, consist of the contact field \( H^c \), the orbital field \( H^l \), the spin-dipolar field \( H^{SD} \), and the supertransferred field \( H^{ST} \).

\[
H_{\text{int}} = H^c + H^l + H^{SD} + H^{ST}. \tag{19}
\]

The contact field \( H^c \) arises from the contribution of the spin density at the nucleus:\(^22\)

\[
H^c = \frac{4\pi}{3} \mu_0 \sum_{a=8} \left[ \left| \chi_{a}(0) \right|^2 - \phi_{a}(0) \right]. \tag{20}
\]

In case that the spin density originates from s-electrons (which have finite charge density \( \varphi (o) \) at the nucleus), eq. (20) can be represented by:\(^23\)

\[
H^c = \frac{4\pi}{3} \mu_0 \varphi (0) < S_s >, \tag{24}
\]

where \( < S_s > \) is the effective spin produced by these s-electrons. On the other hand, if the spin density originates from p- or d-electrons, the spin-paired core-s-electrons may become spin-polarized due to exchange interaction with the p- or d-electrons. Following again Watson and Freeman\(^23\), \( H^c \) then is represented by:

\[
H^c = 2 H^{\text{core}} < S_p,d > + 2 H^{\text{val}} < S_p,d >, \tag{22}
\]

where \( H^{\text{core}} \) and \( H^{\text{val}} \) represent the amount of spin-polarization of core- and valence-s-electrons of the Mössbauer isotope. Both, \( H^{\text{core}} \) and \( H^{\text{val}} \), have to be adjusted to the actual number of d- and p-electrons, because potential shielding effects have considerably influence upon the spin-polarization of the core- and valence-s-electrons\(^23\). From MO calculations the d- and p-population and the effective spin-densities \( < S_p,d > \) and \( < S_p,d > \) are extracted\(^24,25\), thus making the calculation of \( H^c \) straightforward.

The orbital field \( H^l \) arises from the orbital motion of the electrons:

\[
H^l = -2 \mu_B < r^{-3} \times \nabla > L_p, \tag{23}
\]

The total orbital angular momentum \( L_p \) of the electrons around the Mössbauer nucleus is derived according to eq. (12), with usually neglecting cases (ii) and (iii) in section 4.

The spin-dipolar field \( H^{SD} \) is thecontri-
bution from the magnetic moment, which is associated with the spin of the electrons outside the nucleus

\[ H_{\text{pol}} = 2\mu_B \sum_{q} \left( \frac{3p_{q} - \tau_{\text{dip}}}{x_{q}} \right) S_{q} \]  

(24)

Comparing eqs. (24) and (13) it is obvious that the spin-dipolar field is derived in a similar fashion as the EFG. The supertransferred field \( H_{\text{ST}} \) may be evaluated along the lines described by Sawaetzky et al., however, was found to be negligible for the applications presented here.

In Table 3 we summarize the various contributions to \( H_{\text{int}} \) for iron-dithiocarbamate compounds. The comparison with experimental values at the iron nucleus, \( H_{\text{int}}(\text{Fe}(\text{dtc})_2\text{Cl}) = 32.9 \pm 1.0 \) T, \( H_{\text{int}}(\text{Fe}(\text{dtc})_2\text{I}) = 17.2 - 12.4 \) T, and at the iodine nucleus, \( H_{\text{int}}(\text{Fe}(\text{dtc})_2\text{I}) = 5.3 - 6.7 \) T, indicates that the agreement between calculated and measured magnetic data is quite satisfactory. (Further details of the calculation concerning the electronic and magnetic structure of \( \text{Fe}(\text{dtc})_2\text{Cl},\text{I} \) is presented in V.R. Marathe's et al contribution in this volume.)

Table 3: Calculated magnetic data (see text) for \( \text{Fe}(\text{dtc})_2X \) (with \( X = \text{Cl},\text{I} \)) at the iron and iodine nucleus, respectively. Values of \( H \) are given in Tesla. Taken from ref. 27

<table>
<thead>
<tr>
<th>( X = \text{Cl} )</th>
<th>( X = \text{I} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_{3d} )</td>
<td>1.25</td>
</tr>
<tr>
<td>( H_{1s} = 3 \pm 0.2 )</td>
<td>-21.2</td>
</tr>
<tr>
<td>( H_{1s} = 4 \pm 0.2 )</td>
<td>+1.8</td>
</tr>
<tr>
<td>( H_{1d} = 5 \pm 0.2 )</td>
<td>+5.5</td>
</tr>
<tr>
<td>( H_{1d} )</td>
<td>-0.9</td>
</tr>
<tr>
<td>( H_{1d} )</td>
<td>5.7</td>
</tr>
<tr>
<td>( H_{1d} )</td>
<td>5.150.3 (g)</td>
</tr>
</tbody>
</table>

(a) The actual value for \( \langle S_{3d} \rangle \) which is used in the calculation of \( H_{\text{int}} \) contributions is 1.14 - \( \frac{1}{2} \), since at 1.4 K, where measurements have been performed, only the \( \frac{1}{2} \) Kramers doublet is populated.
(b) Calculated with bond order matrix elements instead of orbital charges \( q_{3d} \) and \( q_{4s} \).
(c) Calculated from the LCAO coefficients of the singly occupied MOs. (Includes factor \( \frac{1}{2} \); see (a)).
(d) Overlap contribution which comes from a Mulliken population analysis of singly occupied MOs. (Includes factor \( \frac{1}{2} \); see (a)).
(e) Core polarization contribution.
(f) Direct 5s contribution.
(g) All \( H_{\text{int}} \) contributions are negligible.

8. Magnetic Susceptibility and Gyromagnetic Tensors. Magnetic susceptibility and gyromagnetic tensors (\( \chi_{pq} \) and \( G_{pq} \)) describe the interaction of the magnetic moment of an electronic system with an externally applied magnetic field \( \mathbf{H} \). The temperature dependence of \( \chi_{pq} \) is derived from the expectation value \( \langle \mathbf{L} + 2 \mathbf{S} \rangle \), which is a Boltzmann average over all electronic states. The G-tensor is derived from \( \langle \mathbf{L} + 2 \mathbf{S} \rangle \) by rewriting the interaction

\[ -\mu_B \mathbf{L} = \mathbf{H} \rightleftharpoons \mathbf{G} \rightleftharpoons \mathbf{G} \]

in terms of an effective spin. \( \mathbf{G} \) in general can be asymmetric; in this case a symmetric tensor is constructed by

\[ G_{pq} = \sum_{\alpha=x,y,z} q_{pq} G_{pq} \]

Diagonalization of \( G_{pq} \) corresponds to an operation in \( \mathbb{R}^3 \), which transforms the used basis set into the main axes system of \( G_{pq} \). From the main components \( G_{11}, G_{22}, G_{33} \) then the well-known g-factors are derived

\[ g_{i} = \sqrt{G_{ii}} \quad i = 1,2,3 \]

(From this procedure the sign of \( g_{i} \) cannot be determined.)

For \( K_3\text{Fe(CN)}_6 \), for which also Mössbauer parameters have been derived along the procedure described so far, the powder susceptibility described by \( \chi = \chi_1 + \chi_2 + \chi_3 \) has been evaluated as function of temperature, and was compared with experimental results (Fig. 5). The calculated and measured g-factors for \( K_3\text{Fe(CN)}_6 \) are listed in Table 4. From inspection of Fig. 5 and Table 4 one realizes that theoretical and experimental data are in reasonable agreement.
Fig. 5: Calculated (IEHT-MO-CI) powder susceptibility (solid line) of K$_3$Fe(CN)$_6$ as a function of temperature. Taken from ref. 32. The extrapolation (broken line) leads to a Weiss constant $\theta = 40$ K, which is comparable with the value $\theta_{\text{exp}} = 56$ K from the data of Figgis et al. (ref. 33).

Table 4: g-factors (see text) for K$_3$Fe(CN)$_6$. Taken from ref. 32.

<table>
<thead>
<tr>
<th>calc. results</th>
<th>exp. ESR results (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_1$</td>
<td>Fe$_2$</td>
</tr>
<tr>
<td>$g_1$</td>
<td>2.39</td>
</tr>
<tr>
<td>$g_2$</td>
<td>1.71</td>
</tr>
<tr>
<td>$g_3$</td>
<td>1.08</td>
</tr>
</tbody>
</table>


9. Energies. The orbital energies which were derived using the IEHT approximation are in qualitative agreement with those reported from experimental work (see Table 5).

Table 5: Orbital energies (in cm$^{-1}$) as derived from IEHT calculations and optical experiments. Taken from refs. 20, 32.

<table>
<thead>
<tr>
<th>compound</th>
<th>IEHT</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_3$Fe(CN)$_6$</td>
<td>32000</td>
<td>35000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>compound</th>
<th>IEHT</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeF$_2$</td>
<td>607</td>
<td>873</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Calculated and experimental ionization potentials (in ry = 109737.3 cm$^{-1}$). Taken from ref. 36.

<table>
<thead>
<tr>
<th>molecule</th>
<th>orbital</th>
<th>exp. (a)</th>
<th>calc. (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>a$_1$</td>
<td>-2.37</td>
<td>-2.31</td>
</tr>
<tr>
<td></td>
<td>b$_2$</td>
<td>-1.36</td>
<td>-1.35</td>
</tr>
<tr>
<td></td>
<td>a$_1$</td>
<td>-1.08</td>
<td>-1.05</td>
</tr>
<tr>
<td></td>
<td>b$_1$</td>
<td>-0.93</td>
<td>-0.92</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>3a'</td>
<td>-1.38</td>
<td>-1.27</td>
</tr>
<tr>
<td></td>
<td>1a''</td>
<td>-1.29</td>
<td>-1.11</td>
</tr>
<tr>
<td></td>
<td>4a'</td>
<td>-1.12</td>
<td>-1.11</td>
</tr>
<tr>
<td></td>
<td>5a''</td>
<td>-0.95</td>
<td>-0.96</td>
</tr>
</tbody>
</table>


More accuracy has been achieved with our - compared to the IEHT method - more elaborate model-potential MO calculations$^{12,34}$.

As an example we present energies for H$_2$O and CH$_3$OH in Table 6.

11. Dipole moments and XPS intensities. Dipole moments are derived according to eq. (12) with the operator $\Delta = \hat{F}$. XPS intensities result from

$$I_i = \sum_{\mu, \nu} c_{\mu i} c_{\nu i} \left( \frac{E_{\mu \nu} + E_{\nu \mu}}{2} \right)$$

where $E_{\mu \nu}$ are XPS cross-sections taken from Gelius and Siegbahn$^{35}$. For the two compounds from above, again using the model-potential MO method$^{12}$, the calculated and measured dipole moments and XPS intensities are summarized in Table 7.

Table 7: Calculated and experimental XPS intensities and dipole moments (Debye). Taken from ref. 36.

<table>
<thead>
<tr>
<th>molecule</th>
<th>orbital</th>
<th>XPS (a)</th>
<th>XPS (b)</th>
<th>XPS (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>a$_1$</td>
<td>44.0</td>
<td>44.0</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>b$_2$</td>
<td>5.0</td>
<td>4.4</td>
<td>2.51</td>
</tr>
<tr>
<td></td>
<td>a$_1$</td>
<td>11.2</td>
<td>13.1</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>b$_1$</td>
<td>5.7</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>2a'</td>
<td>27.6</td>
<td>27.6</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td>3a'</td>
<td>12.5</td>
<td>12.4</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>1a''</td>
<td>3.2</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4a'</td>
<td>2.0</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5a''</td>
<td>3.3</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2a''</td>
<td>3.6</td>
<td>5.5</td>
<td></td>
</tr>
</tbody>
</table>

(a) see ref. (a) of Table 6, (b) exp. (c) calc.

11. Summary. On the basis of the IEHT method, with a fixed set of parameters ($\lambda$), electric field gradients, electron densities at the Mössbauer nucleus, internal magnetic fields, susceptibility, g-factors and energies have been derived, which are in reasonable agreement with experiment. This shows that even a relatively simple MO method is able to reproduce satisfactorily experimental results, and thus leads to a deeper understanding of the electronic and magnetic structure of the compounds under study.

The more sophisticated model-potential calculations require much more computer space and time; it is still questionable whether the results justify the effort.

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References

1. Roothan, C. C. J., Rev. Mod. Phys. 23 (1951) 69
3. Hückel, E., Z. Physik 70 (1931) 204
27. V. R. Marathe, Trautwein, A., Kostikas, A., unpublished data
35. Gelius, U., Siegbahn, K., Reprint, Uppsala University, Institute of Physics UUP-794 (1972)