Table 1. *'Theoretical' and experimental structure factors for some 'sum' reflections of* KCl *at* 300 K

hkl	220	222	400	224	442	600	444	800	10,0,0
LDA fit ($\bar{B} = 2.00$ Å^2, $R = 0.0207$)	21.9	18.6	16.2	13.0	9.88	9.88	7.86	5.88	3.17
HF fit ($\bar{B} = 2.01$ Å^2, $R = 0.0255$)	21.9	18.6	16.2	12.9	9.88	9.88	7.86	5.89	3.17
Schmidt *et al.* (1985)	22.0	18.5	15.8	12.9	9.92	9.66	7.81	5.89	3.22
Patomäki & Linkoaho (1969)	21.9	18.4	16.4	12.9	9.78	9.78	7.48	5.91	2.99

factor with the recipe given by Zunger & Freeman (1977) (see footnote 53) agree well with the LDA structure factors for the *static* crystal computed by the latter authors and reasonably well with the X-ray powder data by Merisalo & Inkinen (1966) reduced to the *static* crystal [see Zunger & Freeman (1977), Table IV, last two columns].*

There is a clear tendency in both the theoretical and experimental structure factors at intermediate *hkl* to be higher than the HF free-ion values.

We are most indebted to Professor Colella of Purdue University for making his experimental data available to us prior to publication, and for many stimulating discussions.

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* The resulting tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP39799 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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About the Simultaneous Interpretation of Charge and Spin Density Data

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Abstract

The implications of quantum-chemical concepts for the simultaneous interpretation of charge and spin density data are discussed. It is proposed that the scattering of the electrons involved in the metal-ligand interaction, on which both X-ray and polarized neutron information is available, be expressed in terms of the wavefunction, while the remainder of the electron distribution be described in terms of the multipole formalism. The discussion is based on a three-electron subsystem for metal-ligand bonding. At the restricted molecular orbital level it is shown that the magnitude of the overlap spin density is much larger than that of the overlap charge density, which may be close to zero when the electronegativity difference between metal and ligand is considerable. Spin polarization is introduced at the unrestricted molecular orbital level and implies that different κ parameters should be applied to the α and β electrons. Its effect on the spin and charge distribution is of first and second order respectively. The effect of correlation, described by the mixing of two or more configurations, leads to an apparent increase in covalency. The formalisms discussed may be applied in a stepwise manner, first at the spin-restricted level and subsequently with the inclusion of spin polarization and correlation effects.

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Introduction

One of the main goals of accurate diffraction work is to obtain information on the electronic ground-state wavefunction from the experimental measurements, and to derive from this information a better physical understanding of the bonding in molecules and solids. For magnetic systems we can obtain not only the charge density from the elastic X-ray scattering but also the magnetization distribution by the polarized neutron technique. (See, for example, articles by Brown, Forsyth, Schweitzer in Becker, 1980; Tofield, 1975; Mason, 1982, and recent publications by Figgis and coworkers: Figgis, Williams, Forsyth & Mason 1981; Figgis, Reynolds & Mason, 1983; Figgis, Mason, Smith, Varghese & Williams, 1983). The combination of both techniques is especially powerful and can lead to detailed information on, for example, the nature of metal–ligand bonding (Coppens, Holladay & Stevens, 1982; Holladay, Leung & Coppens, 1983). As charge and spin distributions are manifestations of the same wavefunction, both sets of experimental measurements should be interpreted in a mutually consistent manner.

Let us assume the metal–ligand interaction to be limited to the first neighbors of the metal. We denote the associated electronic wavefunctions, composed of the relevant valence orbitals only, by ψ_A, and the remaining part as ψ_B. Then

$$\Psi = \hat{A}[\psi_A\psi_B], \tag{1}$$

where $\hat{A}$ stands for an antisymmetrizer. If we go from Ψ to the two spin components of the electron density, we may write

$$\rho_\lambda = \rho_{A\lambda} + \rho_{B\lambda} \qquad (\lambda = \uparrow, \downarrow).$$

But B is composed of paired electrons, and as a result

$$\rho_{B\uparrow} = \rho_{B\downarrow} = \rho_B/2.$$

Therefore, the charge density $\rho = \rho_\uparrow + \rho_\downarrow$ and the spin density $s = \rho_\uparrow - \rho_\downarrow$ are only coupled through $\rho_{A\uparrow}$ and $\rho_{A\downarrow}$. We propose, in order to analyze X-ray and polarized neutron results simultaneously, to treat ρ_B at the usual multipole analysis level (Stewart, 1976; Hansen & Coppens, 1978). However, the few-electron subsystem M on which both X-ray and polarized neutron information is available can be interpreted in terms of the wavefunction ψ_A itself.

It is the purpose of the present paper to justify such a treatment and to discuss the complementarity of the two sets of observations.

Wave function description of metal–ligand interaction

In order to get a clear understanding of the problem, we shall restrict the discussion to a simple three-spin system. Such a case occurs for a square-planar complex when one of the d orbitals is coupled with a symmetry-adapted combination of s and p on adjacent ligands.

Molecular orbital scheme

Let φ be the metal orbital and χ the ligand one (in a real case with more electrons, χ could be a combination of ligand orbitals and a metal orbital other than φ). The ionic starting configuration is thus $[\varphi\chi^2]$. The choice of the relevant φ and properly symmetry-adapted χ is dictated by crystal-field effects. The ionic wavefunction is

$$\psi^i = [3!]^{-1/2}|\varphi\chi\bar{\chi}|. \tag{2}$$

As discussed by Freeman & Frankel (1967), the non-orthogonality of φ and χ,

$$S = \langle\varphi|\chi\rangle \neq 0, \tag{3}$$

results in a typical ionic repulsion. Let ζ be the orthogonalized metal orbital ($\langle\zeta|\chi\rangle = 0$):

$$\zeta = (1-S^2)^{-1/2}\{\varphi - S\chi\}. \tag{4}$$

ψ^i can also be written as

$$\psi^i = [3!]^{-1/2}|\zeta\chi\bar{\chi}|. \tag{5}$$

From (5) we get the spin-dependent ionic density:

$$\rho^i_\uparrow = \zeta^2 + \chi^2 \qquad \rho^i_\downarrow = \chi^2. \tag{6}$$

These densities were, at the crystal-field level,

$$\rho^0_\uparrow = \varphi^2 + \chi^2 \qquad \rho^i_\downarrow = \chi^2. \tag{7}$$

We therefore conclude that the ionic interaction only affects the majority spin distribution, through an anti-bonding effect (we expand to second order in S):

$$\rho^i_\uparrow - \rho^0_\uparrow = S^2\varphi^2 + S^2\chi^2 - 2S\varphi\chi. \tag{8}$$

Covalent interaction

The (φ, χ) overlap implies electron hopping between metal and ligand. φ and χ will mix through covalent interaction. Starting from two singly occupied $\varphi_\uparrow$ and $\chi_\uparrow$, such a mixing will have no effect on the $\uparrow$ spin density. The bonding orbital, denoted by η, is written as

$$\eta = [1 + \gamma^2 + 2\gamma S]^{-1/2}\{\chi + \gamma\varphi\}, \tag{9}$$

where the relevant coupling parameter γ could in principle be obtained by energy minimization. The covalent-level wavefunction is thus

$$\psi^c = [3!]^{-1/2}|\zeta\chi\bar{\eta}|, \tag{10}$$

from which we get the spin-dependent densities (up to second order in γ and S):

$$\begin{aligned} \rho^c_\uparrow &= \zeta^2 + \chi^2 = \rho^i_\uparrow \\ \rho^c_\downarrow &= \eta^2 = [1 - \gamma^2 - 2\gamma S]\chi^2 + \gamma^2\varphi^2 + 2\gamma\varphi\chi. \end{aligned} \tag{11}$$

The previous results can be summarized in terms of usual charge and spin densities and deformation densities:

$$\rho^c = \rho^c_\uparrow + \rho^c_\downarrow = \rho^0 + \delta\rho^c$$

$$\rho^0 = \varphi^2 + 2\chi^2 \qquad (12)$$

$$\delta\rho^c = (S^2+\gamma^2)\varphi^2 + (S^2-\gamma^2-2\gamma S)\chi^2 + 2(\gamma - S)\varphi\chi$$

$$s^c = \rho^c_\uparrow - \rho^c_\downarrow = s^0 + \delta s^c$$

$$s^0 = \varphi^2 \qquad (13)$$

$$\delta s^c = (S^2-\gamma^2)\varphi^2 + (S^2+\gamma^2+2\gamma S)\chi^2 - 2(\gamma + S)\varphi\chi.$$

Discussion

In situations with rather strong covalency, γ is larger than S. In such cases, there is a charge transfer from the ligands to the metal, and a charge build up in the internuclear region. But the spin density exhibits an $\uparrow$ spin transfer from the metal to the ligands, with a quite strong depletion in the overlap region. This corresponds to a reduction of the magnetic moment on the metal atom as has often been observed in polarized neutron studies (see for example Rakhecha & Satya Murphy, 1978). The magnitude of the overlap spin density is much larger than that of the overlap charge density. Therefore, though it may be redundant to refine the overlap term in an X-ray determined charge density, the inclusion of the overlap spin density in the polarized neutron data refinement appears essential. It does not imply an extra parameter and cannot easily be expressed though an atom-centered multipolar expansion. This is why we think it preferable to use a scattering formalism based on the 'exact' expansion (12) and (13).

If the covalency is small, we may get $\gamma < S$ (Hubbard, Rimmer & Hopgood, 1966; Watson & Freeman, 1960). In that case, there is still a charge transfer to the metal, but coming from both the ligand and the bond region. It is quite an interesting situation with a covalent interaction and a negative overlap density. The spin density exhibits a transfer from the interatomic region to both the metal and ligand. Therefore, the spin density at the metallic sites is higher than in the non-interacting case, which is opposite to the generally assumed situation where one expects a reduction of the 'ionic magnetic moment' due to covalency. Let us be more quantitative about this situation. Let H be the effective one-electron Hamiltonian. We denote by $\varepsilon_M = \langle\varphi|H|\varphi\rangle$ the energy of an electron localized on the metal, and by $\varepsilon_L = \langle\chi|H|\chi\rangle$ the energy of the electron when localized on the ligand. Let β be the resonance energy $\beta = \langle\chi|H|\varphi\rangle$, which is negative. We can assume $\varepsilon_L < \varepsilon_M < 0$, because the ligand is more electronegative than the metal. To second order in perturbation theory, the energy of the bonding orbital is

$$\varepsilon = \varepsilon_L - \frac{(\beta - \varepsilon_L S)^2}{\varepsilon_M - \varepsilon_L} \quad .$$

and the covalent coupling constant γ becomes

$$\gamma = -\frac{(\beta - \varepsilon_L S)}{\varepsilon_M - \varepsilon_L}.$$

We get

$$\frac{\gamma}{S} = \frac{u-1}{1-x},$$

where $x = \varepsilon_M/\varepsilon_L$ is always smaller than 1, and $u = \beta/\varepsilon_L S$. Thus, the condition becomes

$$\gamma > S \Leftrightarrow \beta < S[2\varepsilon_L - \varepsilon_M].$$

In most semi-empirical methods, one assumes

$$\beta = KS[\varepsilon_L + \varepsilon_M] \qquad \text{with } K \sim 0{\cdot}75.$$

We finally obtain the following condition:

$$\gamma > S \Leftrightarrow \frac{\varepsilon_M}{\varepsilon_L} > \frac{2-K}{1+K}. \qquad (14)$$

In other words, $\gamma < S$ when the electronegativity difference between metal and ligand is large enough for (14) to be contradicted ($x \lesssim 5/7$).

Unrestricted molecular orbital theory-spin polarization

We have assumed that $\uparrow$ and $\downarrow$ spin orbitals were solutions of the same one-electron Hamiltonian H. The mean-field Hartree–Fock Hamiltonian is written as

$$H = T + V_c + V_{\text{ex}}, \qquad (15)$$

where V_c is the Coulomb average potential, T the kinetic energy operator and V_{ex} the average exchange potential between one electron and all the others. But the exchange process can only take place between parallel spins. Since the number of $\uparrow$ and $\downarrow$ spins are different, we expect $V_{\text{ex}}(\uparrow\uparrow) \neq V_{\text{ex}}(\downarrow\downarrow)$. Assuming $\uparrow$ to be the majority spin state, $V_{\text{ex}}(\uparrow\uparrow) < V_{\text{ex}}(\downarrow\downarrow)$. The approximation (15) assumes

$$V_{\text{ex}} = \tfrac{1}{2}[V_{\text{ex}}(\uparrow\uparrow) + V_{\text{ex}}(\downarrow\downarrow)]. \qquad (16)$$

If we relax this constraint, we have to deal with two-coupled spin-dependent Hamiltonians:

$$H\uparrow = H - \delta \qquad H\downarrow = H + \delta$$

with

$$\delta = \tfrac{1}{2}[V_{\text{ex}}(\downarrow\downarrow) - V_{\text{ex}}(\uparrow\uparrow)] > 0. \qquad (17)$$

The first-order wavefunctions become

$$\psi_\uparrow = \psi + x\psi^* \qquad \psi_\downarrow = \psi - x\psi^*, \qquad (18)$$

where ψ^* is normalized and orthogonal to ψ and is a combination of excited states of H; x is given by

$$x = \langle\delta\rangle/\Delta E, \qquad (18')$$

where ΔE is some average excitation energy in the spectrum of the Hamiltonian H. There is a spatial decoupling of paired electrons. This is the spin polarization effect. The charge density for a pair of electrons is

$$\rho(\uparrow\downarrow)=\psi_\uparrow^2+\psi_\downarrow^2=2\psi^2+2x^2\psi^{*2}$$

and the perturbation is therefore of second order and at present beyond any possible experimental observation. However, a small spin density appears,

$$s(\uparrow\downarrow)=\psi_\uparrow^2-\psi_\downarrow^2=4x\psi\psi^*,$$

which is of first order in x. We conclude that spin polarization can only be detected in a spin polarization can only be detected in a spin density distribution.

Let us try to draw some practical guidelines for incorporation of spin polarization in spin density refinement. The qualitative effect is a net ($\uparrow\uparrow$) attraction and thus the occurrence of slight $\downarrow$ spin densities at sites neighboring the magnetic site. Though expected to be small, this is at the origin of the occurrence of ESR at protons in organic radicals (Gillon, 1983; Gillon, Becker & Ellinger, 1983). In the case of transition-metal ions, the effect has been analyzed by Watson & Freeman (1960), who could separate out the radial dependence of $\uparrow$ and $\downarrow$ electrons of the ion: one expects the $\uparrow$ spin wavefunction to contract with respect to the $\downarrow$ spin one. It therefore seems reasonable to decouple the radial dependence of $\varphi_\uparrow$ and $\varphi_\downarrow$ on the metal. This can be achieved through a modification of the screening constant κ (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979):

$$\begin{aligned}&\varphi_\uparrow=\kappa_\uparrow^{3/2}\varphi(\kappa_\uparrow r)\\&\varphi_\downarrow=\kappa_\downarrow^{3/2}\varphi(\kappa_\downarrow r)\\&\kappa_\uparrow=\kappa+\Delta\kappa/2\qquad\kappa_\downarrow=\kappa-\Delta\kappa/2\end{aligned}$$

and κ is the original screening constant.

From Watson & Freeman's calculations, we expect $\Delta\kappa/\kappa\sim 1$ to 2%.

As far as the metal–ligand wavefunction ψ is concerned, we can summarize the results through the following expression, analogous to (11):

$$\begin{aligned}\rho_\uparrow&=[1+S_\uparrow^2](\chi^2+\varphi_\uparrow^2)-2S_\uparrow\varphi_\uparrow\chi\\\rho_\downarrow&=[1-\gamma^2-2\gamma S_\downarrow]\chi^2+\gamma^2\varphi_\downarrow^2+2\gamma\varphi_\downarrow\chi.\end{aligned}\tag{19}$$

To go beyond this approach would imply that we relax condition (1) by assuming

$$\rho_{B\uparrow}\neq\rho_{B\downarrow}.$$

If ρ_B is represented through a multipolar expansion, this could be done by a simple modification of the multipolar expansion at the metal and ligand sites. The metal contribution to ρ_B comes from the core electrons: one may decouple $\uparrow$ and $\downarrow$ spin populations as well as their radial dependences. At the ligands, we should only decouple $\uparrow$ and $\downarrow$ populations.

Beyond the molecular orbital description

So far we have assumed a MO description of the metal–ligand interactions. In a way, the spin polarization effect in the above treatment is equivalent to including correlation among antiparallel spin electrons, but parallel electrons remain uncorrelated. We will give here some indications about the effect of correlation on the spin and charge densities. Following Hubbard *et al.* (1966), let us write the three-electron wavefunctions as

$$\psi=(3!)^{-1/2}[1+\gamma^2+2\gamma S]^{-1/2}\{|\varphi\chi\bar{\chi}|+\gamma|\varphi\chi\bar{\varphi}|\},\tag{20}$$

where covalency appears as the mixing of the two configurations $\varphi\chi^2$ and $\varphi^2\chi$. The latter configuration corresponds to a situation with two electrons on the metal and only one in the ligand: covalency is thus associated with an electron transfer from the ligand to the metal. It is clear that for this $\varphi^2\chi$ configuration the orbitals should be different from those describing the ionic original $\varphi\chi^2$ state. The presence of an extra electron in the metal would cause an expansion of φ to φ' and a corresponding contraction of χ to χ'. Slater's rules would predict a κ effect of the order of 5 to 10%. Thus, while the MO picture is, apart from normalization,

$$\psi^{\mathrm{MO}}=\psi_1+\gamma\psi_2\qquad\psi_1=|\varphi\chi\bar{\chi}|\qquad\psi_2=|\varphi\chi\bar{\varphi}|,$$

the correlated wavefunction is

$$\psi^{\mathrm{cor}}=\psi_1+\gamma'\psi_2'\qquad\psi_2'=|\varphi'\chi'\bar{\varphi}'|.\tag{21}$$

This is of course the first term of an infinite expansion in terms of excited configurations and it cannot be proved that (21) is the leading term (Sugano, Tanaka & Kamimura, 1970). If $\mathscr{H}$ is the total Hamiltonian, one gets

$$\begin{aligned}E^{\mathrm{MO}}&=E_1-\frac{[\langle\psi_1|\mathscr{H}|\psi_2\rangle-E_1\langle\psi_1|\psi_2\rangle]^2}{E_2-E_1}\\\gamma&=\frac{\langle\psi_1|\mathscr{H}|\psi_2\rangle-E_1\langle\psi_1|\psi_2\rangle}{E_2-E_1}\\E^{\mathrm{cor}}&=E_1-\frac{[\langle\psi_1|\mathscr{H}|\psi_2'\rangle-E_1\langle\psi_1|\psi_2'\rangle]^2}{E_2'-E_1}\\\gamma'&=\frac{\langle\psi_1|\mathscr{H}|\psi_2'\rangle-E_1\langle\psi_1|\psi_2'\rangle}{E_2'-E_1}.\end{aligned}\tag{22}$$

Owing to the orbital optimization in the configuration ψ_2', E_2' is significantly smaller than E_2 and thus γ' will be larger than γ, by a factor which may be very significant (γ'/γ can approach 2). It is of course in principle feasible to write down the charge and spin density functions associated with a wavefunction such as (21). The calculation is lengthy but straightforward and will not be further pursued here.

The major pertinent effect is the occurrence of an apparent larger γ' than expected from a MO scheme.

To end this discussion, we should point out that apparent configuration mixing with low-lying excited configurations may also occur through spin-orbit coupling. This has been observed to be of significance in interpreting the ESR spectra of porphyrins and phthalocyanines (Lin, 1979). A comparison of charge and spin density results led Coppens *et al.* (1982) to the conclusion that configuration mixing plays a significant role in the spin-density distribution.

Simplifications for a refinement procedure

So far we have discussed some theoretical implications of the metal-ligand interaction for the simple case of a three-spin system. It appeared opportune to separate the density into two parts, one associated with the metal-ligand interacting orbitals (ρ_A) and the other with the remaining diamagnetic part of the system (ρ_B).

Let M denote the metal site and $L(i)$ $(i=1, n)$ the nearest ligands. We assume that the contribution of B to the charge density is well described in terms of the usual multipole expansion (Hansen & Coppens, 1978).

It is possible to represent $\rho_{B,L(i)}$ in terms of a multipolar expansion, with decoupled populations of valence electrons with different spins.

$$\rho_{B,L(i)}=\rho_{i,\text{core}}/2+\kappa_i^3 P_{\lambda i0}\rho_0(\kappa_i r) + \sum_{lm} P_{\lambda ilm}\kappa_i'^3 R_{il}(\kappa_i' r)y_{lm\pm} \qquad (\lambda=\uparrow \text{ or } \downarrow). \tag{23}$$

A slight contribution to the spin density comes from the difference between $P_\uparrow$ and $P_\downarrow$. This density is restricted to the orbitals that do not contribute to the direct coupling with the metal.

Let us now consider the B orbitals of the metallic site. Its core electrons can be slightly spin decoupled through polarization, at least for $3s$, $3p$ electrons. If we call the normalized core density $\rho_c(r)$, we may write

$$\rho_{B,M\uparrow}=P_{M\uparrow}\kappa_\uparrow^3\rho_{c\uparrow}(\kappa_\uparrow r) \qquad \kappa_\uparrow=1+\Delta\kappa/2$$
$$\rho_{B,M\downarrow}=P_{M\downarrow}\kappa_\downarrow^3\rho_{c\downarrow}(\kappa_\downarrow r) \qquad \kappa_\downarrow=1-\Delta\kappa/2.$$

In terms of form factors let $f_c(S)$ be the form factor associated with ρ_c (**S** is the scattering vector) and $f_c'(S)$ its derivative with respect to S.

$$\begin{aligned} f_{B,M\uparrow}&=P_{M\uparrow}[f_c-(S\Delta\kappa/2)f_c'] \\ f_{B,M\downarrow}&=P_{M\downarrow}[f_c+(S\Delta\kappa/2)f_c']. \end{aligned} \tag{24}$$

The X-ray form factor is up to second order unperturbed:

$$f_{B,M}(\text{X-ray})=(P_{M\uparrow}+P_{M\downarrow})f_c.$$

The neutron form factor is of first order and equal to

$$f_{B,M}(\text{neutrons})=(P_{M\uparrow}-P_{M\downarrow})f_c - (P_{M\uparrow}+P_{M\downarrow})(S\Delta\kappa/2)f_c'. \tag{24'}$$

Notice that the spin polarization over the whole system should sum up to a zero net spin, which will lead to a constraint involving the monopolar population.

We will now deal with the density associated with the metal-ligand wavefunction ψ_A. The Fourier transformation of (19) will involve one-center terms (χ^2 and $\varphi_\uparrow^2$ or $\varphi_\downarrow^2$) and two-center terms ($\varphi_\downarrow\chi$, $\varphi_\uparrow\chi$).

If one starts from Hartree-Fock atomic orbitals (Clementi, 1965; Clementi & Roetti, 1974), it is possible to expand those densities in terms of Gaussian or Slater-type functions (Stewart, 1969, 1970). Within such an expansion, modified by a proper $\kappa_{\uparrow\downarrow}$ rescaling of the radial behavior, the one-center terms can be rigorously expanded as a linear combination of the multipoles. The scattering-vector orientation dependence of the two-center terms is more difficult but one can use, for example, the method already developed by Coppens, Csonka & Willoughby (1971). As stated earlier, it seems sufficient to differentiate $\phi_\uparrow$ from $\phi_\downarrow$ through a linear variation with $\kappa_\uparrow$ and $\kappa_\downarrow$. The great advantage of introducing simultaneously charge and spin density is that it allows examination of the wavefunction behavior associated with the metal-ligand interaction.

In practice, the approximations discussed above should be applied in a stepwise manner. After a critical evaluation of a multipolar refinement, the separation suggested by (1) may be introduced, first at the spin-restricted molecular level, and subsequently with the inclusion of spin polarization and correlation effects.

Finally, the present discussion does not apply to the interesting organic radicals, that have been recently studied (Gillon, 1983). In the case of diphenylpicrylhydrazyl, the alternant nature of the conjugated system reveals itself from the experimntal spin density and one needs an extensive wavefunction that spans the whole conjugated skeleton. We also discarded the case where coupling between metallic sites occurs, for example through an antiferromagnetic coupling (as in yttrium iron garnet; Bonnet, Delaplane, Fuess & Becker, 1979): such cases might be dealt with by a proper combination of the results for individual clusters, each being treated along the lines discussed above.

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Many Algebraic Formulas for the Evaluation of Triplet Phase Invariants from Isomorphous Replacement and Anomalous Dispersion Data

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Abstract

An algebraic analysis is presented for the calculation of triplet phase invariants from isomorphous replacement and anomalous dispersion data. The analysis applies when there is one type or one predominant type of anomalously scattering atoms. The use of the formulas largely parallels a recent approach that is based on a General Rule for evaluating triplet phase invariants. It involves the mixing of terms from isomorphous replacement with various types of terms arising in anomalous dispersion or the mixing of various terms arising in anomalous dispersion alone. The mixing of terms gives rise to a myriad of formulas that can generate values anywhere in the range from $-\pi$ to π. In the tests performed, it was found that the algebraic formulas offered an improvement in accuracy over that obtained from the General Rule. The accuracy is potentially high but depends ultimately on the reliability of the experimental data.

Introduction

Several analyses based on the mathematical and physical properties of diffraction data from isomorphous replacement and anomalous dispersion experiments have led to a large number of formulas for evaluating triplet phase invariants. The formulas are generated by several rules (Karle, 1983, 1984*b*, *c*), which have been generalized and extended by the development of a General Rule (Karle, 1984*d*). In the application of the General Rule, it is possible to combine various sets of isomorphous replacement data or isomorphous replacement data with anomalous dispersion data or various sets of anomalous dispersion data in many different ways. The variety of combinations increases considerably when anomalous dispersion data are collected at more than one wavelength.

A number of tests of the General Rule were performed on exact data computed from the coordinates for cytochrome c550.$PtCl_4^{2-}$ from *Paracoccus denitrificans* (Timkovich & Dickerson, 1976). Values for a variety of different types of triplet phase invariants were computed from combinations of isomorphous replacement and anomalous dispersion data at 2·5 Å resolution by use of the General Rule. The average magnitude of error for thousands of invariants ranged from 30 to 45°. These are significant errors to combine with the experimental error of an actual application and it would evidently be much more desirable if the error inherent in the theory could be reduced.

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