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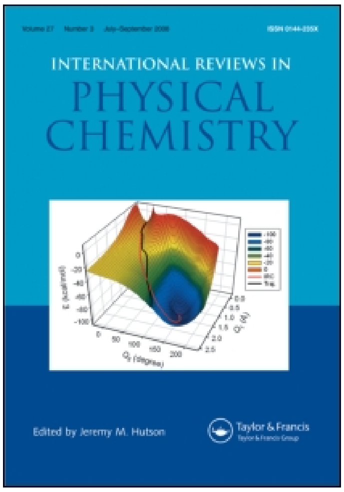

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Wavefunctions in molecular crystals

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Wavefunctions in molecular crystals

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The diffraction experiment provides explicit data which relate directly to the electron density (X-ray scattering) or the magnetization density (polarized neutron scattering). A summary is given of the determination of spin densities in a number of paramagnetic molecular ions with orbitally non-degenerate ground states. The observed densities are compared with theoretical models up to the level of unrestricted Hartree–Fock. Electron correlation is amongst the most important features in the molecular spin densities; observed spin transfer from the metals to the ligands can be matched only with a theory based on a quite extensive basis set.

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1. Introduction

The diffraction experiment provides in principle direct information on the electronic states in molecular and other crystals. X-rays interact with the three-dimensionally periodic electron density while the neutron interacts with atomic nuclei through the strong nuclear interaction and with electrons by virtue of its magnetic moment. In all these cases, elastic scattering cross-sections may be written, within the first Born approximation, in terms of the Fourier transform of the interaction potential. In turn, the elastic cross-section is related to a structure factor which is the Fourier transform of, say, the electron density or of the magnetization density; some specific formalisms are given below.

The modelling of experimental diffraction intensities is almost totally via the atomic scattering factor which, in turn, is based on a self-consistent field calculation of the atomic electron density. The non-bonded, 'at-rest' scattering factor is simply the Fourier transform of the electron density and in its usual form is angularly averaged in conventional X-ray crystallography, no use being made of angular dependent scattering factors. Scattering from an atom is 'allowed' to be anisotropic on account of non-isotropic thermal motions and there is, inevitably, a significant problem in distinguishing anisotropic effects due to vibrational effects and bonding contributions. Two methods have evolved for the X-ray experiment—the so-called X–N and X–X techniques—in the first of which thermal vibrations of electrons and nucleii are assumed identical, while in the second, one constructs the thermal vibration parameters from only those scattering amplitudes which, it is believed, receive little contribution from the valence electrons. Clearly, both methods involve approximations which may play as much of a role in determining significant features of valence electron densities as the increased precision of diffraction intensities. A 'remedial' response is obviously very low-temperature X-diffraction studies.

The information provided by these experiments is usually in the form of so-called deformation electron density maps, representing ideally

$$\rho_{\text{def}} = (\rho_{\text{molecule}} - \rho_{\text{atomic}})$$

Historically, increased accuracy of measurement of diffraction intensities meant the increasingly precise definition of hydrogen atoms and even of lone-pair electron densities. In relation to the accompanying discussions of the structures of hydrogen-bonded dimers, it is interesting that no systematic study has been made of lattice energies and structures of hydrogen-bonded crystals although that of HCN, including its lattice dynamics, is a significant exception. It is perhaps also true that the X-ray diffraction experiment has not as yet provided uniquely valuable and accurate estimates of molecular charge densities and multipole moments—both direct integration and multipole analysis procedures have given charges and moments in reasonable agreement with other measurements, but even for such small molecules as acetylene and formamide, more accurate data are needed to 'stretch' theory.

But let me turn to inorganic systems and ask the question, what do 'd' electrons in complexes look like?

So far as the X-ray experiment is concerned, one has to recognize immediately that few accurate studies are to hand and that the d-valence electron distribution is a small fraction of the total X-ray scattering. There are several reports of deformation densities demonstrating aspherical features around the metal atoms in a way which has been attributed to crystal-field splitting and preferential occupancy of some levels. Coppens and Stevens have used a multipole analysis of diffraction intensities—which I shall return to in a moment—to look at such complexes as FeS_2, $KFeS_2$ and cobalt(II) porphyrins and have obtained orbital occupancies in reasonable agreement with other measurements and, for example, with the local electric field gradients calculated at the iron site both in FeS_2 and $KFeS_2$ which agreed in magnitude and sign with Mossbauer quadrupole splitting measurements (Stevens 1982). But the fact remains that at present accuracies of better than $0{\cdot}1e\,\text{Å}^{-3}$ or so are difficult to achieve so that the test of theoretical wavefunctions and comments on lattice perturbations of molecular charge densities are limited.

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2. Polarized neutron scattering

It is for that reason that the polarized neutron scattering experiment has been developed, for here is a uniquely selective method of exploring unpaired spin densities in the highest, half-filled orbitals of transition metal complexes. The experiment is physically simple, if somewhat expensive. A beam of thermal neutrons is monochromatized and polarized and then passed through a spin 'flipper'; the 'up' or 'down' neutrons are scattered by a magnetically ordered paramagnetic crystal, placed in a strong magnetic field at temperatures of 2–4 K. Magnetic structure factors can be obtained for a good cross-section of the reciprocal lattice essentially by measuring the intensity 'up' and 'down' ratio (Brown *et al.* 1980)

$$R=\frac{\{N(K)+M(K)\}^2}{\{N(K)-M(K)\}^2}$$
$$\simeq\left(\frac{1+\gamma}{1-\gamma}\right)^2,\quad \gamma=\frac{M}{N}$$

The nuclear scattering factors, N, are obtained from the classical unpolarized neutron scattering experiment. We have used two approaches to model the observed magnetic structure amplitudes. The magnetic structure factor is

$$\mathbf{M}(\mathbf{k})=\sum_n f_n(\mathbf{k})\mathbf{M}_n(\exp i\mathbf{k}\cdot\mathbf{r}_n)$$

with $f_n(\mathbf{k})$ the form factor of the nth atom at a distance r_n from the origin and $\mathbf{M}_n$ is its magnetic moment. In turn

$$f(\mathbf{k}) = \frac{\int m(\mathbf{r}) \exp i\mathbf{k}\cdot\mathbf{r}\, dr^3}{\int m(\mathbf{r})\, dr^3}$$

which if the electrons are in a single unfilled shell may be written as

$$f(\mathbf{k}) = \sum_l A_l(\mathbf{k}) \langle j_l(|k|)\rangle$$

with

$$\langle j_l(\mathbf{k})\rangle = \int_0^\infty U^2(r) j_l(kr)\, dr$$

$j_l(kr)$ is the spherical Bessel function of order l and $U^2(r)$ the radial distribution function of electrons in the open shell. $A_l(k)$ are coefficients which depend on the direction of the scattering vector, $\mathbf{k}$, and on the magnetic configuration. For spherical symmetry, only A_0 is finite. For the spin-only case, A_0, A_2 and A_4 are non-zero. So there are three one-electron transforms for d-orbitals, one for s and two for p.

Our first model, then, places electrons in appropriate orbitals on a metal and on the ligands and by a least-squares procedure refines orbital occupancies and the radial exponent of the 'd' electrons—the methods and results are set out by Figgis and Reynolds (1986). Of particular interest in all these studies are the data on isoelectronic complexes such as CrF_6^{3-} and $Cr(CN)_6^{3-}$, $CoCl_4^{2-}$ and $CoBr_4^{2-}$ and, since it represents the first complex on which accurate charge and spin densities are available, $Ni(NH_3)_4(NO_2)_2$. Typically, spin densities are determined with a precision which is 4–5 times greater than charge densities.

At this stage, a comparison of experiment with predictions from various theories can be made in real and reciprocal space—one could construct experimental spin densities from orbital populations and/or one could Fourier transform experimental densities and run a comparison through observed and calculated magnetic structure factors. For reasons as much connected with validating the orbital modelling procedures as with comparing spin densities in a reasonably unbiased way, our second modelling scheme—complementary rather than an alternative—is based on the one-electron density being expressed as a superposition of one-centre density functions expanded as a linear sum of density fragments

$$P_{lm}(r,\theta,\phi) = M_l^m N_l^m Z_l^m(r,\theta,\phi) R_l(r)/4\pi$$

with M, N and Z being multipole populations, normalization factors and Tesseral harmonics, and $R(r)$ the radial wavefunction for the appropriate centre. The magnetic structure factors can be explicitly connected to a least-squares refinement of multipole populations and radial exponents and the results finally presented by the superposition of density fragments within a sphere containing the complex ion. Finally, one notes that multipole populations can be transformed easily into orbital populations (Varghese and Mason 1980).

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Figure 1 shows (i) experimental and calculated (double Zeta, UHF) spin densities in the $CoCl_4^{2-}$ ion. The main features, which are also commented upon by Figgis and Reynolds, appear to be:

(i) more covalence (spin transfer) in the Co–Br bond compared with its Co–Cl counterpart,

(ii) negative spin density concentrated along the Co–X bond axis (this negative spin density is comparable in magnitude with the positive spin transferred from the metal to the ligand),

(iii) diffuse spin density on the metal, reminiscent of '4s' band density in metals of the first transition series,

(iv) less covalence in the Co–Cl theoretical density than that provided by experiment (Chandler *et al.* 1982).

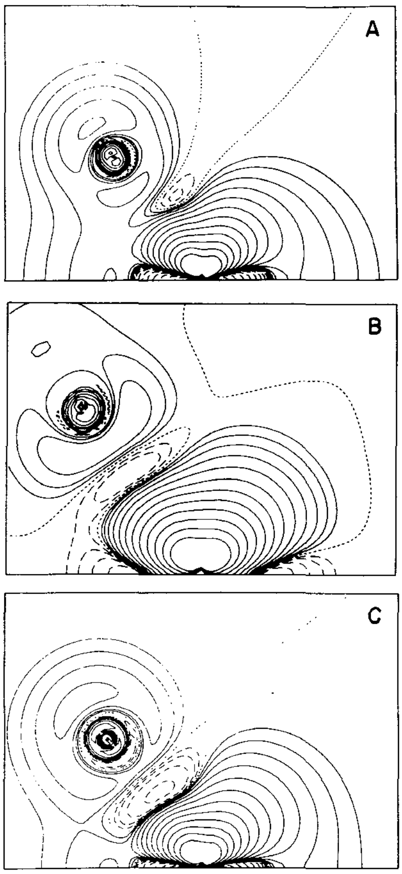

Figure 1. (*a*) Spin density of the model for $CoCl_4^{2-}$. The section is through a Co–Cl bond including the *c*-axis (vertical). Experimental structure factors were used. The contours are logarithmic (12th ≈ 3400 spins nm^{-3}, 1st ≈ 1·64 spins nm^{-3}, factor of 2 between each). In this and subsequent figures solid lines indicate positive, dashed lines negative, and dotted line zero spin density. (*b*) Spin density of $CoCl_4^{2-}$, produced by exact calculation from the theoretical wavefunction. (*c*) Spin-density distribution of the model for $CoBr_4^{2-}$. The section is through a Co–Br bond including the *c*-axis (vertical). The contours are logarithmic (12th ≈ 340 spins nm^{-3}, 1st ≈ 1·63 spins nm^{-3}, factor of 2 between each).

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The latter observation has some generality and together with the observation of spin density in the '4s' orbital is a commentary on the limited basis set of most of the theories that have been described—polarization functions on the ligand and $(n+1)$s/p on the metal are minimal. The negative spin density can be represented only by calculations at the UHF/Xα level or by semi-empirical calculations with explicit consideration of spin polarization and, judged by our experience with pseudopotential theories, does not require the inclusion of really extensive configuration interaction.

A second-order point should be recorded. Most of the complexes we have studied have quasi-cubic symmetry—only small angular and bond length distortions from local T_d or O_h symmetry even though the site symmetry may be as low as C_i. The observed spin densities are significantly different from cubic and we may have a probe of quite small intermolecular interactions in the crystals. But they may not be determined until one has rather closer agreement between observed and calculated densities for idealized and isolated complex ions.

Figure 2 shows the spin density in the $Ni(NH_3)_4(NO_2)_2$ complex. Clearly we have not established the theory of bonding here with the precision available for complexes with simpler ligands. But the observed spin and charge densities do provide a great deal of detail on the charge and spin transfers in the σ- and π-framework and, with other studies of more complex ions, emphasize the future scope of diffraction studies (Chandler *et al.* 1983).

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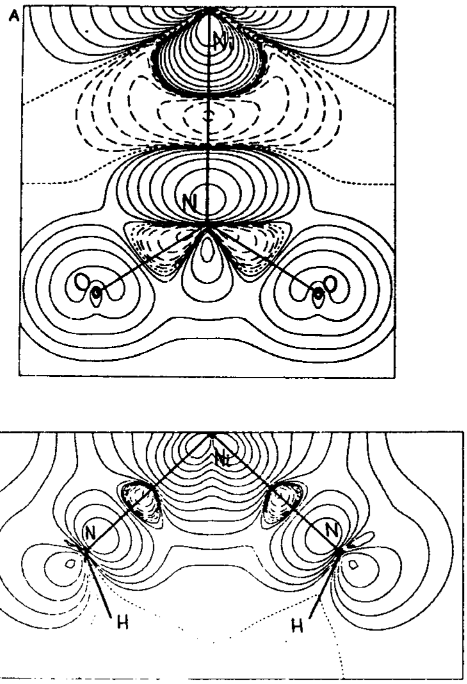

Figure 2. (*a*) Spin density of the fitted model in the *ac* plane, including the nickel and nitro groups. The contours are logarithmic: lowest, 1·64 spin nm^{-3}; increasing by factor 2. Positive, solid contour; negative, dashed; zero, dotted. (*b*) Spin density of the fitted model in the *bc** plane, including the nickel and the amine group.

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