06. X–5 From Spin Densities to the Ground State of Unpaired Electron Systems*

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It is first shown that the parameters which govern charge and spin densities are essentially of same origin and relations among them are specified. However, there are subtilities apparent in the spin density $(\rho_\uparrow - \rho_\downarrow)$ which are hardly seen in the total density $(\rho_\uparrow + \rho_\downarrow)$: these are related to the slight decoupling of the spatial behaviour of ↑ electrons relative to ↓ electrons, as a result of the asymmetry of exchange interactions. After a review of the theoretical aspects and of the possible modelisation of polarized neutron data, a few examples will be discussed, including organic radicals and more common transition metal compounds. The emphasis will be put on the comparison between charge deformation or valence density and unpaired electron density. The case of non pure spin case (occurrence of L-S coupling) will be discussed. The comparison with magnetic resonance data will be commented on specific examples.

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06. X–6 THEORETICAL AND EXPERIMENTAL STUDIES OF MOMENTUM DENSITIES IN METALS, SEMICONDUCTORS AND INSULATORS.* By Vedene H. Smith, Jr., Department of Chemistry, Queen's University at Kingston, Kingston, Ontario, K7L 3N6, Canada.

From Compton scattering of X-rays or γ-rays and from the angular correlation of 2γ-annihilation in positron experiments, one may obtain information about the momentum density, $\Pi(\vec{p})$. Since $\Pi(\vec{p})$ is defined from the square of the electron wavefunction in momentum space whereas $\rho(\vec{r})$ is defined from the square of the electron wavefunction in position space, complementary and independent information to that provided by X-ray and γ-ray diffraction experiments is available. The relationships among these various electron distributions and their transforms ($F(\vec{k})$ and $B(\vec{r})$) will be discussed.

Emphasis will be placed on examples drawn from recent experiments and calculations for metals, semiconductors and insulators.

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06.1–1 AN EMPIRICAL TDS CORRECTION FOR INTEGRATED INTENSITIES FROM SINGLE CRYSTALS WITH UNKNOWN ELASTIC CONSTANTS. By Robert H. Blessing, Medical Foundation of Buffalo, 73 High St., Buffalo, New York 14203, USA.

Step-scanned reflection intensity profiles are analyzed using the minimum σ(I)/I criterion of Lehmann & Larsen (Acta Cryst. A30, 580 (1974)) to locate peak limits for a least-squares fit of peak width anisotropy parameters Q_{ij} according to either a Lorentzian (1) or a Gaussian (2) convolution model.

$$W_i = (Z_k Q_{ijk} Z_j)^{1/2} + T_i \tan\theta \qquad (1)$$

$$W_i = [Z_k Q_{ijk} Z_j + (T_i \tan\theta)^2]^{1/2} \qquad (2)$$

(Repeated index summation convention.) Index i = 1,2 for lower angle ($K\alpha_1$) and higher angle ($K\alpha_2$) half-peaks, respectively. The vector Z is a unit vector perpendicular to the incident and diffracted beam vectors. The Q-tensors are symmetric. The components of the Z-vector and Q-tensors are referred to crystal-fixed Cartesian axes that are coincident with the diffractometer-fixed Cartesian axes at ω=φ=χ=0. The scalar coefficients T are proportional to the spectral line widths.

The net intensity, I_{meas}, above a least-squares straight line background includes the elastic Bragg intensity, I_{Bragg}, and that part, I_{TDS}, of the inelastic thermal diffuse scattering intensity that is included between the peak integration limits and not subtracted with the background.

$$I_{meas} = I_{Bragg} + I_{TDS}$$

$$I_{meas} = I_{Bragg}(1 + \alpha), \quad \alpha = I_{TDS}/I_{Bragg}$$

For a given reflection, we estimate an α value

$$\alpha_{obs} = (I_1/I_2) - 1$$

where I_1 is the net integrated intensity above a *single* least-squares line fitted to the background scans at either side of the peak, and I_2 is the net integrated intensity above a *pair* of least-squares lines, one fitted to the lower angle background scan and one fitted to the higher angle background scan with the constraint that the pair of lines intersect at the abscissa of the intensity-weighted peak centroid. The α_{obs} values are used for a least-squares fit of symmetry-restricted (Harada & Sakata, Acta Cryst, A30, 77 (1974); A32, 426 (1976)) TDS correction tensors α_{ij},

$$\alpha = (1/4) h_i h_j a^*_i a^*_j \alpha_{ij}$$

The fit is weighted toward the low angle reflections, for which the model is a fair approximation. Results will be presented for X-ray measurements at 20°C on LiF, NaCℓ, KBr, NaF, and KCℓ, and for the neutron measurements on ZnS at six temperatures up to 1000°C (Moss, Roberts, McMullan & Koetzle, J. Chem. Phys. 78, 7503 (1983)). Supported by NIH grant no. AM19856.