

17.7-01 SHORT BONDS - THE RESULT OF DISORDER, NOT LIBRATION. By A.D. Rae, School of Chemistry, University of New South Wales, Kensington, 2033 N.S.W., Australia.

It has generally been assumed in crystal structure analyses that least-squares refinement locates atoms at their mean positions. Consequently, when libration is seen to occur, it has been considered necessary to make corrections to atomic positions to obtain correct bond lengths. Analysis of the cumulant expansion model shows that if third order cumulant terms are omitted, the atom refines to a position between the mean and the mode. Reasonable weighting schemes can be devised so that the refined position of the atom corresponds to the mode and not the mean of the scattering density. Consequently if bonds are observed to be abnormally short, this phenomenon must be associated with a disordering phenomenon, not a riding motion. To correctly describe the mean and the most probable nuclear position, using multivariate probability distributions, it is necessary to include third order cumulant terms and an algebraically simplified formalism for this term will be given. The third order cumulant term for an atom has

$$-\frac{i}{6} \sum_{jkl} 3_{k,jkl} t_j t_k t_l = -i \sum_{j \neq k \neq l} \lambda_j^j (\sigma^{kk})^2 t_j t_k t_l (\sigma^{kk} + \sigma^{ll})^{-1}$$

Where t_j , λ_j and σ_j are defined relative to the principal axes of the variance covariance matrix σ which is the *libration only* component of the overall variance covariance matrix U . λ_j is the associated displacement of the mean from the mode for this component motion.