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X-ray High-Order Refinements of Hydrogen Atoms: A Theoretical Approach

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Abstract

Recent work in X-ray crystallography has demonstrated that reasonable nuclear H positional parameters can be obtained by refinements using high-order data only. A theoretical model for high-order refinements of H atoms has been developed which simulates the experimental results. For a suitable choice of the lower sin θ/λ cut-off, the H atoms are shown to refine to their actual nuclear positions. The calculations imply that the proper cut-off is indeed dependent on the type of atom to which the H is bonded, in agreement with experimental results.

Introduction

In covalently bonded H atoms a substantial fraction of the electron density is located at the bond region in the space between the atoms. Owing to this acentric density distribution, standard least-squares refinements of positional parameters in X-ray crystallography tend to displace the H towards the atom to which it is bonded. Usually, X—H bond lengths obtained in X-ray structure determinations are about 0·1–0·2 Å shorter than the internuclear distance.

Various modifications of the spherical description of the H atom density have been attempted without going beyond a one-centre expansion (Stewart, 1969). The results are not entirely satisfactory, however. This work investigates the error brought about by a simple one-centre model, assuming a two-centre expansion of the true density.

In many-electron atoms, one may partition the electron density into an inner 'core' electron density and an outer, more diffuse 'valence' electron density. For an atom in a molecule, the core density can be assumed to remain unchanged, whereas the valence electrons are redistributed when the molecule is formed. The influence of this aspherical valence electron density on structure parameters may be reduced by using only high-order data in the refinement procedure since valence scattering is negligible at high sin θ/λ values. Such procedures are now becoming standard routines in accurate X-ray work.

The low scattering power of H at high sin θ/λ values usually prevents the inclusion of H parameters in high-order refinement. However, in a number of recent accurate investigations (Hope & Ottersen, 1978; Ottersen & Hope, 1979) it has been demonstrated that H positional parameters do indeed refine to reasonable values if only data with sin θ/λ above a certain cut-off are used. The actual numeric value for this cut-off seems to be dependent on the type of atom to which the H is bonded (Hope, Poling & Ottersen, 1976).

The experimental results indicate that the observation/parameter ratio must be very high, about 60:1, in order to obtain accurate H parameters. This makes the data collection for most structures extremely time-consuming and in many cases prohibitive. A theoretical model for refinements of bonded H atoms will be important in determining the sin θ/λ ranges to be emphasized in the data collection when accurate H parameters are of prime concern. In this way the model may help in reducing data-collection times and may also give a better understanding of the best way to perform a high-order refinement of H parameters.

Theory

In simple MO theory, a covalent X—H bond may be described in terms of a localized doubly occupied molecular orbital;

$$\varphi = c_{\rm H}\,\chi_{\rm H} + c_X\,\chi_X. \tag{1}$$

χ_X and $\chi_{\rm H}$ are basis functions (atomic orbitals) centred on atoms X and H respectively. Without loss of generality one may assume the atom H to be located at the origin. The electron density associated with that MO is then

$$\varphi^2 = 2(c_{\rm H}^2\,\chi_{\rm H}^2 + 2c_{\rm H}\,c_X\,\chi_{\rm H}\,\chi_X + c_X^2\,\chi_X^2). \tag{2}$$

The corresponding contribution to the X-ray scattering is obtained as

$$(2\pi)^{-3/2}\int \varphi^2 \exp(i\mathbf{k}.\mathbf{r})\,{\rm d}\mathbf{r} = 2c_{\rm H}^2\,I_{\rm HH} + 4c_{\rm H}\,c_X\,I_{X{\rm H}} + 2c_X^2\,I_{XX}. \tag{3}$$

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In conventional X-ray structure analysis the entire molecular electron density is described in terms of spherical atomic-charge distributions. In the present case it would seem reasonable to assume that a least-squares refinement includes the term $c_X^2 I_{XX}$ in the description of the density at atom X. The least-squares procedure thus fits a model scattering factor for H,

$$F_{\text{mod}} = \exp(i\mathbf{k}.\mathbf{D})\, f_{\text{H}}(k), \tag{4}$$

to the remaining two terms of the transformed orbital density in (3). The quantity **D** is the vector displacement of the refined H atom position from the true one, at our disposal in the refinement procedure.

For the purpose of this work, it seems justified to simulate the refinement on a discrete set of $F_{\mathbf{k}}$ values by the minimization of a somewhat generalized R factor:

$$R = \int' |\Delta F|^2\, \mathrm{d}\mathbf{k}; \tag{5}$$

in which

$$\Delta F = 4c_{\text{H}}\, c_X\, I_{X\text{H}} + 2c_{\text{H}}^2\, I_{\text{HH}} - qF_{\text{mod}}. \tag{6}$$

The primed integral sign in (5) is used to indicate that the refinement may involve only a limited part of k space. The factor q multiplying F_{mod} accounts for the possibility of a scale-factor refinement. Minimizing R with respect to the displacement D yields

$$\frac{\mathrm{d}R}{\mathrm{d}D} = 2 \int' \Delta F \frac{\mathrm{d}\Delta F^*}{\mathrm{d}D}\, \mathrm{d}\mathbf{k} = 0. \tag{7}$$

Introducing polar coordinates for the integration in k space, one obtains (taking $\theta = 0$ for the bond direction)

$$\int' \Delta F \cos\theta F_{\text{mod}}^*\, k^3 \sin\theta\, \mathrm{d}k\, \mathrm{d}\theta\, \mathrm{d}\varphi = 0. \tag{8}$$

The limitations on the integration range are taken to be

$$a \leq |\mathbf{k}| \leq b. \tag{9}$$

Assuming the bond density to be cylindrically symmetric around the bond the φ integration may now be performed:

$$\int' \Delta F(k,\theta)\, f_{\text{H}}(k) \exp(-ikD\cos\theta) \times k^3 \sin\theta \cos\theta\, \mathrm{d}k\, \mathrm{d}\theta = 0 \tag{10}$$

$$\int_a^b \int_0^\pi [(4c_{\text{H}}\, c_X\, I_{X\text{H}} + 2c_{\text{H}}^2\, I_{\text{HH}}) \exp(-ikD\cos\theta) \times f_{\text{H}}(k)\, k^3 \sin\theta\cos\theta]\, \mathrm{d}\theta\, \mathrm{d}k - q \int_a^b f_{\text{H}}^2(k)\, k^3 \int_0^\pi \sin\theta \cos\theta\, \mathrm{d}\theta\, \mathrm{d}k = 0. \tag{11}$$

The second integral in (11) is zero, and the explicit q dependence is thus eliminated from the equations.

By equation (11), D is defined as a function of the integration limits (a,b). With a reasonable choice of $I_{X\text{H}}$, I_{HH} and f_{H}, one may solve this equation for various values of a and b. The experimental findings for $R_{X\text{H}}$ as a function of a can thus be compared with theoretical results.

Results and discussion

Apparent X—H distances as functions of the lower $\sin\theta/\lambda$ cut-off angle [a in equation (11)] are shown in Fig. 1. For C and N, the experimental results obtained by Hope & Ottersen are shown for comparison.

When selecting the basis set in equation (1), χ_{H} has been chosen as a (scaled) H 1s orbital:

$$\chi_{\text{H}} = \left(\frac{Z^3}{\pi}\right)^{1/2} \exp(-Zr). \tag{12}$$

This yields

$$I_{\text{HH}} = (2\pi)^{-3/2}[1 + (k/2Z)^2]^{-2}. \tag{13}$$

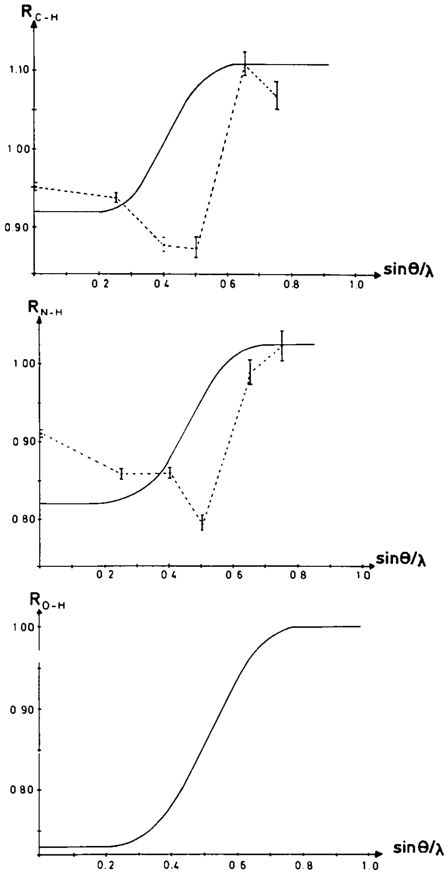

Fig. 1. Theoretical estimates of refined X—H distances as functions of the lower $\sin\theta/\lambda$ cut-off for X = C, N and O. The dashed curves show average values from experimental work, with e.s.d.'s.

For χ_X an sp^3 hybrid of exponential $2s$ and $2p$ type basis functions was used, with orbital exponents chosen in accordance with Slater's (1930) rules.

It seemed realistic to set the scattering factor for H equal to the 'observed' one, *i.e.*

$$f_{\rm H}(k) = I_{\rm HH}(k). \tag{14}$$

For the bond overlap density $4c_{\rm H}c_X\chi_{\rm H}\chi_X$, the use of exponential basis functions leads to some numerical complications, as the Fourier transform of such a charge distribution cannot be expressed analytically. Therefore, it was decided to replace the overlap density by a simpler function. Previous experience, both theoretical and experimental, indicates that such bond densities have approximately spherical symmetry. In this work, a single Gaussian function has been used to describe the overlap charge distribution:

$$\chi_{\rm H}\chi_X \Longrightarrow S_{X{\rm H}}\left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha(\mathbf{r}-\mathbf{R}_1)^2]. \tag{15}$$

Here, $S_{X{\rm H}}$ is the overlap between χ_X and $\chi_{\rm H}$,

$$S_{X{\rm H}} = \int \chi_X\chi_{\rm H}\,{\rm d}\mathbf{r} \tag{16}$$

and $\mathbf{R}_1$ represents the location of the centre of this charge density. The scattering from such a charge distribution is known to be

$$I_{X{\rm H}} = S_{X{\rm H}}(2\pi)^{-3/2}\exp(i\mathbf{k}.\mathbf{R}_1 - 0{\cdot}25k^2/\alpha). \tag{17}$$

Inserting (14) and (17) in (11) and performing the angular integration leads to

$$\{4c_X\exp(-0{\cdot}25k^2/\alpha)\,g[k(D-R_1)] + 2c_{\rm H}\,f_{\rm H}(k)\,g(kD)\}\,f_{\rm H}(k)\,k^3\,{\rm d}k = 0 \tag{18}$$

in which

$$g(x) = \int_0^\pi \exp(ix\cos\theta)\sin\theta\cos{\rm d}\theta = 2i[\sin(x) - x\cos(x)]/x^2. \tag{19}$$

It must be kept in mind that the computational strategy outlined here involves a number of adjustable parameters. Some effort has been devoted, therefore, to an investigation of the influence of those parameters on the final results and conclusions.

In equation (1), the ratio between the MO coefficients $c_{\rm H}/c_X$ is an ambiguous parameter that must be selected. The curves shown in Fig. 1 were obtained with $c_X = c_{\rm H}$, *i.e.* assuming a non-polar X—H bond. In order to check whether this assumption was crucial, the coefficients were changed to give a gross charge on H of +0·3 e. The largest effect of this modification was to shorten $\mathbf{R}_{X{\rm H}}$ by 0·01–0·02 Å for low cut-off values, whereas the curves for $a > 0{\cdot}4$ Å^{-1} were practically identical.

The upper integration limit [b in equation (11)] was also varied in the calculations. For $b > 1{\cdot}1$–$1{\cdot}2$ Å^{-1}, no dependence of $\mathbf{R}_{X{\rm H}}(a)$ upon b could be observed. Series-termination effects may thus be assumed to constitute a minor problem in experimental investigations on this subject. Similarly, the orbital exponent for H [Z in equation (12)] was varied within reasonable limits (1·0–1·5) without significant effect on the calculated curves.

A minimal basis set has been used to expand the localized bond orbital in equation (1). It is known that an MO calculation using such a basis sometimes gives quite strange orbitals and, accordingly, a poor representation of the density in the molecule. However, in the present case the coefficients c_X and $c_{\rm H}$ in equation (1) are not variationally determined, but are assumed optimal for the expansion of the localized MO, and thus for the density. Accordingly, many defects encountered when a minimal basis is used in an MO calculation are not to be expected with the present model. Nevertheless, the approximate nature of the present model must always be kept in mind.

It is tempting to believe that the shift of H atoms from their true positions in usual X-ray work is due to the expansion of the density in one-centre terms. Therefore, the modification of the model by a two-centre term [albeit approximated, *cf.* equation (15)] is likely to improve the results qualitatively. For more quantitative agreement with experiment a much more refined model must be used, but this is not within the scope of the present work.

Conclusions

Recent experimental work indicates a spectacular effect on refined X—H distances by excluding low-angle data from the least-squares refinement. The distances remain in error by 0·1–0·2 Å when the lower cut-off limit is raised from zero to about 0·5 Å^{-1}, and then suddenly shift to apparently correct values within a quite narrow interval. This behaviour is confirmed by the present theoretical investigations. The calculations also indicate a higher cut-off limit for this shift with heavier atoms, consistent with the experimental findings. The slight minima in the experimental curves for $a \approx 0{\cdot}5$ Å^{-1} are not reproduced by the calculations, however.

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