SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1983). A**39**, 422

Conditions for direct structure imaging in silicon carbide polytypes. Erratum.

By David J. Smith and M. A. O'Keefe, *High Resolution Electron Microscope, University of Cambridge, Free School Lane, Cambridge CB*2 3*RQ, England*

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Abstract

As a result of a printer's error, Figs. 9(*a*) and 9(*b*) in Smith & O'Keefe [*Acta Cryst.* (1983), A**39**, 139–148] have been transposed, so that (*a*) is labelled (*b*) and (*b*) is labelled (*a*).

All information is given in the *Abstract*.

Acta Cryst. (1983). A**39**, 422–424

A cusp-constrained scattering factor for bonded hydrogen atoms.

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Abstract

A simple one-parameter form factor that satisfies a cusp condition has been developed. A one-parameter form factor, based on a 1*s*-type density function, is more tractable in a least-squares analysis than the corresponding cusp-constrained form factor. Application of both form factors for bonded hydrogen atoms to X-ray diffraction data of sucrose revealed a more contracted density for H bonded to C compared to H bonded to O.

At a NATO-sponsored international school on electron and magnetization densities in molecules and crystals (Becker, 1980) held in Arles, France, in August 1978, a number of exercises were distributed by the participants. One exercise, proposed by Professor Hirshfeld, was to develop an atomic form factor which satisfies the electron–nuclear cusp condition. The present communication is an approximate solution to the problem for a bonded hydrogen atom.

The electron–nuclear cusp condition,

$$\lim_{\mathbf{r}_j \to 0} [(\partial\bar{\rho}/\partial\mathbf{r}_j)/\bar{\rho}] = -2Z_j, \tag{1}$$

is a consequence of satisfying the many-electron *non-relativistic* Schrödinger equation (Kato, 1957; Steiner, 1963; Pack & Brown, 1966). In (1) $\bar{\rho}$ is the one-electron density spherically averaged about the *j*th nucleus with atomic number Z_j. The $\mathbf{r}_j$ is a scalar radial length in atomic units (1 a.u. = 0·529177 Å). One possible form for ρ is

$$\rho(\mathbf{r}) = A_o e^{-\gamma\mathbf{r}} \sum_{n=0}^{N} (A_n/A_o)\, \mathbf{r}^n/4\pi. \tag{2}$$

For (2) to satisfy (1),

$$A_1/A_0 = \gamma - 2Z. \tag{3}$$

For $\rho(\mathbf{r})$ normalized to unity,

$$A_o = 1\Big/\left[(2/\gamma)^3 (1 - 3Z/2\gamma) + \sum_{n=2}^{N} (A_n/A_0)\,(n+2)!/\gamma^{n+3}\right]. \tag{4}$$

To maintain simplicity, we set all A_n/A_0 equal to zero for $n \geq 2$. This gives a simple one-parameter function which normalizes to one and satisfies (1):

$$\rho(\gamma, \mathbf{r}) = (\gamma/2)^3 (1 - 3Z/2\gamma)^{-1} e^{-\gamma\mathbf{r}}[1 + (\gamma - 2Z)\,\mathbf{r}]/4\pi. \tag{5}$$

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The form factor for (5) is

$$f(\gamma, \mathbf{K}) = \{1 + [Z/(2\gamma - 3Z)]\,(\mathbf{K}/\gamma)^2\}/[1 + (\mathbf{K}/\gamma)^2]^3, \quad (6)$$

where $\mathbf{K} = 4\pi \sin\theta/\lambda$ in a.u.*

We note in (6):

$$\underset{\mathbf{K}\to\infty}{f(\gamma, \mathbf{K})} = 16\pi\rho(\gamma; 0)\, Z/\mathbf{K}^4 + O(\mathbf{K}^{-6}) \quad (7a)$$

and

$$\lim_{\mathbf{K}\to 0} f(\gamma, \mathbf{K}) = 1, \quad (7b)$$

From (7*a*) we see that $f(\gamma, \mathbf{K})$ satisfies the cusp condition (Goscinkski & Linder, 1970) and from (7*b*) that the function normalizes to 1. For $\gamma = 2Z$, (6) reduces to a hydrogenic form factor.

We set Z equal to one and concentrate on (6) as a form factor for a bonded hydrogen atom. For $\gamma > 2$, (5) is a positive-definite function for all $\mathbf{r}$. For $0 < \gamma < 1{\cdot}5$, ρ [(5)] is negative for all $\mathbf{r}$ and cannot be an acceptable density function. For $1{\cdot}5 < \gamma < 2$, ρ has a node at $\mathbf{r} = (2 - \gamma)^{-1}$ and becomes negative when $\mathbf{r}$ exceeds $(2 - \gamma)^{-1}$, which occurs for $\mathbf{r} > 2$ a.u. (1·058 Å). Although this feature is undesirable, the density from neighbouring atom may offset the negative density contribution. If the total charge density in the molecule or crystallographic cell is positive definite, then $\rho(\gamma, \mathbf{r})$ $(1{\cdot}5 < \gamma < 2)$ may be claimed as an acceptable density function for a bonded hydrogen atom. But, it is clear that ρ given by (5) is acceptable for $\gamma > 2$ and gives a contracted density near the proton compared to an isolated H atom. As a general rule of thumb, one expects a contraction of the charge density for bonded H atoms (Stewart, Davidson & Simpson, 1965).

An optimum value of γ was found for a mean-square fit to an accurate density for $H_2(^1\Sigma_g^+)$ reported by Stewart, Davidson & Simpson (1965). For this case, $\gamma = 2{\cdot}7606$ with a relative root-mean-square error, R_w, of 0·157.

$$R_w = \{\textstyle\int (\rho_{H_2} - 2\rho_H)^2\, d\tau / \int \rho_{H_2}^2\}^{1/2}. \quad (8)$$

By contrast, a 1*s*-type density function has an optimum value of $\alpha = 2{\cdot}332$ with $R_w = 0{\cdot}166$. A best spherical-atom, centered on the protons, fit to H_2 affords an $R_w = 0{\cdot}151$. It is interesting that the simple one-parameter function in (5) is almost as good as the best sphere, based on an R_w criterion. Although the single function for H by itself satisfies the cusp condition, (1), the $\rho_{2H}(\mathbf{r}) = \rho_H(\gamma, |\mathbf{r} + \frac{1}{2}\mathbf{R}|) + \rho_H(\gamma|\mathbf{r} - \frac{1}{2}\mathbf{R}|)$ does not. ($|\mathbf{R}|$ is the internuclear distance in H_2, and $\mathbf{r}$ has its origin at the bond midpoint.) The cusp at $\mathbf{r}_a = 0$ has a contribution from $\rho_H(\gamma, \mathbf{R})$. For $\gamma = 2{\cdot}7606$, $[(\partial\bar{\rho}_{2H}/\partial\mathbf{r}_a)/\bar{\rho}]_{\mathbf{r}_a=0} = -1{\cdot}917$, which is not -2. The corresponding cusp-condition value for the optimum 1*s* density function is $-2{\cdot}246$, which reveals a much larger discrepancy than does the $\rho_H(\gamma, \mathbf{r})$ model. To the extent that neighboring atoms contribute charge density on the proton, the cusp condition cannot be rigorously satisfied. The use of (6) as a hydrogen-atom form factor in conjunction with atomic form factors for heavier atoms provides an approximate solution to the cusp condition at the protons.

As a basis for comparison, hydrogen atoms may be assigned a 1*s*-type density function,

$$\rho_H(\alpha, \mathbf{r}) = \alpha^3 \exp(-\alpha\mathbf{r})/8\pi, \quad (9)$$

with a corresponding form factor,

$$f(\alpha, \mathbf{K}) = [1 + (\mathbf{K}/\alpha)^2]^{-2}. \quad (10)$$

We note that (9) is a positive-definite density function for all $\alpha > 0$, is normalised [(10) is unity for $\mathbf{K} = 0$], but only satisfies the cusp condition when α is two. For $\alpha > 2$, the density is contracted compared to an isolated hydrogen atom. It is useful to compare the behavior of $f(\alpha, \mathbf{K})$ [(10)] to $f(\gamma, \mathbf{K})$ [(6) with $Z = 1$] as functions of both α or γ and $\mathbf{K}$. Fig. 1 is a display of each one-parameter form factor as a three-dimensional graph. At $\gamma = 2$ a.u., $\partial f/\partial\gamma$ is zero for all $\mathbf{K}$. Above $\gamma = 2$ a.u., $\partial f/\partial\gamma$ is nearly constant and positive over much of $\mathbf{K}$. For the same regions of $\mathbf{K}$ space, $\partial f/\partial\alpha$ is positive and typically ten times larger than $\partial f/\partial\gamma$. At γ less than 2 a.u., the slope of $f(\gamma, \mathbf{K})$ along γ becomes negative and steep, whereas $\partial f/\partial\alpha$ in the same region is positive. The second derivative, $\partial^2 f/\partial\gamma^2$, is also small for $\gamma > 2$ a.u. in most of the $\mathbf{K}$ space; corresponding $\partial^2 f/\partial\alpha^2$ values are typically twenty times larger. We see that the cusp-constrained form factor has rather small variational behavior in its γ parameter in contrast to the 1*s*-type form factor. It can be anticipated that, in least-squares application to diffraction data, optimum γ's will have rather larger estimated standard deviations than corresponding optimum α's.

In order to get a calibration for γ values in application to real X-ray diffraction data, we have applied (6) to X-ray data from sucrose (Hope, 1971). The first and second cumulants for the oxygen, carbon and hydrogen nuclei, based on a refinement of neutron diffraction data, have been reported by Brown & Levy (1973). Sucrose has 14 hydrogens bonded to carbon and 8 bonded to oxygen. Of the eight OH's, all but one participate in hydrogen bonding in the

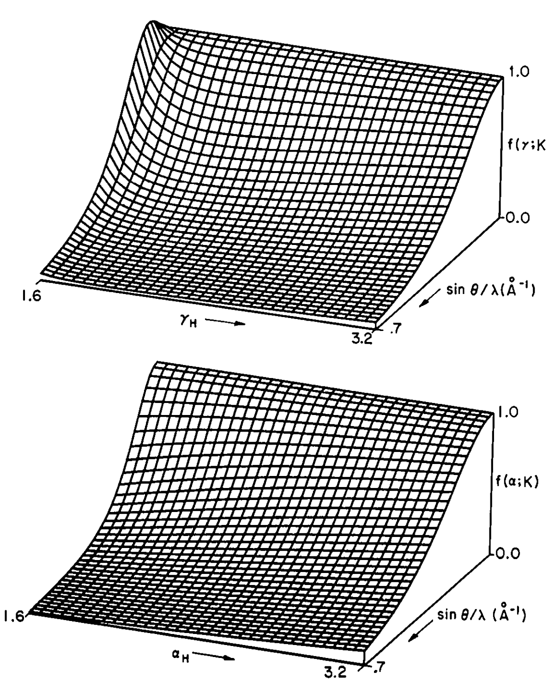

Fig. 1. Three-dimensional graphs of the cusp-constrained, $f(\gamma; \mathbf{K})$, and of the 1*s*-type, $f(\alpha; \mathbf{K})$, hydrogen-atom form factors. Grid in γ_H and α_H is 0·05 a.u. Grid for $\sin\theta/\lambda$ is 0·02 Å^{-1}.

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* 1 a.u. = 1·88973 Å^{-1}.

Table 1. *Mean optimum values for γ_H and α_H in sucrose with neutral atoms*

S is the standard deviation of the *distribution*; the estimated standard deviation of the mean $\sigma = S/\sqrt{N}$.

Atom type	N	$\bar{\gamma}_H$ or $\bar{\alpha}_H$	S	σ	Largest	Smallest	R_w
γ_H (C)	14	2·86	0·13	0·03	3·16	2·72	0·0489
γ_H (O)	8	2·19	0·23	0·08	2·55	2·00	
α_H (C)	14	2·42	0·085	0·02	2·63	2·33	0·0487
α_H (C)	8	2·05	0·14	0·05	2·27	1·87	

* $R_w = \{\sum_H (|F_H^o|^2 - k|F_c|^2)^2/\sum_H (|F_H^o|^2)^2\}^{1/2}$.

crystal lattice. From an earlier study on the isotropic amplitudes of motion of the hydrogen atoms found in sucrose (Stewart, 1976), based on a refinement of X-ray diffraction data reported by Hanson, Sieker & Jensen (1973), we expect the hydrogens bonded to C atoms to fall into a distinctly different class from those bonded to O atoms. In particular, we expect the former to have a more contracted charge density compared to the hydrogens bonded to oxygens.

Optimum values of γ for the 22 hydrogen atoms were determined by a mean-square fit to the $|F_H|^2$ with weights $\sigma^{-2}(|F_H|^2)$, as provided by Hope (1971). The data extend to a maximum of 0·7 Å^{-1} in $\sin\theta/\lambda$. The proton positions and mean-square amplitudes of motion were fixed at the neutron refinement results (Brown & Levy, 1973). An overall scale factor as well as first and second cumulants for the carbon and oxygen atoms were included as variables. Each atom was constrained to be neutral. The Hessian of the mean-square-error function included explicit second-derivative terms, which proved to be critical for variations in γ near the value of two. Convergence to a least-squares solution was found to be slow (~10 cycles). This is primarily due to the near constancy of $\partial f/\partial \gamma$ for $\gamma > 2$ a.u. Optimum values for α were found in the same way as for γ. A solution was found in three cycles and estimated standard deviations were about one-tenth of corresponding γ values.

Table 1 is a summary of the results. As expected (*vide supra*), the optimum γ or α values fall into two distinct classes that are easily correlated with the atom (C or O) to which the hydrogen is covalently bonded. Note that the largest and smallest values in γ_H or α_H for each subset do not overlap. It is clear that the Hope (1971) data for sucrose give a more contracted density for H bonded to C than for H bonded to O with the neutral-atom model that we have used here. Moreover, for H bonded to O(4) and γ_H (2·55) and α_H (2·27) are the largest in the subset for H atoms bonded to oxygens. It is this particular OH that does not form a hydrogen bond in the crystal structure. With the exception of H(O′1), all other $\gamma_H(0)$ or $\alpha_H(0)$ are lower by at least 0·1. It is interesting that H(O′1) and H(O′6), which form the two intramolecular hydrogen bonds in sucrose, have γ_H, α_H which are the high (2·54, 2·22) and low (2·00, 1·87) values among the OH's that form hydrogen bonds.

We emphasize that our results are with respect to a neutral-atom model. One may interpret the diffuse densities (Small γ or α) for the hydrogens bonded to oxygen as having less charge per unit volume compared to the contracted densities about the hydrogens bonded to carbon. Extension to variable monopole population parameters has been pursued (van der Wal, 1982). Very large correlations between H-atom populations and the nonlinear parameters, γ_H or α_H, were found. With the neutral-atom model we see that for sucrose the H-atom form factor for C—H is rather different than for O—H. The cusp-constrained form factor $f_H(\gamma; \mathbf{K})$ is less tractable in computational applications than is the 1**s**-type form factor $f_H(\alpha; \mathbf{K})$.

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