Short Communications

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A convolution method for the calculation of bond scattering factors.

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The X-ray scattering factor of bond electrons in a diatomic molecule is calculated from Fourier transforms of atomic wave functions, by the use of the convolution theory. For the hydrogen molecule, it is shown that the contribution of bond electrons is large for the scattering vector in the direction of the molecular axis.

The electron cloud in an atom contained in a molecule or a crystal may differ from spherical symmetry by chemical bonds or other effects. McWeeny (1952, 1953, 1954) calculated the scattering factors of hydrogen and carbon atoms involving H–H and C–C bonds, respectively. Tomiie (1958) discussed the electron distribution in C–H bonds for various electronic states of the carbon atom using a valence bond method. Stewart (1969) reported the generalized form factors of products of self-consistent-field atomic orbitals for first-row atoms. Also, several calculations were attempted concerning the X-ray scattering due to bonding electrons in covalent-bond crystals having the diamond structure (*e.g.* Raccah, Euwema, Stukel & Collins, 1970). The present paper presents a simplified method of calculating the bond scattering factors by the convolution theory. The electron distribution of a bonded atom pair a–b is given, by either the valence bond method (VB) or the molecular orbital method (MO), as,

$$\varrho_{ab}=n_a\varphi_a^*\varphi_a+n_b\varphi_b^*\varphi_b+(n_{ab}/S_{ab})\varphi_a^*\varphi_b\,, \tag{1}$$

where φ_a and φ_b are the atomic wave functions of atoms a and b respectively, n_a and n_b the electron populations localized at the atoms a and b respectively, n_{ab} the bond electron population and S_{ab} the overlap integral. $\varphi_a^*\varphi_a$ and $\varphi_b^*\varphi_b$ are the spherical parts of valence electrons belonging to the atoms a and b respectively, and $\varphi_a^*\varphi_b$ represents a spherical part due to bonding. We define the bond scattering factor as,

$$f_B(\mathbf{S})=\int\varphi_a^*\varphi_b\exp\left(2\pi i\mathbf{S}\,.\,\mathbf{r}\right)\mathrm{d}\mathbf{r}\,, \tag{2}$$

where **S** and **r** are reciprocal and real space vectors respectively. The Fourier transforms of atomic wave functions φ_a^* and φ_b are given by,

$$g_a^*(\mathbf{S})=\int\varphi_a^*\exp\left(-2\pi i\mathbf{S}\,.\,\mathbf{r}\right)\mathrm{d}\mathbf{r}\,,$$

$$g_b(\mathbf{S})=\int\varphi_b\exp\left(2\pi i\mathbf{S}\,.\,\mathbf{r}\right)\mathrm{d}\mathbf{r}\,. \tag{3}$$

According to the convolution theory, $f_B(\mathbf{S})$ is given as,

$$f_B(\mathbf{S})=\int g_a^*(\mathbf{M})\,.\,g_b(\mathbf{M}\text{–}\mathbf{S})\,\mathrm{d}\mathbf{M}\,. \tag{4}$$

If we denote the part of electron distribution, due to bond electrons only, by $\varrho_{BL}(\mathbf{X})$, it is given as

$$\varrho_{BL}(\mathbf{X})=(1/V)\sum_{\mathbf{H}}F_B(\mathbf{H})\exp\left(-2\pi i\mathbf{H}\,.\,\mathbf{X}\right), \tag{5}$$

where

$$F_B(\mathbf{H})=\sum_j f_{Bj}\exp\left(2\pi i\mathbf{H}\,.\,\mathbf{X}_j\right), \tag{6}$$

and V is the volume of a unit cell, **H** the reciprocal lattice vector, $\mathbf{X}_j$ the position of the jth bond electron in the unit cell and f_{Bj} the jth bond scattering factor.

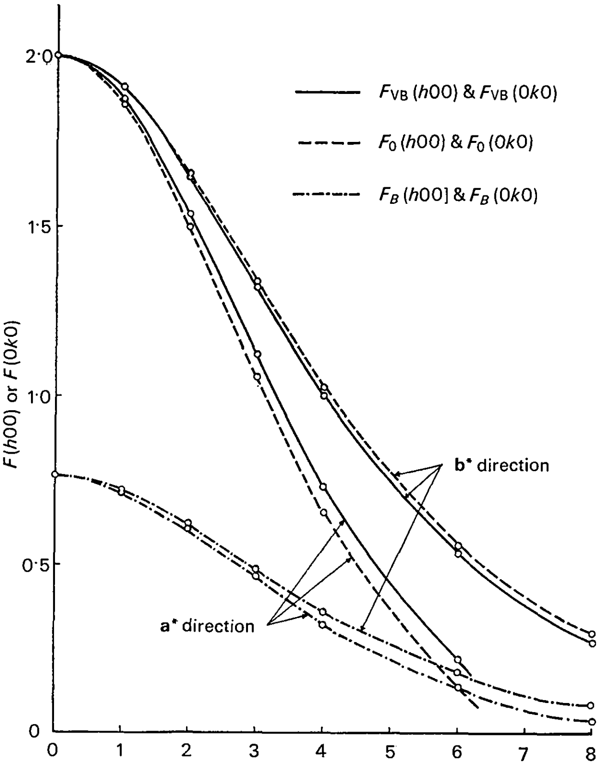

Fig. 1. F_B, F_{VB} and F_0 of a hypothetical H_2 crystal for the **a*** and **b*** directions.

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* Deceased 31 May 1967.

Now we consider hypothetical three-dimensional periodic functions $\Phi^*_{aL}(\mathbf{X})$ and $\Phi_{bL}(\mathbf{X})$ composed of φ^*_a and φ_b respectively. Then $\varrho_{BL}(\mathbf{X})$ is given by

$$\varrho_{BL}(\mathbf{X}) = \Phi^*_{aL}(\mathbf{X}) \,.\, \Phi_{bL}(\mathbf{X}).$$

We define $\Phi^*_{aL}(\mathbf{X})$ and $\Phi_{bL}(\mathbf{X})$ as,

$$\Phi^*_{aL}(\mathbf{X}) = (1/V)\sum_{\mathbf{H}} G^*_a(\mathbf{H}) \exp(2\pi i\mathbf{H}\,.\,\mathbf{X})\,, \tag{7}$$

$$\Phi_{bL}(\mathbf{X}) = (1/V)\sum_{\mathbf{H}} G_b(\mathbf{H}) \exp(-2\pi i\mathbf{H}\,.\,\mathbf{X})\,,$$

where

$$G^*_a(\mathbf{H}) = \sum_j g^*_{aj} \exp(-2\pi i\mathbf{H}\,.\,\mathbf{X}_j)\,,$$

$$G_b(\mathbf{H}) = \sum_j g_{bj} \exp(2\pi i\mathbf{H}\,.\,\mathbf{X}_j)\,. \tag{8}$$

Equations (7) and (8) correspond to equations (5) and (6) respectively, that is, $G(\mathbf{H})$ is a 'structure factor of the atomic wave function' and g_j is the Fourier transform of the jth atomic wave function as defined by equation (3). Using the convolution theory we have

$$F_B(\mathbf{H}) = \frac{1}{V}\sum_{\mathbf{K}} G^*_a(\mathbf{K})\,.\,G_b(\mathbf{K}\text{–}\mathbf{H})\,. \tag{9}$$

If the Fourier transforms of the atomic wave function, g's, are obtained, the bond structure factor can be calculated from equations (8) and (9).

As a simple example, we consider a hypothetical crystal composed of H_2 molecules which are located at corners of unit cells of a simple cubic lattice with their molecular axis along the **a** direction. The lattice constant of 20 atomic units (a.u.) and the H–H distance of 1·4 a.u. were assumed, then the fractional coordinate of the hydrogen nucleus is $x = 0{\cdot}70/20 = 0{\cdot}035$. From equations (8) and (9) we obtain

$$F_B(hkl) = (1/V)\sum_{h',k',l'} g^*(h',k',l')g(h'-h,k'-k,l'-l) \times \cos 2\pi(2h'-h)\,x\,. \tag{10}$$

$g(hkl)$ is given from the Slater wave function,

$$\varphi(1s)\;(1/\sqrt{\pi}) \exp(-r),$$

by

$$g(hkl) = 8\sqrt{\pi}(1+4\pi^2 d^{*2}_{hkl})^{-1}\,, \tag{11}$$

where d^*_{hkl} is the reciprocal of the spacing of reflection plane (hkl). Calculated values of $F_B(hk0)$ for **a*** and **b*** directions in which $g(h'k'l')$ is taken from $h',k',l' = 0$ to $h',k',l' = 10$ are shown in Fig. 1. It is found that the contour map of $F_B(hk0)$ which is identical with the bond scattering factor f_B in the simple cubic lattice has an anisotropy enlongated in the **b*** direction.

In order to see the contribution of the bond scattering factor f_B, we consider the structure factor $F_0(hkl)$ without the contribution of f_B. $F_0(hkl)$ of the crystal is given by

$$F_0(hkl) = 2f_H \cos 2\pi hx\,, \tag{12}$$

where

$$f_H = \int \varphi^*(1s)\varphi(1s) \exp(2\pi i\mathbf{H}\,.\,\mathbf{X})d\mathbf{X} = (1+\pi^2 d^{*2}_{hkl})^{-1}\,.$$

From equation (1) we obtain

$$F_{\mathrm{VB}}(hkl) = (n_a+n_b)\,f_H \cos 2\pi hx + (n_{ab}/S_{ab})f_B, \tag{13}$$

where $n_a = n_b = 1/(1+S_{ab})^2 = 0{\cdot}6382$ and $n_{ab} = 2S^2_{ab}/(1+S^2_{ab}) = 0{\cdot}7235$ $(n_a+n_b+n_{ab}=2)$ using the VB method, and $S_{ab} = \int\varphi^*_a(1s)\varphi_b(1s)dr = 0{\cdot}7529$. The comparison between $F_{\mathrm{VB}}(hk0)$ and $F_0(hk0)$ for the **a*** and **b*** directions is shown in Fig. 1. We can see clearly that the contribution of bond electrons for the **a*** direction is larger than that for the **b*** direction. This result is reasonable because the molecular axis of H_2 is assumed to lie along the **a** direction, and is similar to the result of McWeeny (1952).

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References

McWeeny, R. (1952). *Acta Cryst.* **5**, 463.
McWeeny, R. (1953). *Acta Cryst.* **6**, 631.
McWeeny, R. (1954). *Acta Cryst.* **7**, 180.
Raccah, P. M., Euwema, R. N., Stukel, D. J. & Collins, T. C. (1970). *Phys. Rev.* **B1**, 756.
Stewart, R. T. (1969). *J. Chem. Phys.* **51**, 4569.
Tomiie, Y. (1958). *J. Phys. Soc. Japan*, **13**, 1030.

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Small-angle X-ray scattering by solutions: the calculation of radial electron density distributions for long cylinders.

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It is pointed out that a method recently suggested for evaluating the radial density distribution of long rods is not new and the necessary conditions for its application are emphasized by a simple treatment.

Fedorov & Aleshin (1966) described a Hankel transform method of calculating the radial electron density distribution $\varrho(r)$ for long rigid cylindrical molecules with a cylindrical symmetry of $\varrho(r)$ about the rod axis. Carlson & Schmidt (1969), using this method, have examined the relationship between theoretical models for $\varrho(r)$ and calculated distributions when data for the intensity of scattering by dilute solutions are available over a limited range of scattering angle ($s=0$ to $s=s_{\max}$, $s = 2\sin\theta/\lambda$, θ being the Bragg angle).

It is the purpose of the present note to point out that Fedorov & Aleshin's method is not a new one and that the complexities of their analysis can be avoided. In consequence the necessary assumptions for the method to be valid are clarified.

The Fedorov & Aleshin method is a variant of the Fourier—Bessel transform method used, for example, to