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The smearing function and the Edgeworth map. By G. S. Pawley, *Department of Natural Philosophy, University of Edinburgh, Edinburgh, Scotland*

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The recently introduced Edgeworth map is exactly the same as the smearing function for an atom. The most generally understood name for this function is the probability density function. The identity above is demonstrated for the specific case of BaF_2, which is cubic. Demonstration for the general case is straightforward but is not given.

Cooper, Rouse & Willis (C.R.W.) (1968) have presented a section through the vibrating fluorine atom in BaF_2. The vibration is considered in terms of a smearing function $t_j(\mathbf{r})$, where $t_j(\mathbf{r})\,dx\,dy\,dz$ is the probability of finding the atom within the volume $dx\,dy\,dz$ (Å^3) at a displacement $\mathbf{r}=(x,y,z)$ from its equilibrium position. The same result could be obtained by calculating an Edgeworth map as described by Johnson (1969).

The smearing function is given by

$$t_F(\mathbf{r})=\left(\frac{\alpha_F}{2\pi k_BT}\right)^{3/2}\exp\{-[V_F(\mathbf{r})-V_{0F}]/k_BT\} \quad (1) \quad \text{(C.R.W.: 3)}$$

(the subscript F refers to the fluorine atom in BaF_2) when the atomic potential function is

$$V_F(\mathbf{r})=V_{0F}+\tfrac{1}{2}\alpha_F(x^2+y^2+z^2)+\beta_F(x\,y\,z)\,, \quad (2) \quad \text{(C.R.W.: 2)}$$

where k_B is Boltzmann's constant and T is the temperature. Substituting equation (2) in equation (1) and expanding the exponential involving the small quantity β_F to first order in β_F:

$$t_F(\mathbf{r})=\left(\frac{\alpha_F}{2\pi k_BT}\right)^{3/2}\left[1-\frac{\beta_F}{k_BT}x\,y\,z\right]\times\exp\left\{-\frac{\alpha_F}{2k_BT}(x^2+y^2+z^2)\right\}. \quad (3)$$

Let us now transform to fractional coordinates u^1,u^2,u^3, where $u^1=x/a$, $u^2=y/a$ and $u^3=z/a$.

Let $\Psi(u^1,u^2,u^3)du^1\,du^2\,du^3$ be the probability of finding the atom in the volume $du^1du^2du^3$, then equation (3) becomes:

$$\Psi(u^1,u^2,u^3)=\left(\frac{\alpha_Fa^2}{2\pi k_BT}\right)^{3/2}\left[1-\frac{\beta_Fa^3}{k_BT}u^1\,u^2\,u^3\right]\times\exp\left\{-\frac{\alpha_Fa^2}{2k_BT}\sum_{i=1}^{3}(u^i)^2\right\}. \quad (4)$$

We can now write down Johnson's (1969) equation (10) for the Edgeworth map. The coefficients in this equation are called the cumulants which are obtained from diffraction data by structure-factor least-squares refinement. For the particular case of the fluorine atom in BaF_2 its position is uniquely determined and the first cumulant term vanishes. This leaves

$$\Psi(u^1,u^2,u^3)=\left[1-\tfrac{1}{6}\sum_{ijk}{}^3\kappa^{ijk}\frac{\partial^3}{\partial u^i\partial u^j\partial u^k}\right]\Phi(u^1,u^2,u^3), \quad (5) \quad \text{(J.: 10)}$$

$$\Phi(u^1,u^2,u^3)=\left(\frac{\det\mathbf{p}}{8\pi^3}\right)^{1/2}\exp\left\{-\tfrac{1}{2}\sum_{ij}p_{ij}u^iu^j\right\}, \quad (6) \quad \text{(J.: 1)}$$

where in equation (6) we have taken as origin the position of the fluorine atom. The matrix $\mathbf{p}$ is related to the inverse of the anisotopic temperature factor matrix $\mathbf{b}$. For the fluorine atom $\mathbf{b}$ is diagonal with identical components, so let us write $b=b_{11}=b_{22}=b_{33}$. Then $p_{11}=p_{22}=p_{33}=2\pi^2/b$, $\det\mathbf{p}=8\pi^6/b^3$ and the relationship with the coefficients of equation (4) is

$$b=\frac{2\pi^2k_BT}{a^2\alpha_F}\,. \quad (7) \quad \text{(C.R.W.: 6)}$$

Equation (6) reduces to:

$$\Phi(u^1,u^2,u^3)=\left(\frac{\pi}{b}\right)^{3/2}\exp\left\{-\frac{\pi^2}{b}\sum_i(u^i)^2\right\}. \quad (8)$$

Before substituting in equation (5) we note that the only non-vanishing third cumulant is ${}^3\kappa^{123}$ ($=\kappa$, say). The coefficient $\frac{1}{6}$ cancels on summing over the combination of equivalent κ's and we get:

$$\Psi(u^1,u^2,u^3)=\left[1+\frac{8\pi^6\kappa}{b^3}u^1\,u^2\,u^3\right]\Phi(u^1,u^2,u^3)\,. \quad (9)$$

Equations (8) and (9) then agree with equation (4) taking equation (7) for the second cumulant b. The relation for the third cumulant is therefore

$${}^3\kappa^{123}=\kappa=-\frac{k_B^2T^2\beta_F}{a^3\alpha_F^3}\,, \quad (10)$$

in agreement (except for sign) with Johnson's footnote.

The smearing function and the Edgeworth map are identical except for the neglected and certainly negligible terms in the expansion to get equation (3). This is the approximation in the Edgeworth series expansion. Their different names obscure their identity. Agreement on one term – probability density function (Johnson 1969) – would be advantageous.

References

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