Chemistry 208—Spring 2008 **Problem Set 6**
Professor K. N. Raymond **Answer Key**

1.
For the conversion of raw data into structure factors and their standard deviations:

What are the units of F_o^2? *counts*

What are the units of $F_{(hkl)}$? *electrons*

What are the units of F_c^2? *counts*

How do we scale our observations into what we need? *A Wilson plot can be used, as well as the data from the final refinement*

What are the units of the standard deviation of F_o^2? *Counts*

What are the units of the variance of F_o^2? *Counts*

Why do we add variances and not standard deviations?
Because the sum of the squares of the deviations add

Why is there a difference in the dependence of the ratio (r) of time (or pixels) for raw count collection (P) versus background (B) when calculating I versus σ(I)?
[e.g. if I = P –rB what is the dependence of σ(I) on r?]

σ^2 contains r^2

What is the relative size of I versus σ(I) typical of X-ray sturctures?
Generally 1-2%

2.

The following formulae are useful to remember / know for this problem

$$F_{hkl} = \sum_{j=1}^{N} e^{2\pi i(hx_j + ky_j + \ell z_j)} = A + iB$$

$$e^{2\pi i} = \cos\theta + i\sin\theta$$

$$\cos\theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$$

$$\sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2}$$

$$e^{ab} = e^a e^b$$

$$\cos(\theta + \phi) = \cos\theta\cos\phi - \sin\theta\sin\phi$$

$$\sin(\theta + \phi) = \sin\theta\cos\phi + \cos\theta\sin\phi$$

$$e^{n\pi i} = (-1)^n \quad (\forall n \in Z)$$

(a). Cc

General positions: $(x, y, z), \quad (x+1/2, y+1/2, z)$
$(x, \bar{y}, z+1/2), \quad (x+1/2, \bar{y}+1/2, z+1/2)$

i) From the symmetry in this space group, we can change the sum from 1 to N to 1 to N/4 atoms

$$F_{hkl} = \sum_{j=1}^{N/4} f_j \left[e^{2\pi i(hx_j + ky_j + \ell z_j)} + e^{2\pi i(h(x_j+1/2) + k(y_j+1/2) + \ell z_j)} + e^{2\pi i[hx_j + k\bar{y} + \ell(z_j+1/2)]} + e^{2\pi i[h(x_j-1/2) + k(\bar{y}_j - 1/2) + \ell(z_j+1/2)]} \right]$$

$$but, \quad e^{2\pi i[h(x_j+1/2) + k(\bar{y}_j+1/2) + \ell(z_j+1/2)]} = e^{2\pi i[(hx_j + k\bar{y}_j + \ell(z_j+1/2)) + 1/2(h+k)]} = e^{\pi i(h+k)} e^{2\pi i(hx_j + k\bar{y}_j + \ell z_j)}$$

$$\Rightarrow F_{hkl} = \sum_{j=1}^{N/4} f_j \left\{ e^{2\pi i(hx_j + ky_j + \ell z_j)} + e^{2\pi i(hx_j + k\bar{y}_j + \ell(z_j+1/2))} + e^{\pi i(h+k)} \left[e^{2\pi i(hx_j + ky_j + \ell z_j)} + e^{2\pi i(hx_j + k\bar{y}_j + \ell(z_j+1/2))} \right] \right\}$$

$$F_{hkl} = A + iB$$

$$For\ h + k = even, \quad F_{hkl} = 0$$

$$For\ h = 0, \quad F_{0kl} = 2\sum_{j=1}^{N/4} f_j \left[(\cos 2\pi(ky_j + lz_j)) + (-1)^k \cos 2\pi(-ky_j + lz_j) \right] = 0 \quad for\ k\ odd.$$

The intensities are related to the structure factor by the following

$$I_{hk\ell} = |F_{hk\ell}|^2 = F_{hk\ell} \cdot F_{hk\ell}^*$$

So for Cc we have

$$I_{hk\ell} = I_{h\bar{k}\ell} = I_{\bar{h}\bar{k}\bar{\ell}} = I_{\bar{h}k\bar{\ell}}$$

(b). Applying the symmetry operations in $P2_12_12_1$, the number of atoms can be reduced further from N/2 to N/8. We now have the equivalent positions (related by the screw axes)

$$
\begin{aligned}
&(x, y, z), \quad (x+1/2, \bar{y}+1/2, \bar{z}+1/2) \\
&(\bar{x}, y+1/2, \bar{z}+1/2), \quad (\bar{x}+1/2, \bar{y}, z+1/2)
\end{aligned}
$$

The structure factor becomes

$$
\begin{aligned}
F_{hkl} &= \sum_{j=1}^{N/2} f_j I e^{2\pi i\left(hx_j+ky_j+\ell z_j\right)}, \quad \textit{with} \quad I = \left(1+(-1)^{h+k+\ell}\right) \\
F_{hkl} &= \sum_{j=1}^{N/8} f_j I \left[e^{2\pi i\left(hx_j+ky_j+\ell z_j\right)} + e^{2\pi i\left[h\left(x_j+1/2\right)+k\left(\bar{y}_j+1/2\right)+\ell\bar{z}_j\right]} + e^{2\pi i\left[h\bar{x}_j+k\left(y_j+1/2\right)+\ell\left(\bar{z}_j+1/2\right)\right]} + e^{2\pi i\left[h\left(\bar{x}_j+1/2\right)+k\bar{y}_j+\ell\left(z_j+1/2\right)\right]} \right] \\
F_{hkl} &= \sum_{j=1}^{N/8} f_j I \left[e^{2\pi i\left(hx_j+ky_j+\ell z_j\right)} + e^{\pi i(h+k)} e^{2\pi i\left(hx_j+k\bar{y}_j+\ell\bar{z}_j\right)} + e^{\pi i(k+\ell)} e^{2\pi i\left(h\bar{x}_j+ky_j+\ell\bar{z}_j\right)} + e^{\pi i(h+\ell)} e^{2\pi i\left(h\bar{x}_j+k\bar{y}_j+\ell z_j\right)} \right]
\end{aligned}
$$

So the reflection conditions for the 2_1 axes are:

$2_1 \parallel x \rightarrow h\ 0\ 0 : h = 2n$
$2_1 \parallel y \rightarrow 0\ k\ 0 : k = 2n$
$2_1 \parallel z \rightarrow 0\ 0\ l : l = 2n$

Note that due to the 2-fold symmetry along each axis,

$$I_{hk\ell} = I_{h\bar{k}\bar{\ell}} = I_{\bar{h}k\bar{\ell}} = I_{\bar{h}\bar{k}\ell}$$

Remember that

$$I_{hk\ell} = I_{\bar{h}\bar{k}\bar{\ell}}$$

So the intensities, we have that

$$I_{hk\ell} = I_{h\bar{k}\bar{\ell}} = I_{\bar{h}k\bar{\ell}} = I_{\bar{h}\bar{k}\ell} = I_{\bar{h}\bar{k}\bar{\ell}} = I_{\bar{h}k\ell} = I_{h\bar{k}\ell} = I_{hk\bar{\ell}}$$

This is an example of a diffraction pattern with mmm symmetry despite the fact that $P2_12_12_1$ is a chiral space group.

(c). Pbca. The equivalent positions are: (note that the bottom row are related to the top by inversion)

$$
\begin{aligned}
&(x, y, z), \quad (\bar{x}+1/2, \bar{y}, z+1/2), \quad (\bar{x}, y+1/2, \bar{z}), \quad (x+1/2, \bar{y}+1/2, \bar{z}+1/2) \\
&(\bar{x}, \bar{y}, \bar{z}), \quad (x+1/2, y, \bar{z}+1/2), \quad (x, \bar{y}+1/2, z), \quad (\bar{x}+1/2, y+1/2, z+1/2)
\end{aligned}
$$

$$F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i\left(hx_j + ky_j + \ell z_j\right)}$$

$$F_{hkl} = \sum_{j=1}^{N/8} f_j \begin{bmatrix} e^{2\pi i\left(hx_j + ky_j + \ell z_j\right)} + e^{2\pi i\left[h\left(-x_j + 1/2\right) + k\left(-y_j\right) + \ell\left(z_j + 1/2\right)\right]} + e^{2\pi i\left[h\left(-x_j\right) + k\left(y_j + 1/2\right) + \ell\left(-z_j\right)\right]} + e^{2\pi i\left[h\left(x_j + 1/2\right) + k\left(-y_j + 1/2\right) + \ell\left(-z_j + 1/2\right)\right]} \\ + e^{-2\pi i\left(hx_j + ky_j + \ell z_j\right)} + e^{-2\pi i\left[h\left(-x_j + 1/2\right) + k\left(-y_j\right) + \ell\left(z_j + 1/2\right)\right]} + e^{-2\pi i\left[h\left(-x_j\right) + k\left(y_j + 1/2\right) + \ell\left(-z_j\right)\right]} + e^{-2\pi i\left[h\left(x_j + 1/2\right) + k\left(-y_j + 1/2\right) + \ell\left(-z_j + 1/2\right)\right]} \end{bmatrix}$$

Factoring out the constant terms in the exponents and grouping the terms (i.e. term #1 with #5 etc), and using the fact that $e^{i\theta} + e^{-i\theta} = 2\cos\theta$.

$$F_{hkl} = \sum_{j=1}^{N/8} 2 f_j \begin{bmatrix} \cos 2\pi h\left(hx_j + ky_j + \ell z_j\right) + e^{\pi i(h+l)} \cos 2\pi\left(-hx_j - ky_j + \ell z_j\right) \\ + e^{\pi i \ell} \cos 2\pi\left(-hx_j + ky_j - \ell z_j\right) + e^{\pi i(h+k+l)} \cos 2\pi\left(hx_j - ky_j - \ell z_j\right) \end{bmatrix}$$

$$F_{hkl} = 2\sum_{j=1}^{N/8} f_j \begin{bmatrix} \cos 2\pi h\left(hx_j + ky_j + \ell z_j\right) + (-1)^{(h+k)} \cos 2\pi\left(-hx_j - ky_j + \ell z_j\right) \\ + (-1)^{(\ell)} \cos 2\pi\left(-hx_j + ky_j - \ell z_j\right) + (-1)^{(h+k+\ell)} \cos 2\pi\left(hx_j - ky_j - \ell z_j\right) \end{bmatrix}$$

Reflection conditions:

n glide ⊥ a → $0\ k\ l : k+l = 2n$
a glide ⊥ c → $h\ k\ 0 : h = 2n$

$$F_{0kl} = 2\sum_{j=1}^{N/8} f_j \begin{bmatrix} \cos 2\pi h\left(ky_j - \ell z_j\right) + (-1)^{(l)} \cos 2\pi\left(-ky_j + \ell z_j\right) \\ + (-1)^{(\ell)} \cos 2\pi\left(ky_j - \ell z_j\right) + (-1)^{(k+\ell)} \cos 2\pi\left(-ky_j + \ell z_j\right) \end{bmatrix}$$

$$F_{0kl} = 2\sum_{j=1}^{N/8} f_j \left[\left[(-1)^{(l)}\right] \cos 2\pi\left(ky_j - \ell z_j\right) + (-1)^{(l)}\left[1 + (-1)^{(k)}\right] \cos 2\pi\left(-ky_j + \ell z_j\right)\right]$$

If $k + l = 2n + 1$, $F_{0kl} = 0$ gives systematic absences from n glide ⊥ a

$$F_{hk0} = 2\sum_{j=1}^{N/8} f_j \begin{bmatrix} \cos 2\pi h\left(hx_j + ky_j\right) + (-1)^{(h+k)} \cos 2\pi\left(hx_j + k\bar{y}_j\right) \\ + (-1)^{(k)} \cos 2\pi\left(h\bar{x}_j + ky_j\right) + (-1)^{(h)} \cos 2\pi\left(h\bar{x}_j + k\bar{y}_j\right) \end{bmatrix}$$

$$F_{hk0} = 2\sum_{j=1}^{N/8} f_j \left[\left[1 + (-1)^{(h)}\right] \cos 2\pi\left(hx_j + ky_j\right) + (-1)^{(k)}\left[1 + (-1)^{(h)}\right] \cos 2\pi\left(hx_j + k\bar{y}_j\right)\right]$$

If $h = 2n + 1$, $F_{hk0} = 0$ gives systematic absences from a glide ⊥ c

Pnma is centrosymmetric, as shown by the structure factor expression since only cosine terms are present to describe the phase information.

Therefore,

$$\left|F_{hk\ell}\right| = \left|F_{\bar{h}\bar{k}\bar{\ell}}\right|$$

The point group is mmm, which implies that

$$F_{hk\ell} = F_{\bar{h}k\ell} = F_{h\bar{k}\ell} = F_{hk\bar{\ell}}$$

From this, we know that

$$I_{hk\ell} = I_{\bar{h}k\ell} = I_{h\bar{k}\ell} = I_{hk\bar{\ell}} = I_{\bar{h}\bar{k}\bar{\ell}} = I_{h\bar{k}\bar{\ell}} = I_{\bar{h}k\bar{\ell}} = I_{\bar{h}\bar{k}\ell}$$