

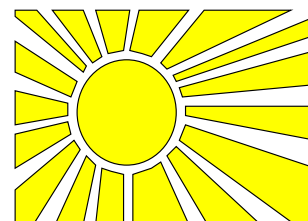
**EPCC-SS99-09**

**Crystal structure determination from powder diffraction**

**Daniel Wilson**

**Abstract**

This project involved implementing the Ewald Sum in SNIFFER, a code which determines crystal structures from powder diffraction. The Ewald Sum is a method for the calculation of the lattice energy of a crystal. For ionic-like systems in which the Coulombic interactions were dominant, the Ewald sum converged far more rapidly than the direct summation.



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## 1 Introduction

X-ray diffraction is the technique of determining the structure of a crystal by shining x-rays onto a sample and measuring the scattering angles, amplitudes and phases of the diffracted rays.

*Single Crystal X-ray diffraction* is the simplest method. It gives a characteristic 3D pattern from which the crystal structure can be routinely determined. However, in some cases growing single crystals can be difficult, whereas a powder may be obtained more readily.

The powder diffraction pattern has the same information as the single crystal pattern, but projected onto 1-dimension. Information is lost through peak overlap, so for all but the simplest cases, the crystal structure cannot be determined directly.

Using computational techniques, a possible structure can be modelled, then its powder diffraction pattern can be simulated and checked against the experimental results. Reitveld refinement, in which the structure is repeatedly improved upon, can be used to converge on the final structure.

A number of tests are performed on the possible structures so that some can be discarded on grounds of thermodynamic instability or geometrical improbability. One such test is to determine the lattice energy of the crystal. The aim of this project was to alter the code of SNIFFER<sup>1</sup> to determine this energy using the Ewald summation rather than the original direct method.

## 2 Background theory

### 2.1 Crystal structure

A crystal is material in which the atoms or molecules form a regular, gridlike, pattern throughout its volume. The structure can be described by splitting it into a lattice and a unit cell, the contents of the unit cell appearing on every lattice point.

The unit cell can consist of a number of symmetry copies of the asymmetric cell, the primitive repeated unit, which is usually a single molecule or atom. Figure 1 shows this diagrammatically.

### 2.2 Diffraction patterns

A diffraction pattern is the result of interference between the x-ray waves reflected from a crystal. The peaks in the pattern are where the waves combine in phase, the troughs where the waves combine out-of-phase and cancel each other out.

The relation between the scattering angle and the distance between the planes of lattice points for a given wavelength of light was found by Bragg to be,

$$n\lambda = 2d\sin\theta \tag{1}$$

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<sup>1</sup>Original code by Dr Robert Hammond and Dr Robert Docherty.

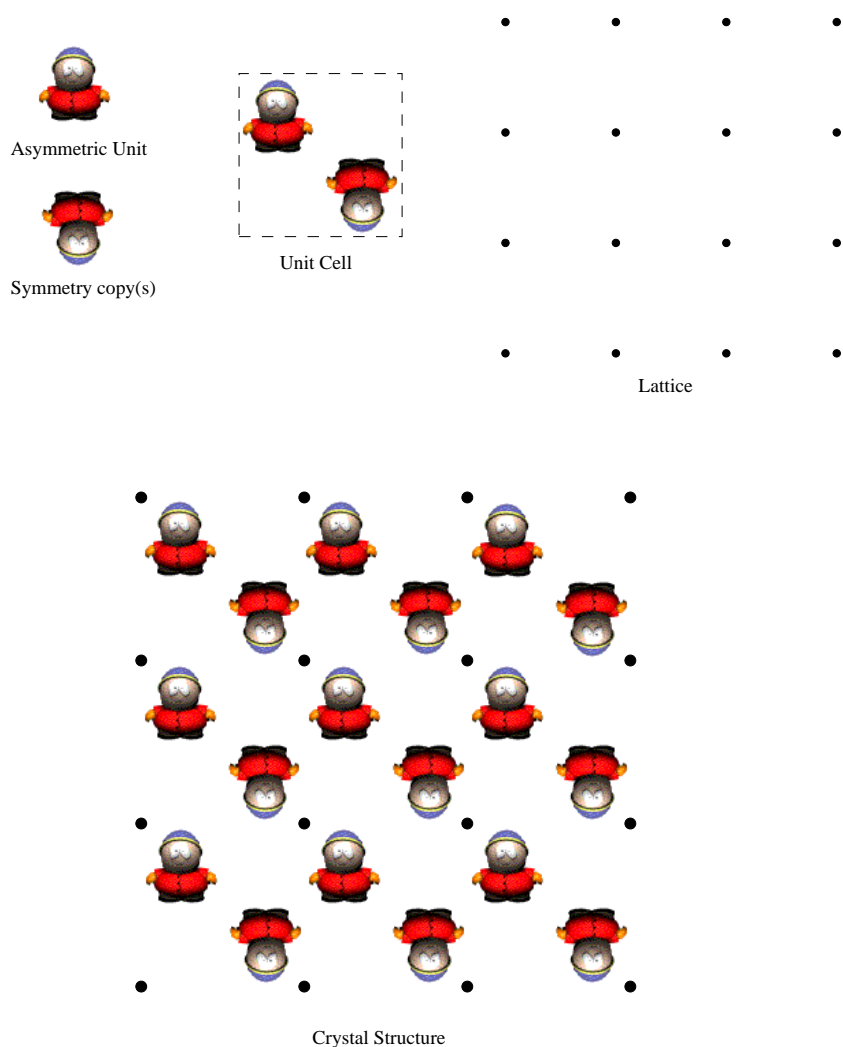


Figure 1: Illustration of Crystal Structure.

where  $n$  is the order of the reflection,  $d$  is the spacing of the planes and  $\theta$  is the scattering angle. For normal crystalline dimensions X-rays are perfect for determining the structure as their wavelength,  $\lambda$  is similar to  $d$ .

The positions of the peaks determine the space group of the crystal. In powder diffraction the 3-dimensional pattern is averaged into a single dimension. In this projection information is lost through peak overlap.

### 2.3 Calculating lattice energy

The lattice energy is the binding energy of the crystal itself, ignoring intra-molecular contributions, that is, it is the energy evolved when a gas changes to a crystal. During a typical run of SNIFFER, the lattice energy is calculated thousands of times, hence even a small reduction in calculation time can have a significant effect on the overall run time of the code.

The lattice energy is calculated by summing all the interactions between all molecules in the

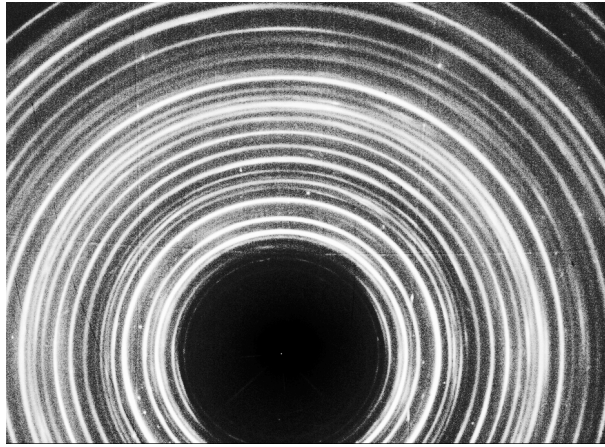


Figure 2: Powder Diffraction Pattern.

crystal.

All the interactions fall-off with distance, so all summations have a pay-off between speed and accuracy. This is defined by the radial cut-off distance, which determines how many atoms are included in the summation.

Three interactions are considered by SNIFFER.

The **Van der Waals potential** is a semi-empirical law to model the interactions between uncharged atoms.

It takes the form:

$$U = \frac{A}{r^6} + \frac{B}{r^{12}} \quad (2)$$

where  $A$  and  $B$  are constants that depend on the elements in question, and  $r$  is the distance between the atoms.

Being of the form  $r^{-6}$  the Van-der-Waals interaction is short-ranged and the sum converges quickly.

The interactions associated with **Hydrogen Bonding** are treated separately. These are due to the influence of other atoms on the electrons attached to the hydrogen atoms. This is a stronger interaction than the Van der Waals interaction, and has the form:

$$U = \left( \vec{a} \cdot \vec{b} \right)^4 \left( \frac{A}{|\vec{b}|^{12}} - \frac{B}{|\vec{b}|^{10}} \right) \quad (3)$$

This interaction is also very short ranged, so converges quickly.

In an ionic system the **Coulomb interaction** is due to the charged ions attracting each other electrostatically.

It takes the form:

$$U = \frac{q_1 q_2}{4\pi\epsilon_0 r} \quad (4)$$

Where  $q_1$  and  $q_2$  are the charges on the atoms/ions and  $\epsilon_0$  is a constant.

This interaction is also present in molecular crystals. The presence of other atoms/molecules can alter the electron density of the molecule, inducing slight partial-charges in the molecule.

Being of the form  $r^{-1}$  the sum converges very slowly.

### 2.3.1 The Ewald sum

The Ewald Sum is an effective alternative for summing the interactions between molecules and its periodic images.

It superimposes a broad spherically symmetric distribution of charge with equal magnitude but opposite sign over each point charge in the system. This has a screening effect so the interactions become short-ranged. A cancelling distribution is then added, which is rapidly convergent in *reciprocal* space.

Mathematically it converts the  $\frac{1}{r}$  sum above into two separate sums using the following equality.

$$\frac{1}{r} = \frac{f(r)}{r} + \frac{1-f(r)}{r} \quad (5)$$

For the case of the Coulomb sum  $f(r)$  is taken to be  $erfc(\frac{r}{\kappa})$ , where  $erfc$  is the complementary error function and  $\kappa$  is the Ewald parameter that alters the weighting of the two sums. The first term in equation 6 converges rapidly and the second converges rapidly if summed in reciprocal space.

$$U = \frac{2\pi}{V} \sum_{\mathbf{k}} \left\{ \left[ \sum_i q_i \cos(\mathbf{k} \cdot \mathbf{r}_i) \right]^2 + \left[ \sum_i q_i \sin(\mathbf{k} \cdot \mathbf{r}_i) \right]^2 \right\} \frac{e^{-\left(\frac{k\kappa}{2}\right)^2}}{\kappa^2} - \frac{1}{2\kappa} \sum_{i,j} q_i q_j \frac{erfc(\mathbf{r}_{ij})}{\mathbf{r}_{ij}} - \frac{1}{\pi^{\frac{3}{2}} \kappa} \left( \sum_i (q_i)^2 \right) \quad (6)$$

## 3 Results

### 3.1 Timings

Despite the high overheads associated with the reciprocal space sum, the Ewald sum is much faster for most ionic-like systems.

For a typical ionic system the direct, non-Ewald, sum may have to extend to  $\sim 500\text{\AA}$ ; the Ewald sum need only extend to  $\sim 50\text{\AA}$ . As figure 3 shows, as the cutoff distance increases, the number of atoms that have to be included goes up as  $\sim r^3$  in the calculation, and the sum gets correspondingly slower.

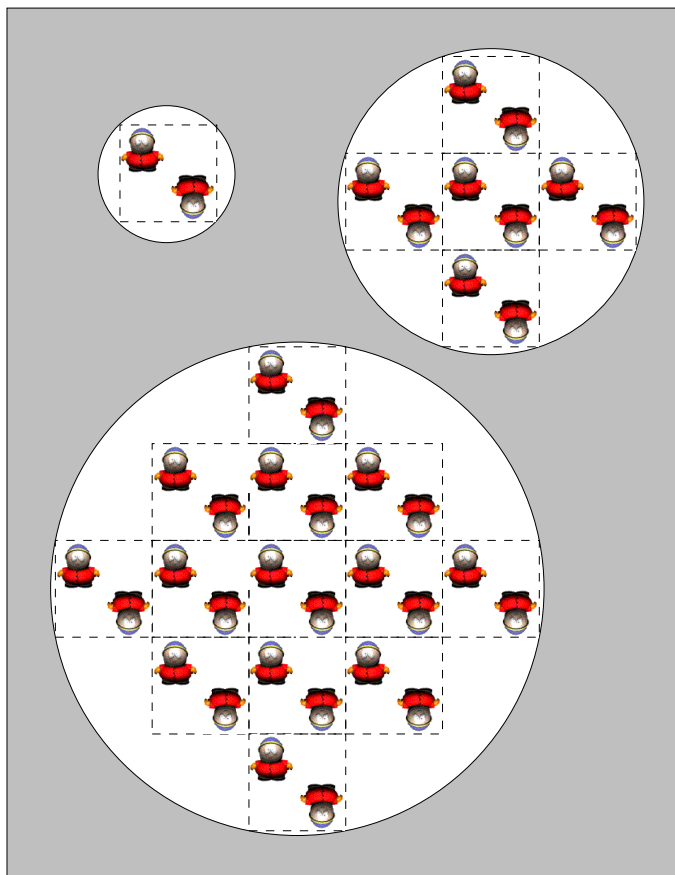


Figure 3: Illustration of the cut-off sphere.

### 3.1.1 Sodium Chloride

The main system that was used for testing purposes was a slightly modified version of NaCl. Since SNIFFER can only deal with one molecule in the asymmetric unit, this had to be taken as a  $Na^+Cl^-$  molecule.

Figure 4 illustrates the interactions that are calculated by SNIFFER. The blue arrows depict interactions between the sodium ion in the unit cell and all other ions within the cut-off sphere. Similarly, the purple arrows depict interactions between the chloride ion in the unit cell, and all other ions in the cut-off sphere. These are characteristic of the interactions of every sodium ion and chloride ion in the lattice. What SNIFFER does not calculate is the ‘intramolecular’ interactions shown in red. These would be included in the lattice energy calculation for the unmodified sodium chloride lattice.

Figure 5 show the convergence of the Ewald sum (for two values of  $\kappa$ ) and the original direct method. It can be seen that the Ewald sum converges rapidly; for  $\kappa = 0.35$  the sum converges in

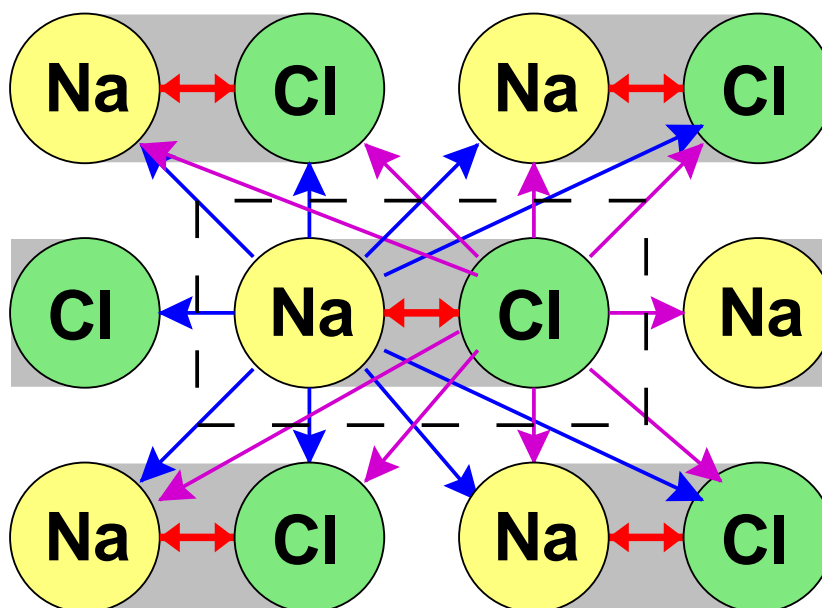


Figure 4: Illustration of the calculated interactions for (modified) NaCl.

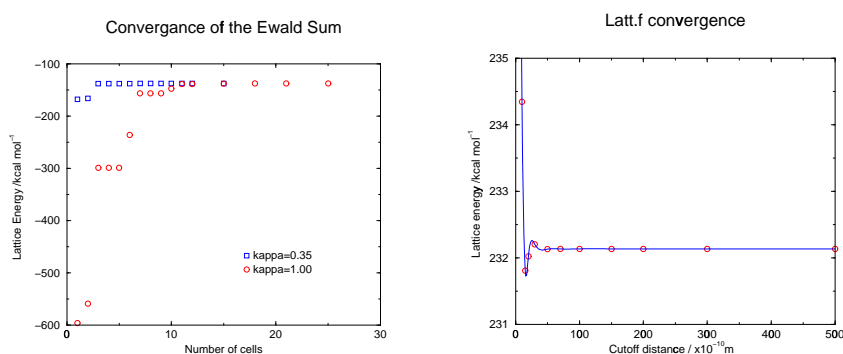


Figure 5: Convergence of the Ewald sum [left] and the original method [right] for NaCl.

around 4 cells which, for NaCl corresponds to around  $20\text{\AA}$ . The direct method failed to converge even with a cut-off sphere of radius of up to  $500\text{\AA}$ .

The optimum value of  $\kappa$  can be determined prior to running the program by performing short tests.

Method	Lattice Energy( $kcal\ mol^{-1}$ )	Time/s
Ewald	-137.77	0.62
Non-Ewald	232.14	140

These results also correspond exactly with results given by HABIT, a code in which the Ewald sum has already been implemented.



### 3.1.2 Benzophenone

The other system that the code was tested with was benzophenone.

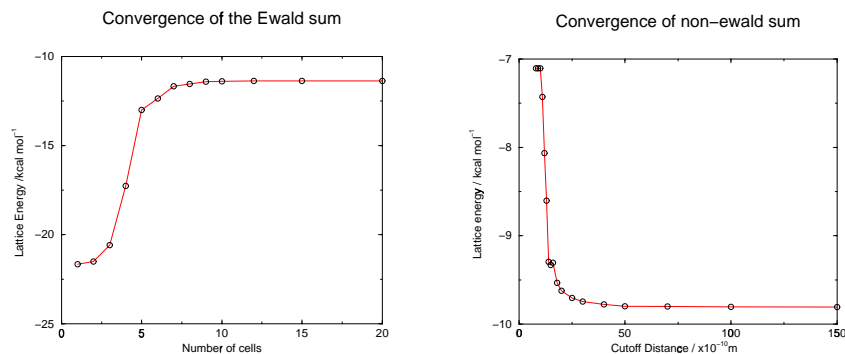


Figure 6: Convergence of the Ewald sum [left] and the original method [right] for benzophenone.

These results also agreed with HABIT. The convergence is shown in figure 6.

As benzophenone is a relatively uncharged organic system, the Coulomb sum was less significant than the Van der Waals attractions, so the original method is quicker at calculating the lattice energy.

The structure of benzophenone is shown in figure 7.

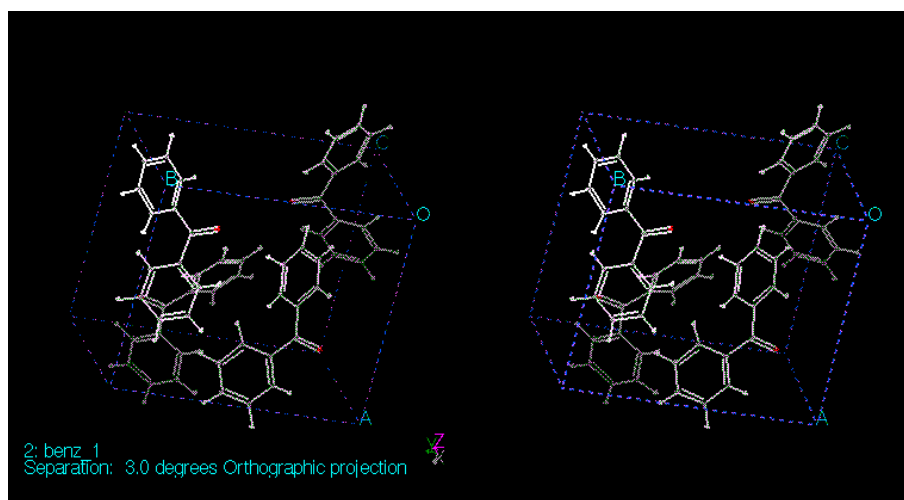


Figure 7: Stereoscopic view of the unit cell of Benzophenone.

## 3.2 Plug'n'play

The subroutines that were written to calculate the Ewald sum were written in to ensure reasonable portability to other versions of SNIFFER, such as the MPI version or the Monte Carlo version.

## 4 If more time were available...

Due to time constraints the routine was not tested as rigorously as I would have liked. Given more time, it would have been useful to test the program with a system for which the Ewald sum would have given significantly faster results than the original method. A system such as Sodium Chlorate, which is less ionic than NaCl, might have been a good choice as it would probably converge, albeit slowly, using the direct method, unlike the NaCl. The Ewald sum should converge significantly faster.

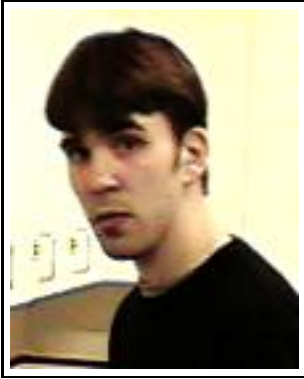
Also, importing the Ewald sum into the MPI version of SNIFFER written by Sam Carr [3], would have given me the opportunity to attempt to solve previously unknown structures.

## 5 Conclusion

The addition of the Ewald sum to the set of SNIFFER modules is very useful in that it opens up the class of ionic-like systems for structure determination. Some of these were not originally possible, others were extremely slow.

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I am currently studying for a Masters degree in Chemical Physics at The University of Edinburgh.

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