Calculating the Density Map

- Once we know the phases we can calculate an electron density map for the whole unit cell

$$\rho(x,y,z) = \sum_h \sum_k \sum_l \boldsymbol{F}_{hkl}\, \mathrm{e}^{\mathrm{i}\alpha_{hkl}}\, \mathrm{e}^{2\pi\mathrm{i}(hx+ky+lz)}$$

- Structure ↔ amplitudes and phases

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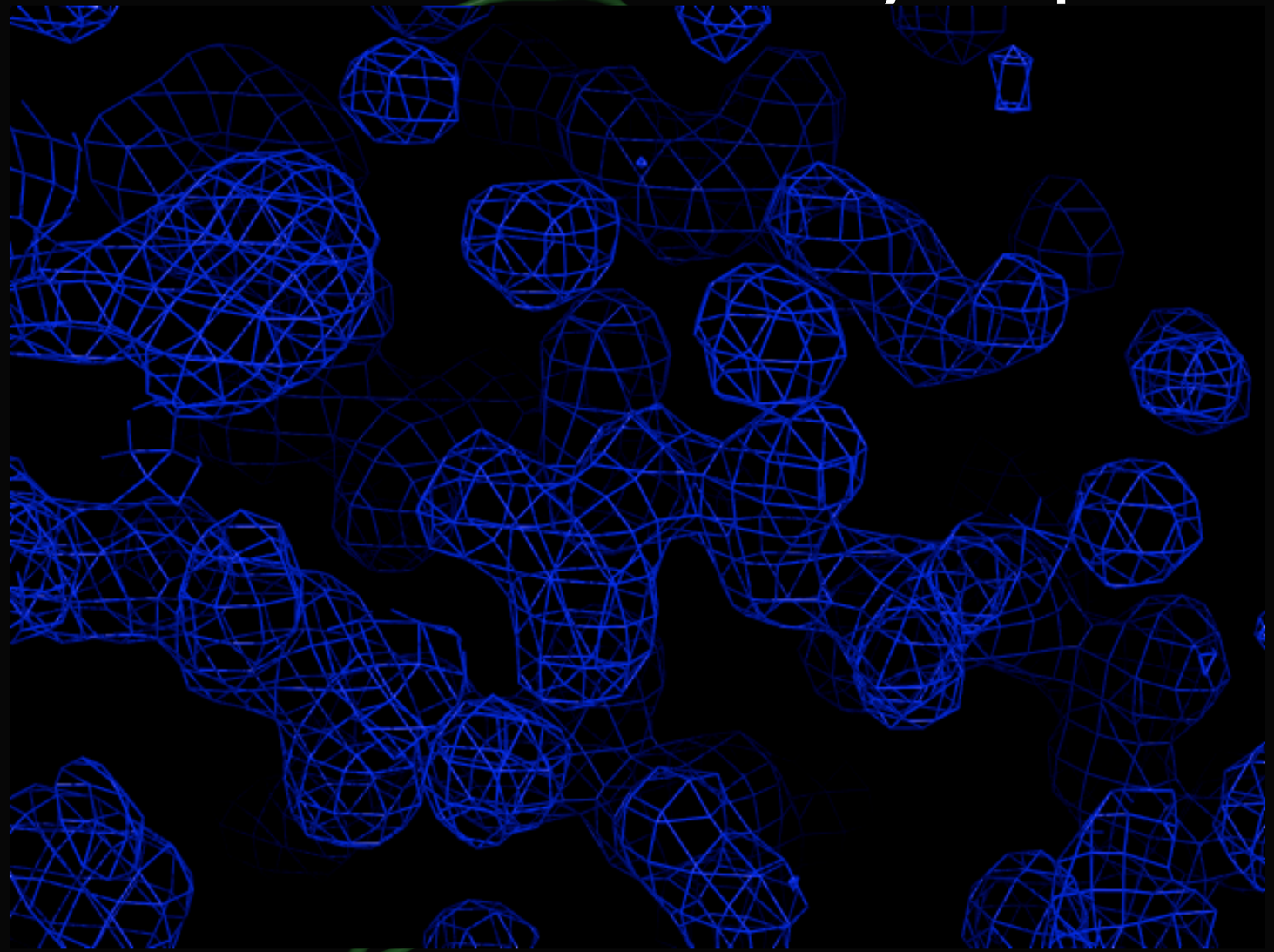
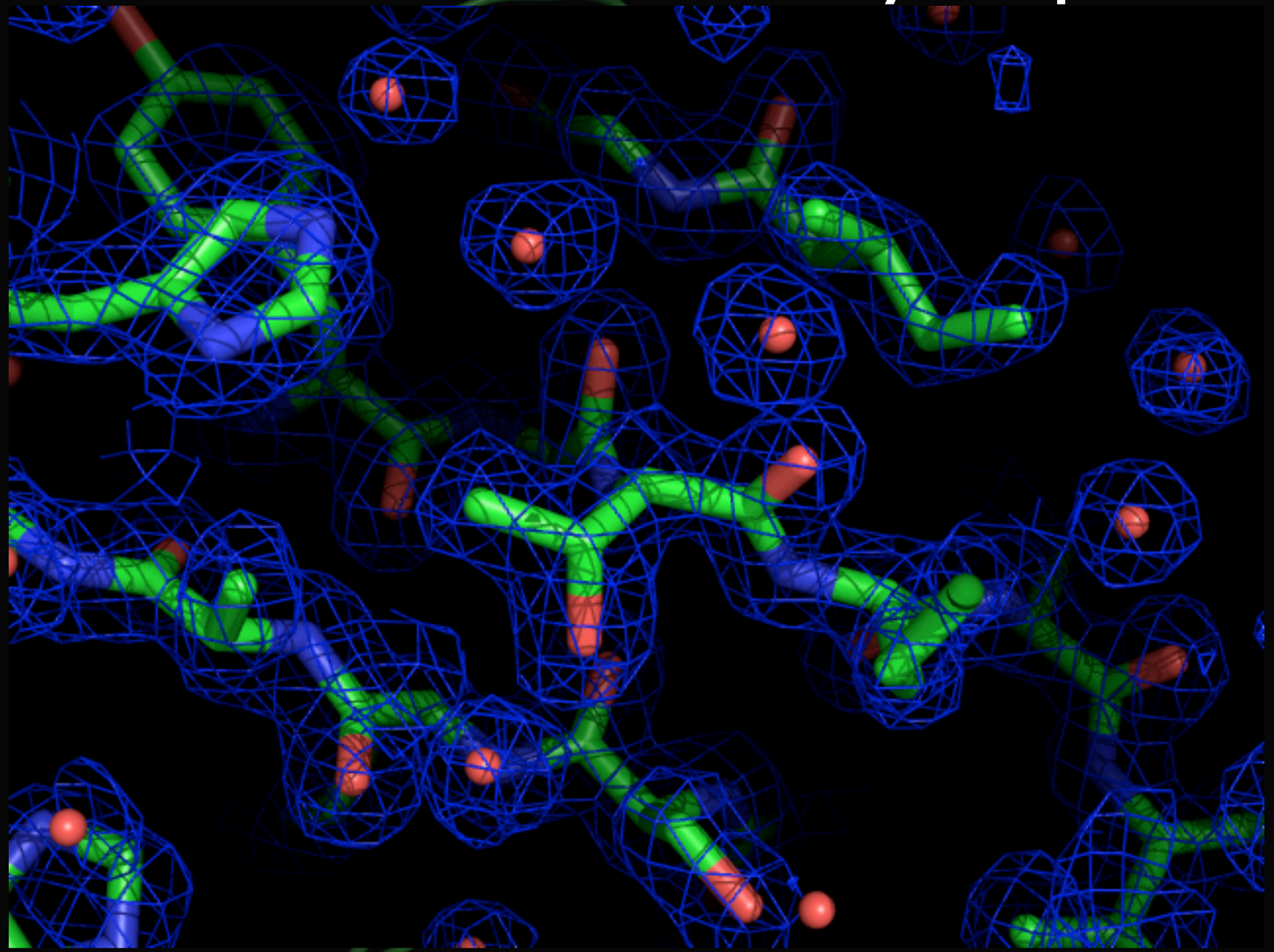
From intensities

From molecular replacement solution

The electron density map

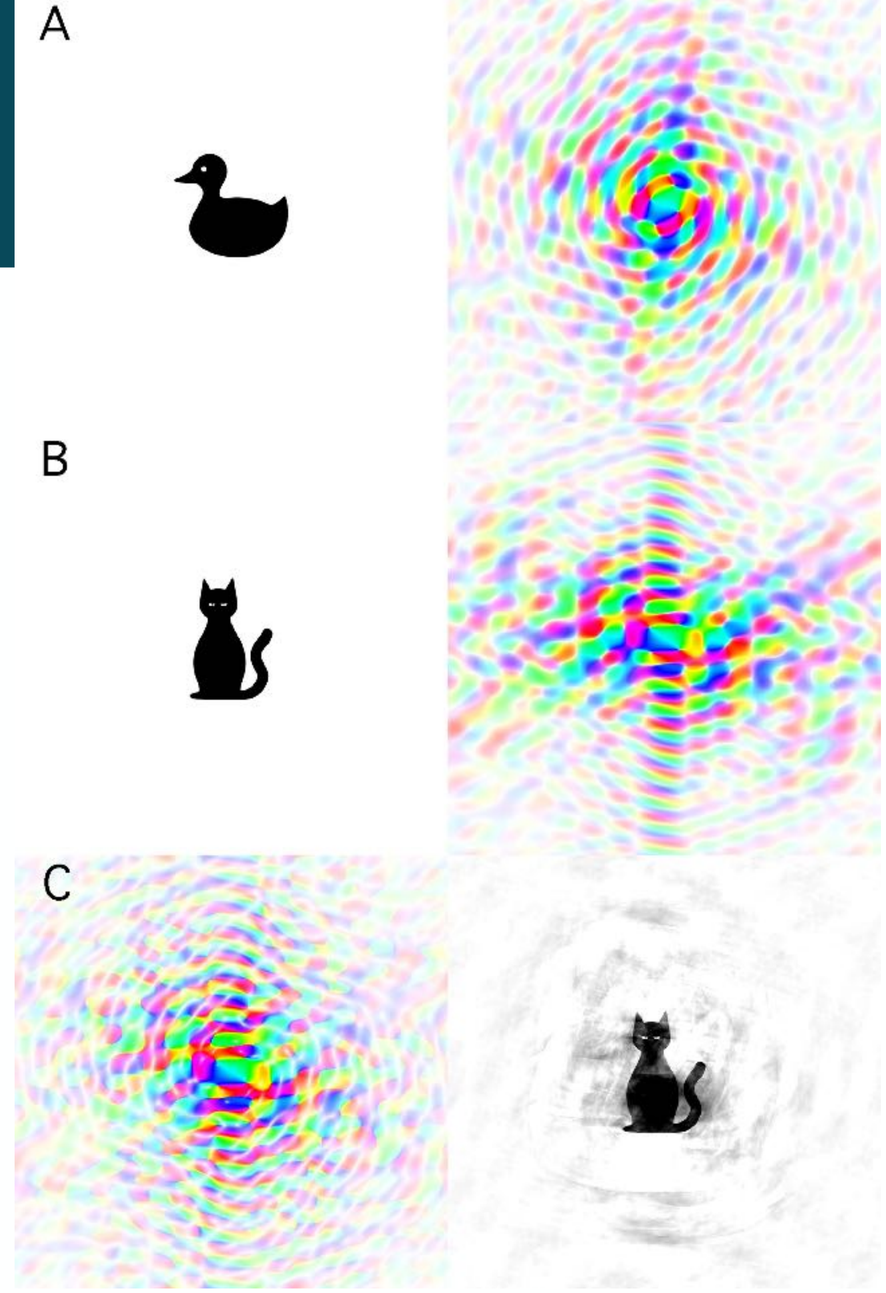


The electron density map



Model Bias

- Phases dominate the appearance of the map
- Phases are calculated from the model!



Duck amplitudes,
cat phases

InfraLife

Countering Model Bias

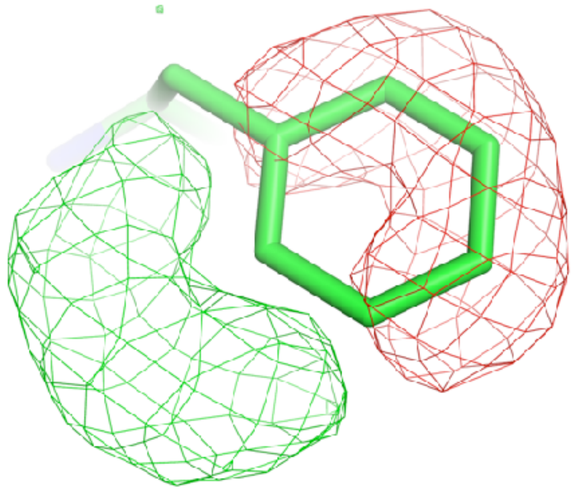
$2F_o$-F_c maps

$$\rho(x,y,z) = \sum_h \sum_k \sum_l \left(2\left|\mathbf{F}^{\text{obs}}_{h,k,l}\right| - \left|\mathbf{F}^{\text{calc}}_{h,k,l}\right| \right) \mathrm{e}^{\mathrm{i}\alpha_{\text{calc}}} \mathrm{e}^{2\pi\mathrm{i}(hx+ky+lz)}.$$

σ_a weighting

$$\mathbf{F} = (2m|\mathbf{F}_{\text{obs}}| - D|\mathbf{F}_{\text{calc}}|)\mathrm{e}^{i\alpha_{\text{calc}}}$$

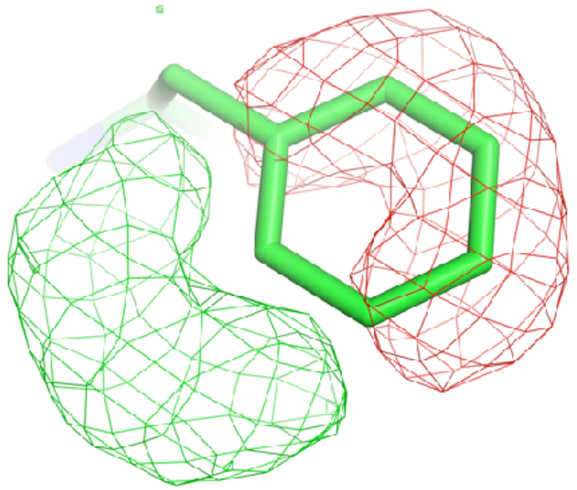
Difference (mF_o-DF_c) maps



- Positive (green) density → Something in data missing in model
- Negative (red) density → Something in model not consistent with data

InfraLife

Difference (mF_o-DF_c) maps



σ_a weighting used here too

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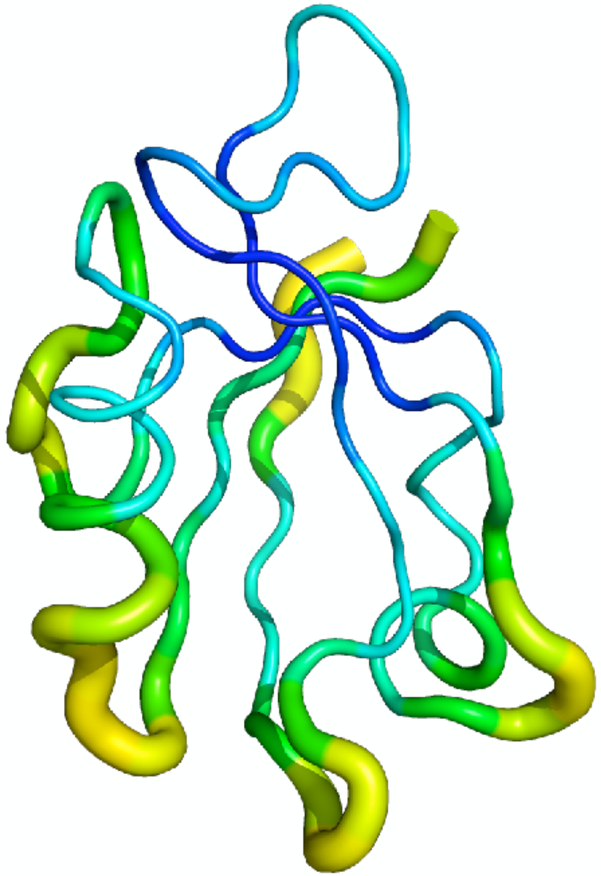
Crystallographic refinement

- Optimise calculated scattering from model to fit data
- Prior chemical knowledge → Restrain bond lengths & angles
- Model the disorder of scatterers

Modelling disorder – Atomic Displacement Factors



$$B = 8\pi^2 U$$

B (Å^2)	√U (Å)
10	0.36
20	0.50
30	0.62
40	0.71
50	0.80

Crystallographic refinement – Data vs. parameters

1. Data
   1.1. Observed structure factors
   1.2. Restraints on bond lengths & angles
2. Parameters
   2.1. Coordinates (3/atom)
   2.2. Atomic Displacement Factors (1/atom isotropic, 6/atom anisotropic)
   2.3. Occupancies (1/atom)

Crystallographic refinement – Data vs. parameters

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   - 1.1. Observed structure factors — From the experiment
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Crystallographic refinement – Data vs. parameters

1. Data
   - 1.1. Observed structure factors — From the experiment
   - 1.2. Restraints on bond lengths & angles — From prior chemical knowledge
2. Parameters
   - 2.1. Coordinates (3/atom)
   - 2.2. Atomic Displacement Factors (1/atom isotropic, 6/atom anisotropic)
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Crystallographic refinement – R-values

$$R = \frac{\sum_{h,k,l} [|\mathbf{F}_{\text{obs}}| - |\mathbf{F}_{\text{calc}}|]}{\sum_{h,k,l} [|\mathbf{F}_{\text{obs}}|]}$$

From the model

- Crystallographic residual – how different the model is from data
- Global indicator
- R_{work} → reflections used in refinement
- R_{free} → reflections not used in refinement → independent cross-validation

Crystallographic refinement – R-values

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