

# X-ray Wavefunction Refinement

Dylan Jayatilaka

School of Chemistry and Biochemistry  
University of Western Australia

Asian Charge Density Workshop, IISc Bangalore, 2015

# X-ray Wavefunction Refinement

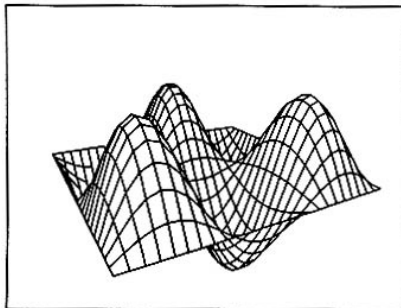
This talk is based on material in Jayatilaka (2012) in *Modern Charge Density Analysis* eds. Gatti & Macchi.

If you want the Tonto program:

- ▶ Download executables from:  
`https://github.com/dylan-jayatilaka/tonto/`
- ▶ It also comes as part of CrystalExplorer: `http://hirshfeldsurface.net/`
- ▶ And in a development version of Olex2: `http://www.olexsys.org/`

# What is a wavefunction $\Psi$ ?

- ▶  $\Psi(\mathbf{x}_1 \dots \mathbf{x}_N)$  is a function of the coordinates of all  $N$  particles in our system.
- ▶ It tells us where the particles are, and more generally it tells us how to calculate the results of experimental measurements.
- ▶ It obeys Schrödinger's wave equation, and looks like a wave or a vibrating membrane, except in many dimensions. It has  $4N$  dimensions for  $N$  electrons, including time.

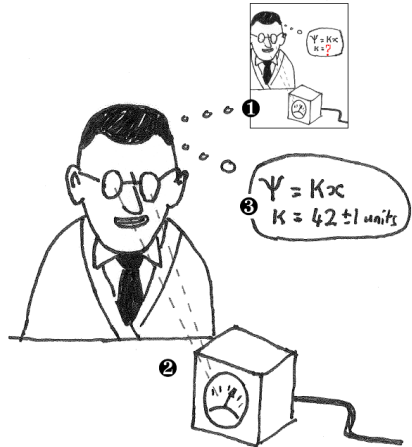


# Is it possible to measure the wavefunction?

YES.

Do it like any measurement.

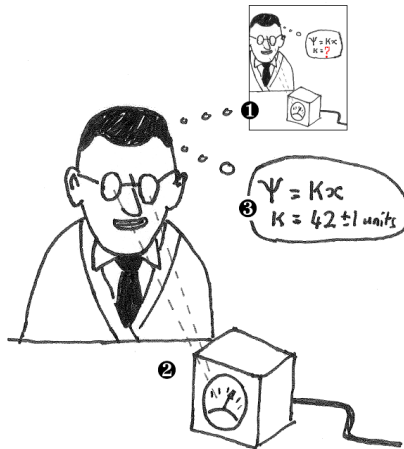
- ① Think of a model with parameters, and a corresponding experiment to find those parameters.
- ② Do the experiment.
- ③ Find the parameters.



# Should we measure wavefunctions?

The answer depends on who you talk to.

- ▶ Theorists want to calculate  $\Psi$  as was intended by theory. Good idea. Can replace real experiments.
- ▶ Experimentalists want to model their experiments. Good idea. They know theorists' wavefunctions are just models—for a subset of the real system—and with bonus approximations.
- ▶ The wavefunction is the best model: it can predict the results of multiple experiments *simultaneously*.
- ▶ Only use  $\Psi$  for single-state systems. Otherwise do dynamics or quantum statistical mechanics.



# Examples of model wavefunction determinations

- ▶ One-particle wavefunctions (LUSO) from polarized neutron diffraction. Strictly: model of the  $z$  spin density.

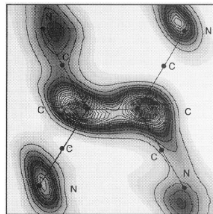
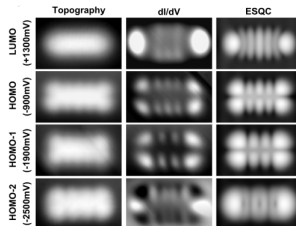


Figure 1. Maximum Entropy (MaxEnt) reconstruction of the spin density. Projection onto the  $[\text{TCNE}]^{4-}$  molecular ( $xy$ ) plane.

Zheludev et al. (1994) JACS

- ▶ One-particle wavefunctions (Dyson orbitals) from atomic transmission microscopy of adsorbed pentacene. Strictly: model of the orbital magnitude.



Soe et al. (2009) PRL

# Examples of model wavefunction determinations

- Direct reconstruction of a photon wavefunction by “weak measurement”.

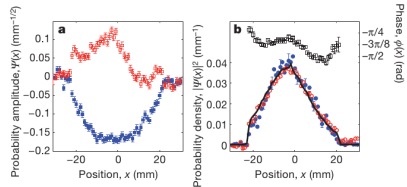
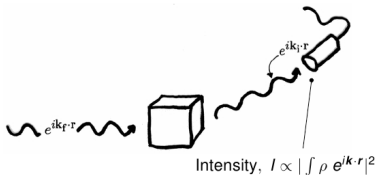


Figure 2 | The measured single-photon wavefunction,  $\Psi(x)$ , and its modulus squared and phase. **a**,  $\text{Re}\Psi(x)$  (solid blue squares) and  $\text{Im}\Psi(x)$

Lundeen et al (2011) Nature

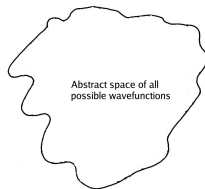
# How we get our model wavefunctions

- ▶ We use an indirect method: fitting to the (electron) density. Actually, we use its Fourier transform from X-ray diffraction experiments.

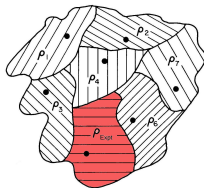


- ▶ According to Levy, the true  $\Psi$  is the one which minimizes  $E$  and gives the experimental density  $\rho^{expt}$

$$E = \min_{\Psi \rightarrow \rho^{expt}} \langle \Psi | H | \Psi \rangle$$



- ▶ To apply this formula we have to *constrain* the wavefunction to the **red** part, and minimize in there to produce the true  $\Psi$  (the dot).





# What $\Psi$ model to use?

- ▶ We want to use an *ab initio*  $\Psi$ ,  
i.e. one that has been calibrated and is known to be reliable.
- ▶ We want to use a simple model  
because *ab initio*  $\Psi$ 's are a lot of work [human and computer].
- ▶ Single determinant wavefunctions are the first (and last?) choice:
  - Hartree-Fock
  - Density functional theory (DFT) wavefunctions e.g. BLYP
- ▶ Ideally we should take into account crystalline periodicity  
because experiments are on crystals.
- ▶ Currently we use a self-consistent embedded-crystal-field method.

# Do you know your $\psi$ ?

Mean absolute deviation (MAD) for HF, BLYP and MP2, for 32 first row atom molecules [6-31G\* basis]; compared with the best CCSD(T) theory on 28 diatomics [W4 method; cc-pV5Z, relativistic]

Method	bond length /Å	dipole /D
HF	0.020	0.29
BLYP	0.020	0.25
MP2	0.014	0.23
CCSD(T)	0.002	0.02

Johnson, Gill, Pople (1994) JCP.  
Karton et al (2010).

## Conclusions:

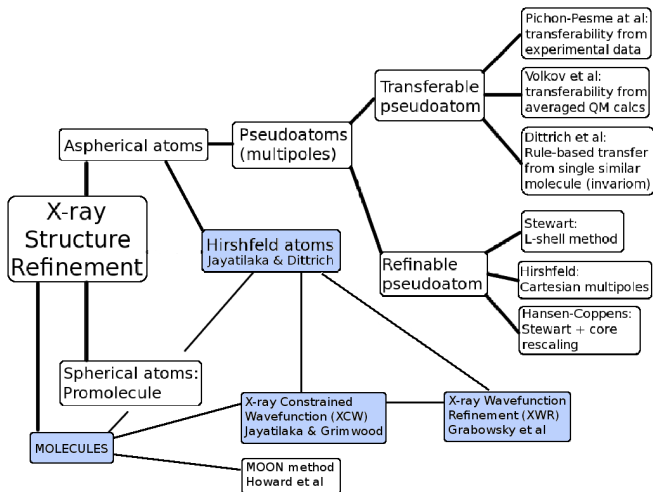
- ▶ The best methods can reduce errors by 10, but only at enormous cost.
- ▶ Experiment easily produces better geometric information.
- ▶ The experiment may well produce better dipole moments.  
Munshi (2007) CPC.
- ▶ There is scope for using X-rays to improve HF and BLYP  $\psi$ 's.

Do you know your  $\Psi$ ?



No way to improve this Psy.

# Taxonomy of X-ray refinement methods



# X-ray Wavefunction Refinement

## 1. *Refine geometry (HAR).*

- ▶ Positions, ADPs and anharmonic constants refined using Hirshfeld atom refinement (HAR).
- ▶ Use a “good” wavefunction; at least a wavefunction self-consistently embedded in the crystal-field of its own atomic charges and dipoles; and use a DFT method e.g. BLYP with at least a triple-zeta basis set.

## 2. *Refine electron distribution (XCW).*

- ▶ Constrain/restrain orbital coefficients to X-ray data for fixed geometric and ADP parameters (including anharmonic ADPs where needed) using the X-ray constrained wavefunction (XCW) method.
- ▶ Terminate fit when  $\chi_{\text{free}}^2$  is a minimum and/or when other indicators e.g. Meindl-Henn fractal dimension residual density analysis, or the Hamilton-Skeve plot, or visual inspection of plots, or all of these, indicate overfitting or pathologies.

Jayatilaka & Dittrich (2008) Acta **A64** 383 (harmonic HAR)

Bak & Grabowsky & Chen & Woinska & Jayatilaka (2015) (anharmonic HAR)

Jayatilaka & Grimwood (2001) Acta **A57** 76 (harmonic XCW)

Bak & Grabowsky & Chen & Woinska & Jayatilaka (2015) (anharmonic XCW)

# X-ray Wavefunction Refinement

Summary:

$$\text{XWR} = \text{Hirshfeld atom refinement (HAR)} + \text{X-ray constrained wavefunction (XCW)} = \text{X-ray Wavefunction Refinement (XWR)}$$

The diagram illustrates the combination of two refinement methods to form X-ray Wavefunction Refinement (XWR). On the left, the text "XWR =" is followed by an image of a silver adjustable wrench, labeled "Hirshfeld atom refinement (HAR)". This is followed by a plus sign and an image of a silver frying pan containing a spoon and a spatula, labeled "X-ray constrained wavefunction (XCW)". Finally, an equals sign is followed by an image of a pink delivery van, which represents the final result, X-ray Wavefunction Refinement (XWR).



# Hirshfeld Atom Refinement (HAR)

Minimize  $\chi^2$  wrt geometric and experimental correction parameters  $\mathbf{p}$   
(but *not*  $\Psi$  electronic parameters)

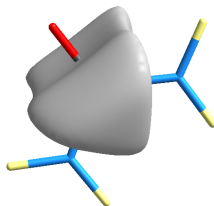
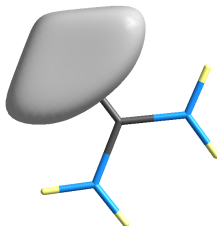
$$\chi^2(\mathbf{p}, \{F_{\text{obs}}\}) = (N_r - N_p)^{-1} \sum_{\mathbf{k}} \left( \frac{F_{\text{model}}(\mathbf{k}; \mathbf{p}) - F_{\text{obs}}(\mathbf{k})}{\sigma(\mathbf{k})} \right)^2$$

- ▶ Always look at  $\chi^2$ , it has better statistical properties than  $R$ .
- ▶ When refining hydrogen ADPs,  $R$  may hardly change, but the ADPs and X-H bond lengths are as accurate as from neutron diffraction (Capelli & Bürgi & Dittrich & Grabowsky & Jayatilaka (2014), IUCrJ **1** 361).



# What are Hirshfeld atoms?

- ▶ The HAs are atomic densities extracted from the wavefunction via Hirshfeld's formula.
- ▶ Here they are for C and O in urea when the weight function (which cuts them out of the density) is set to 0.5.
- ▶ The density and the HAs must be recalculated when the atoms move during the refinement. This is expensive!
- ▶ To save work:  $\Psi$  is recalculated only after convergence with fixed structure factors, i.e. a two-step refinement.



# Hirshfeld Atom Refinement (HAR)

Model X-ray structure factor magnitudes are:

$$F_{\text{model}}(\mathbf{k}) = s \cdot X(\xi, |F(\mathbf{k})|) \cdot \sum_A^{\text{atoms}} n_A^{-1} \sum_{\{\mathbf{S}, \mathbf{t}\}}^{\text{symops}} \bar{f}_A(\mathbf{S}^T \mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}_A} e^{i\mathbf{k} \cdot \mathbf{t}}$$

where:

$\mathbf{k}$	=	Scattering vector (cartesian)
$s$	=	Scale factor
$\xi$	=	Larsen extinction parameter
$\{\mathbf{r}_A\}$	=	Asymmetric unit atom positions
$\{\mathbf{S}, \mathbf{t}\}$	=	Rototranslational symop
$n_A$	=	Atom symmetry counting/masking factor
$\bar{f}_A(\mathbf{k})$	=	$f_A(\mathbf{k}; \{\mathbf{r}_A\}; \Psi) \times \text{TF}(\mathbf{k})$
	=	Thermally-averaged aspherical HA form factor
$f_A(\mathbf{k} \dots)$	=	Static aspherical HA form factor; from $\Psi$
$\text{TF}(\mathbf{k})$	=	Temperature factor (Gram-Charlier form)
	=	$e^{-\frac{1}{2!} \mathbf{U}^2 : \mathbf{k}} \left[ 1 - \frac{i}{3!} \mathbf{U}^3 : \mathbf{k} + \frac{1}{4!} \mathbf{U}^4 :: \mathbf{k} \right]$
$\mathbf{U}^2, \mathbf{U}^3, \mathbf{U}^4$	=	Atomic displacement parameters, ADPs



# X-ray Constrained Wavefunction (XCW)

Minimize the Lagrangian

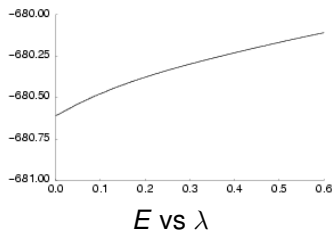
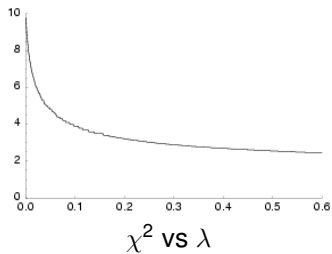
$$L = E_{QM}[\Psi(\mathbf{c})] + \lambda \chi^2[\Psi(\mathbf{c})]$$

with respect to the orbital parameters  $\mathbf{c}$ .

The term  $\lambda \chi^2$  is a penalty; it enforces the  $\rho$  fitting constraint.

- ▶ Choosing  $\lambda = 0$  gives an *ab initio* QM calculation.
- ▶ Choosing  $\lambda = \infty$  gives a (regularized) least squares fit.

# The effect of $\lambda$ in XCW on $\chi^2$ and $E$



# How to choose $\lambda$ and end the fit

You are finished if:

- ▶  $\chi^2$  is as small as you can get
- ▶ And:  $\chi^2_{\text{free}}$  has not increased
- ▶ And: you get *reasonable fit indicators* (see later)
- ▶ And: you didn't notice anything else suspicious.
- ▶ *Don't interpret  $\lambda$ , it is meaningless.* Interpret the  $\chi^2$ .

# X-ray Wavefunction Refinement

Summary:

$$\text{XWR} = \text{Hirshfeld atom refinement (HAR)} + \text{X-ray constrained wavefunction (XCW)} = \text{X-ray Wavefunction Refinement (XWR)}$$

The diagram illustrates the combination of two refinement methods to form X-ray Wavefunction Refinement (XWR). On the left, the text "XWR =" is followed by a wrench icon, which is labeled "Hirshfeld atom refinement (HAR)". This is followed by a plus sign and a cooking pot icon containing a spoon and spatula, labeled "X-ray constrained wavefunction (XCW)". Finally, an equals sign leads to a pink delivery van icon, which represents the final result, X-ray Wavefunction Refinement (XWR).