Images of unpaired electron density in molecular crystals obtained using experimentally constrained wavefunctions

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Outline

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1. The constrained wavefunction idea

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2. The polarised neutron diffraction (PND) experiment

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3. PND constrained wavefunctions and a preliminary application

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1. The constrained wavefunction idea
2. The polarised neutron diffraction (PND) experiment
3. PND constrained wavefunctions and a preliminary application
4. Polarisabilities and refractive indices from X-ray constrained wavefunctions

The constrained wavefunction idea

Key motivations

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We want a better model for electron densities in solids.

The constrained wavefunction idea

Key motivations

We want

- to make full use of our quantum mechanical knowledge about the electron density

The constrained wavefunction idea

Key motivations

We want

- to make full use of our quantum mechanical knowledge about the electron density
- to get more information out of experimental data which probes electrons in solids

The constrained wavefunction idea

The constrained wavefunction idea

To get a quantum mechanical wavefunction which fits the diffraction data.

The constrained wavefunction idea

Theoreticians minimise the energy:

$$E(\boldsymbol{c}) = \langle \Phi(\boldsymbol{c}) | H | \Phi(\boldsymbol{c}) \rangle$$

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Wavefunction parameters

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$$\chi^2(\boldsymbol{c})$$

The constrained wavefunction idea

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$$E(\boldsymbol{c}) = \langle \Phi(\boldsymbol{c}) | H | \Phi(\boldsymbol{c}) \rangle$$

Energy

Wavefunction parameters

Experimentalists minimise the error:

$$\chi^2(\boldsymbol{c})$$

Experimental model parameters

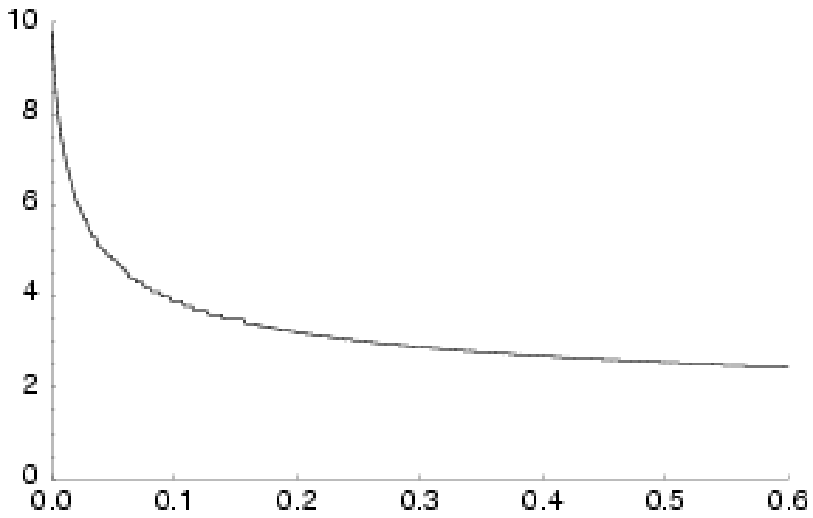
The constrained wavefunction idea

We minimise a weighted sum of both:

$$E(\boldsymbol{c}) + \lambda\chi^2(\boldsymbol{c})$$

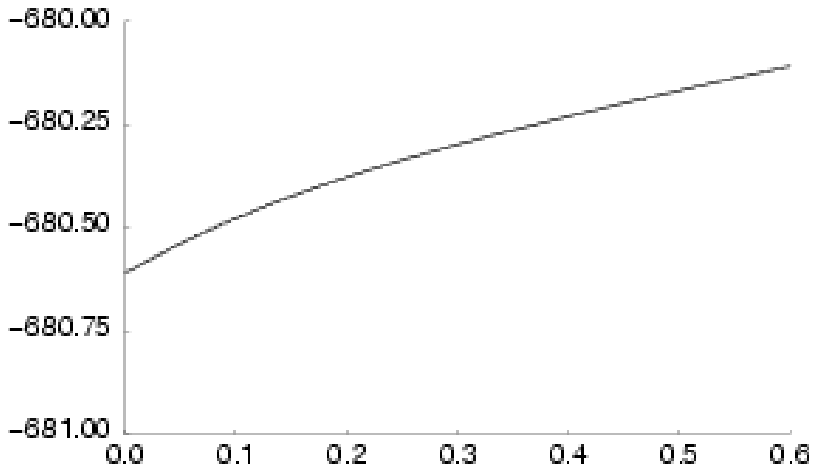
The constrained wavefunction idea

The χ^2 goes down when the adjustable weight λ increases.



The constrained wavefunction idea

The energy E goes up the smallest possible amount, as λ increases.



The constrained wavefunction idea

The constrained wavefunction idea

We get a wavefunction which reproduces the experimental data.

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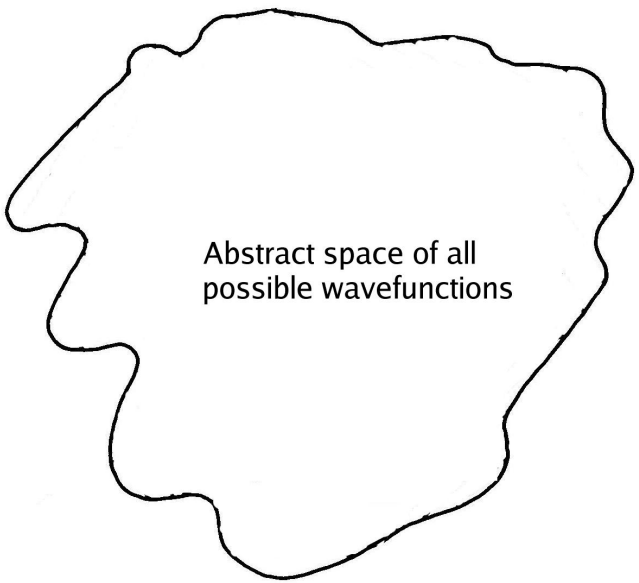
We get a wavefunction which reproduces the experimental data.

We get a wavefunction which has the best possible energy.

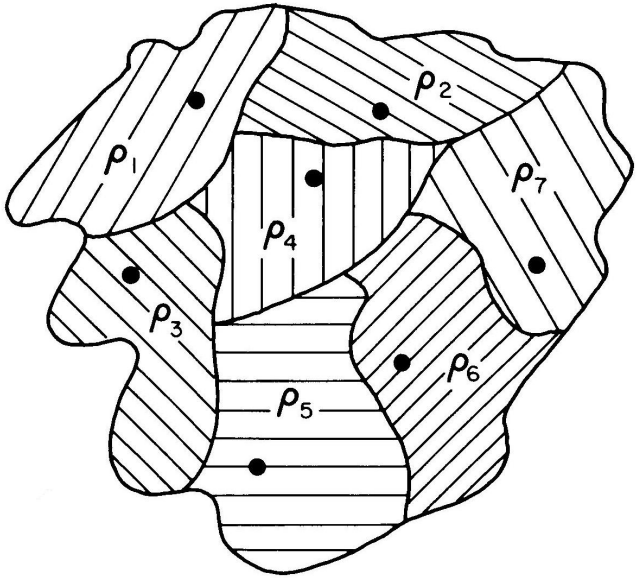
The constrained wavefunction idea

There are infintely many wavefunctions for a given system.



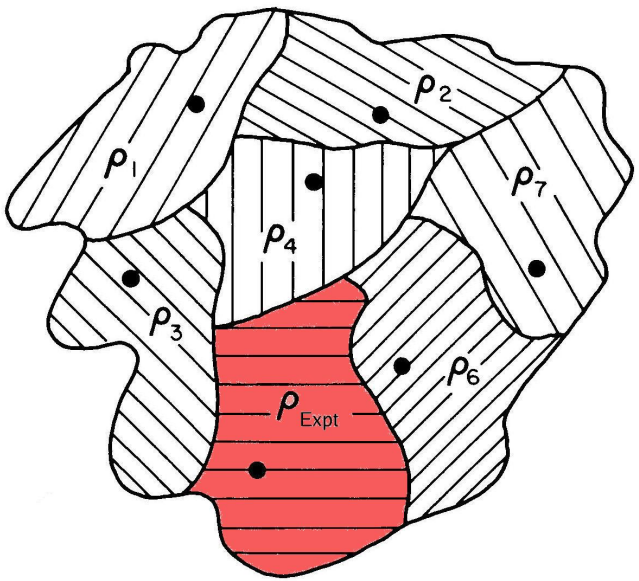
The constrained wavefunction idea

There are even infinitely many which have a given density ρ_i



The constrained wavefunction idea

We restrict our attention to those which yeild the experimental density ρ_{Expt}. We find the one with minimum energy.



What has been achieved so far?

Some highlights

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Some highlights

- Structure factors from constrained wavefunctions agree better with accurate correlated calculations

What has been achieved so far?

After fitting, structure factors agree better with accurate calculations

χ^2 values between $F_{\mathbf{k}}$'s obtained from the constrained Hartree-Fock wavefunction, and MP2 and BLYP calculations:

$F_{\mathbf{k}}$ method	Ammonia	Urea	Alloxan
HF (no constraint)	6.4	3.5	0.7
MP2	4.4	2.9	0.6
BLYP	5.3	2.7	0.6

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- The effects of the crystalline lattice can be modelled

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Ammonia: recovery of cluster size effects

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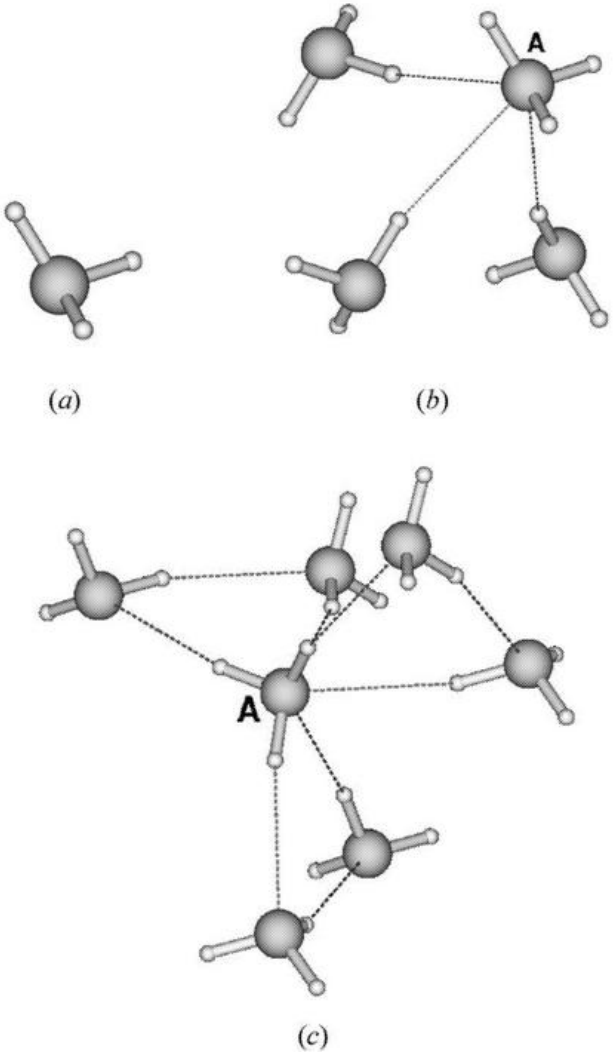


What has been achieved so far?

Ammonia: effect of cluster size on constrained fit

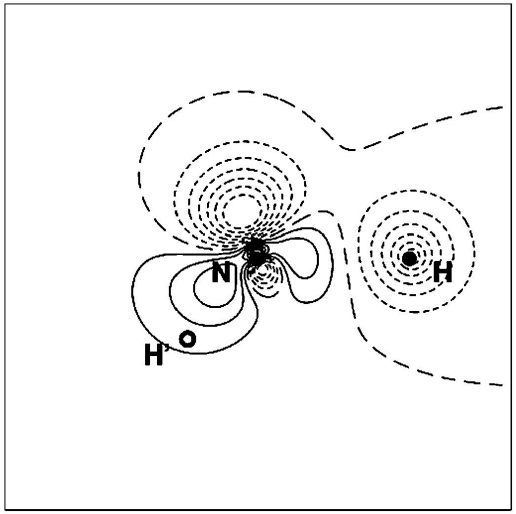
χ^2 statistics for HF structure factors, for the different clusters, *before* fitting..

Model	χ^2
$(NH_3)_1$	10.9
$(NH_3)_4$	11.3
$(NH_3)_7$	8.0

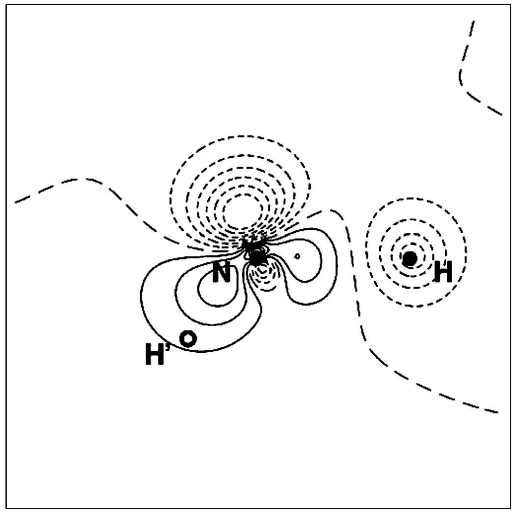
What has been achieved so far?

Ammonia: effect of cluster size on constrained fit

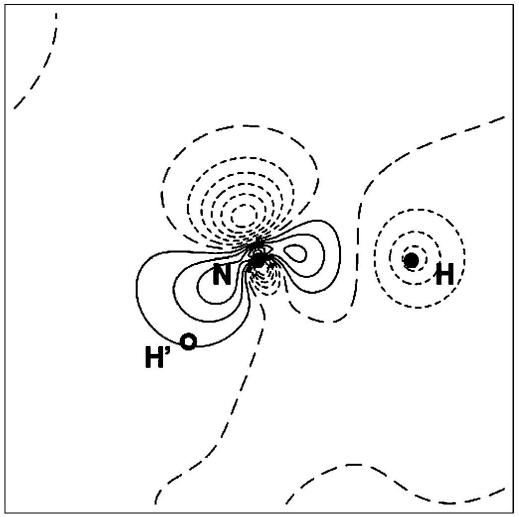
Difference density plots for fitted wavefunctions:



$(NH_3)_1$



$(NH_3)_4$



$(NH_3)_7$

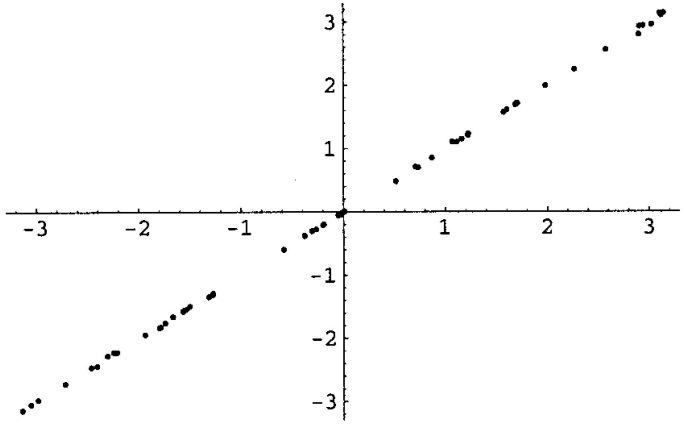
What has been achieved so far?

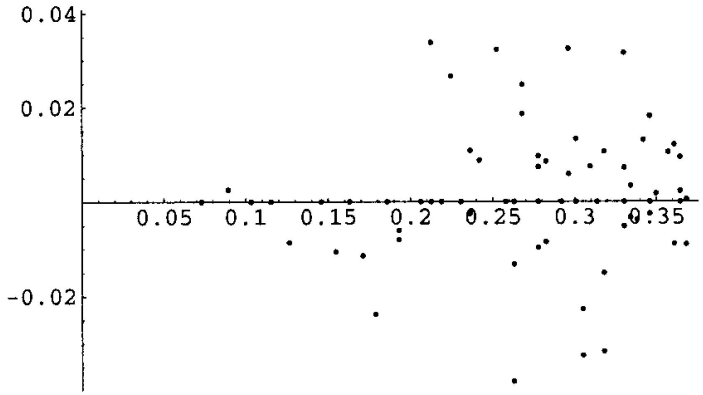
- Structure factors agree better with accurate correlated calculations, than with the original Hartree-Fock results.
- The effects of the crystalline lattice can be modelled
- For non-centrosymmetric structures, the phases obtained for the structure factors are hardly perturbed—even in the presence of noisy data

What has been achieved so far?

Recovery of phase information

Phases of fitted versus unfitted wavefunctions (NH_3):





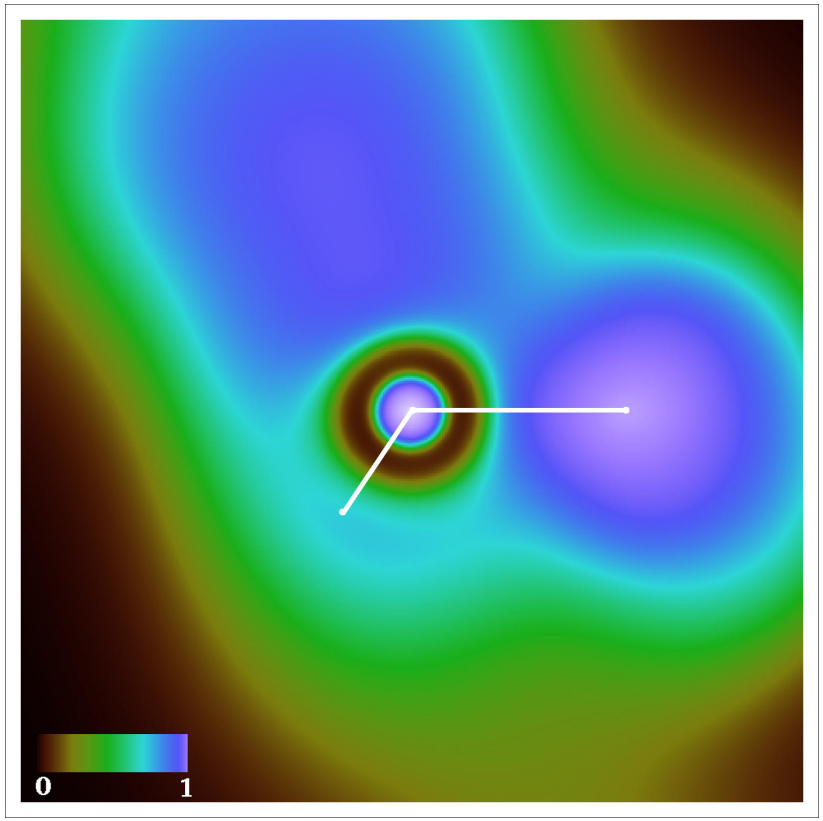
What has been achieved so far?

- Structure factors agree better with accurate correlated calculations, than with the original Hartree-Fock results.
- The effects of the crystalline lattice can be modelled
- For non-centrosymmetric structures, the phases obtained for the structure factors are hardly perturbed in the presence of noisy data
- Properties related to the density matrix (e.g. kinetic energy, kinetic energy densities, and electron localisation functions) can be obtained

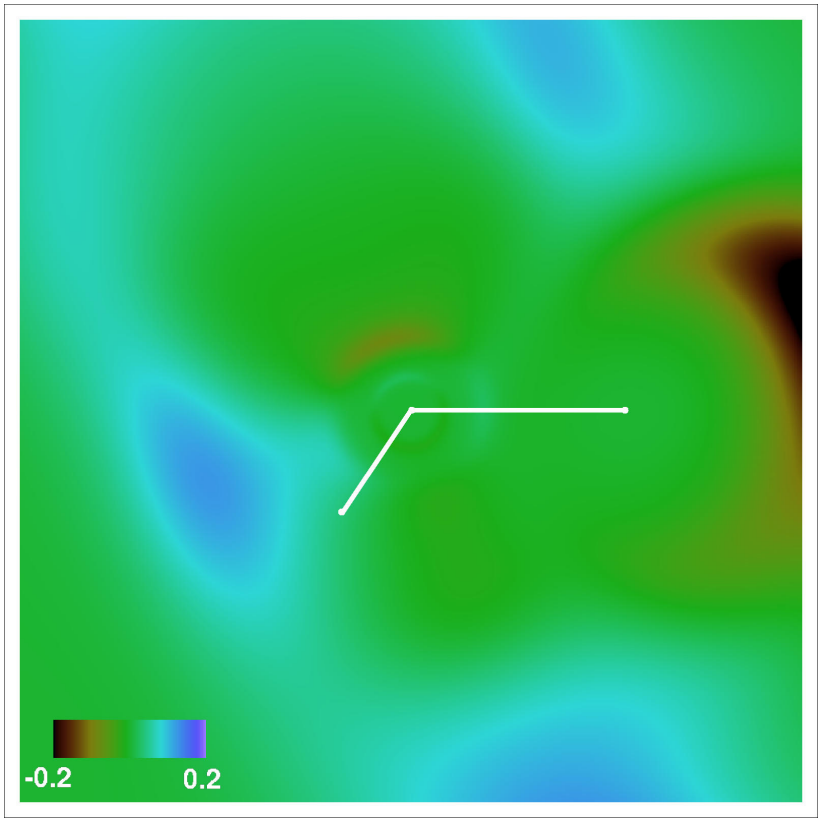
What has been achieved so far?

Properties from the density matrix

The ELF for Ammonia.



ELF

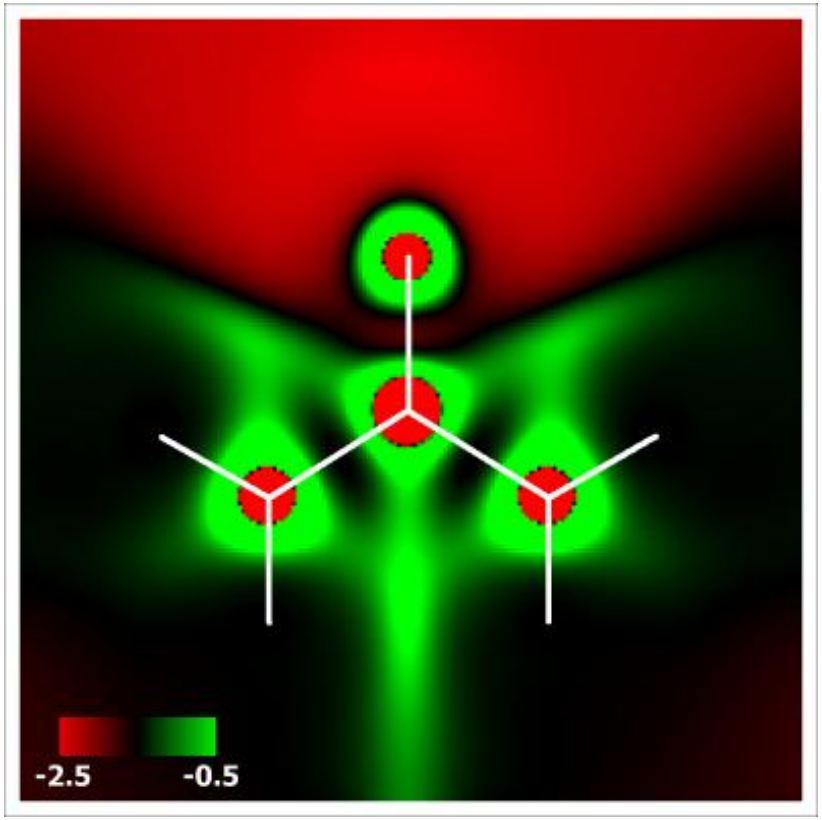


Change due to fitting

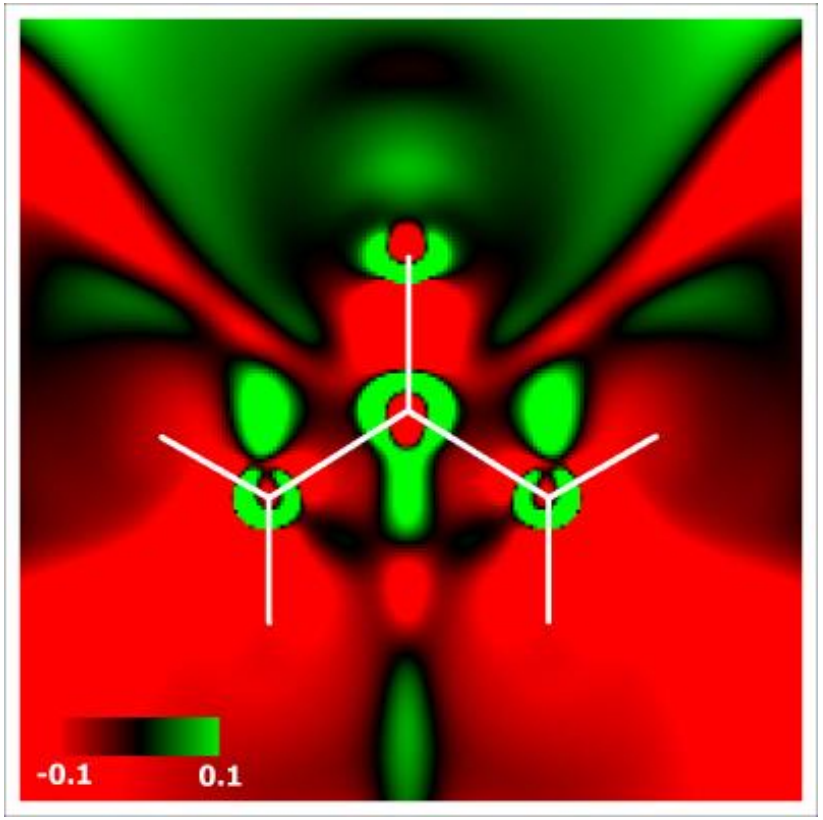
What has been achieved so far?

Properties from the density matrix

The Fermi-hole mobility function for Urea (FHMF).



FHMF



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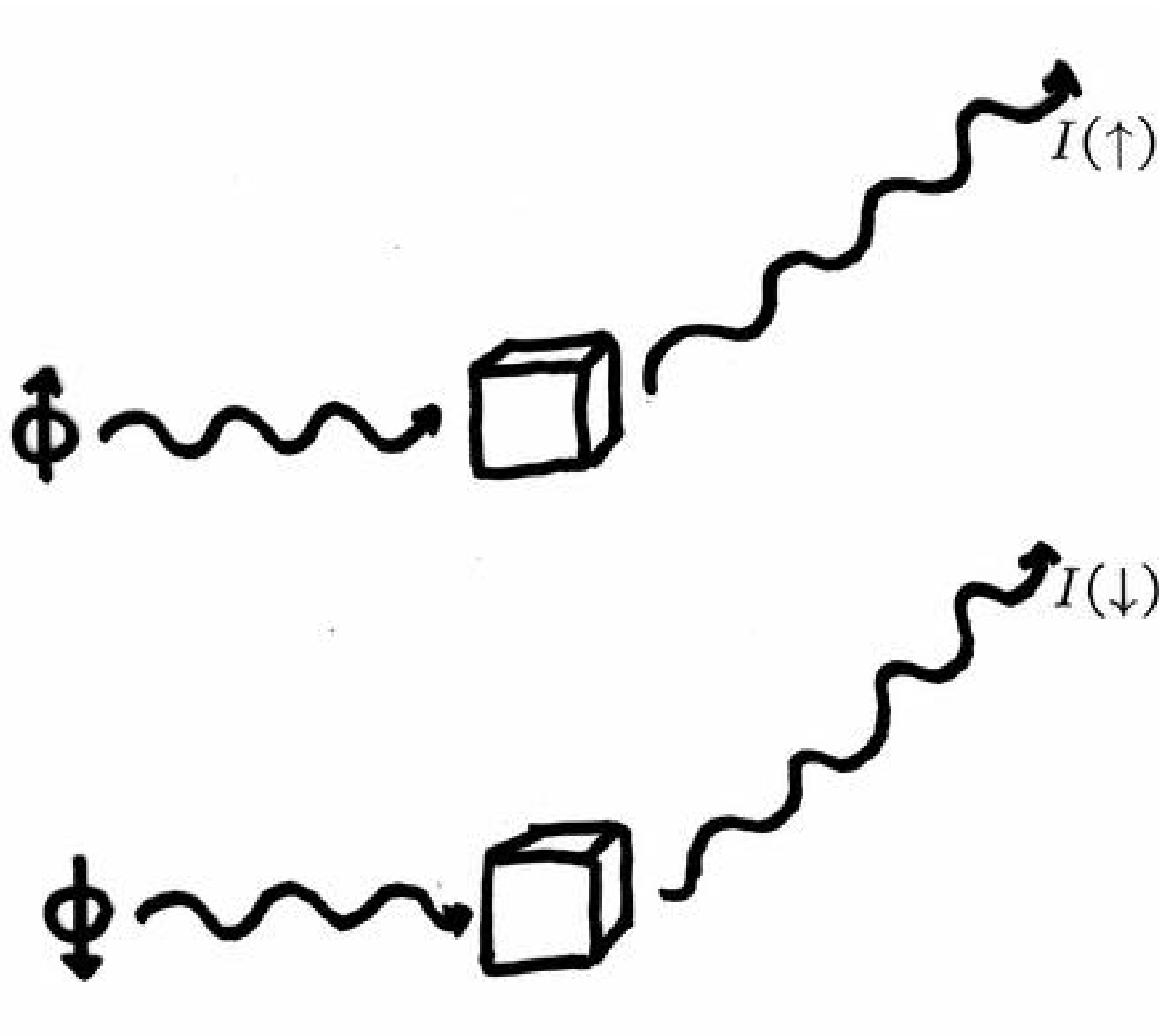
The calculations are not quick: limited to about 40 light atoms on a PC

The calculations require good data and errors — for χ^2

The PND experiment

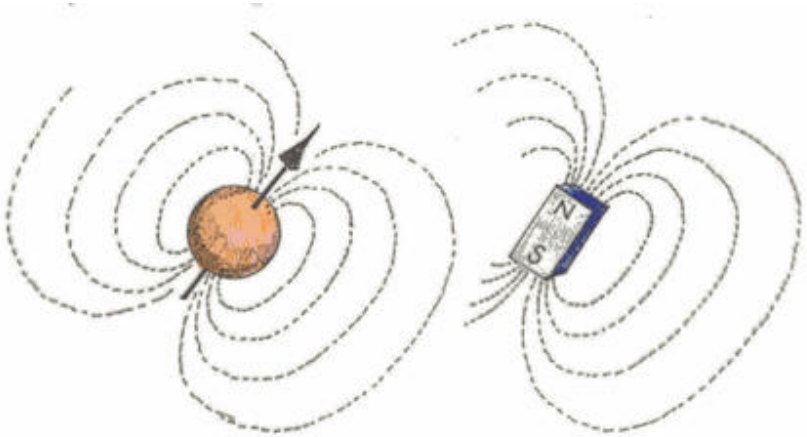
The PND experiment



What does the PND experiment tell us?

The PND experiment

Neutrons are sensitive to the magnetic field in the crystal.



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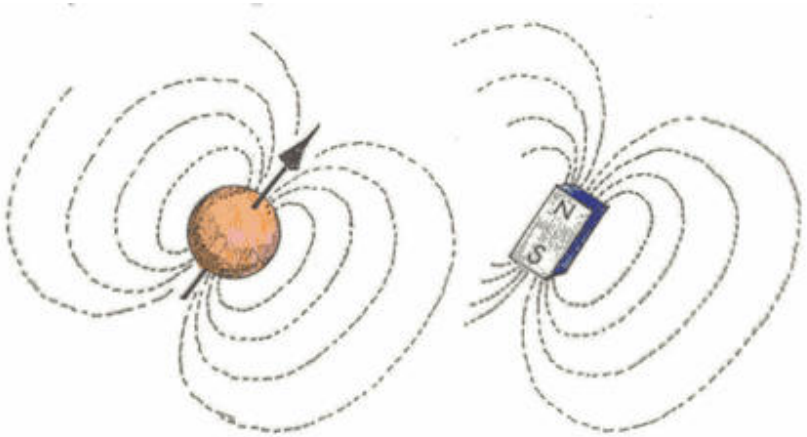


Neutrons are also sensitive to the positions of the nuclei.

The PND experiment

$$I(\boldsymbol{P}) = |F_N - \boldsymbol{P} \cdot \bar{\boldsymbol{B}}|^2 + |\boldsymbol{P} \times \bar{\boldsymbol{B}}|^2$$

Polarisation of Neutron

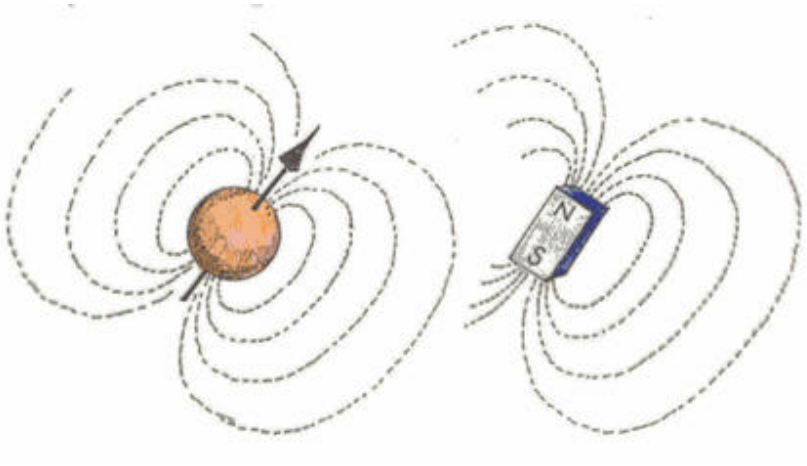
Nuclear Part

Magnetic Part.

The PND experiment

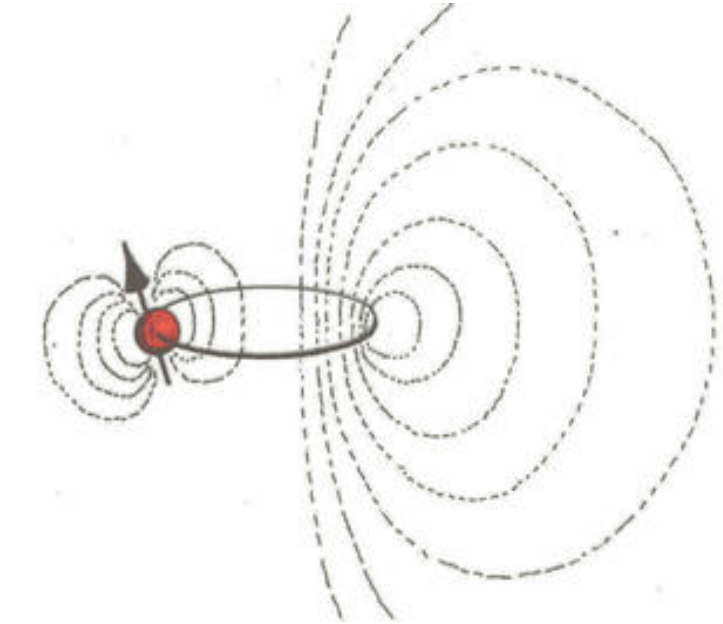
In the PND experiment the magnetic part of the scattering comes from the Fourier transform of the magnetic field density in the crystal $\bar{\boldsymbol{B}}$.

The PND experiment



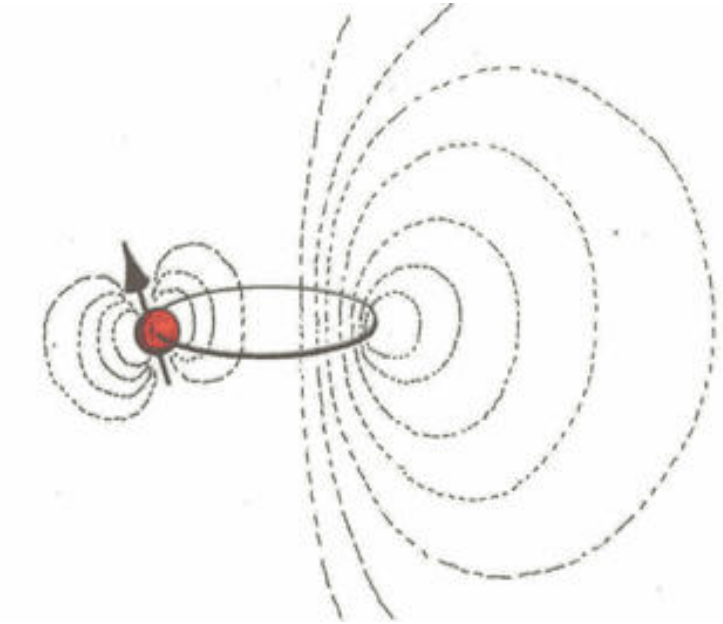
Where do the magnetic fields come from, in a crystal?

The PND experiment



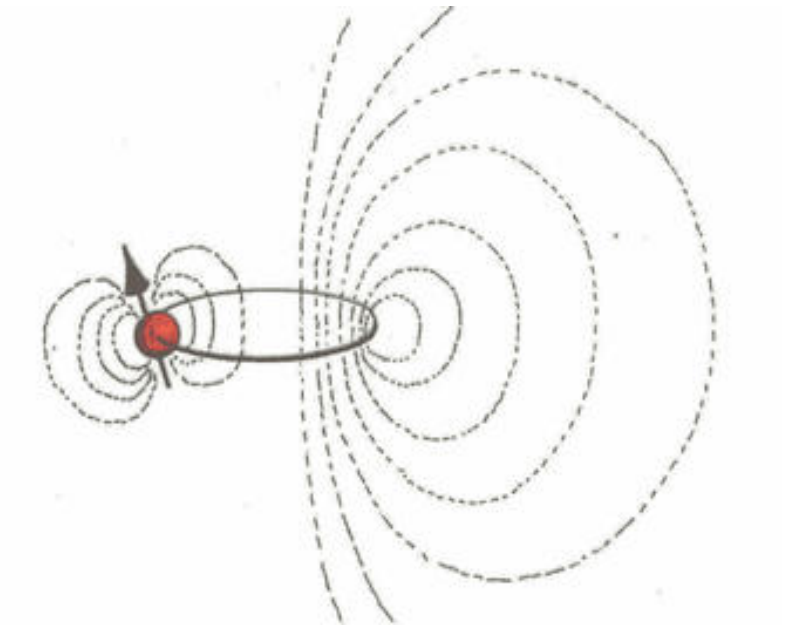
The magnetic field in crystals is due to unpaired spins and currents due to electron motion.

The PND experiment



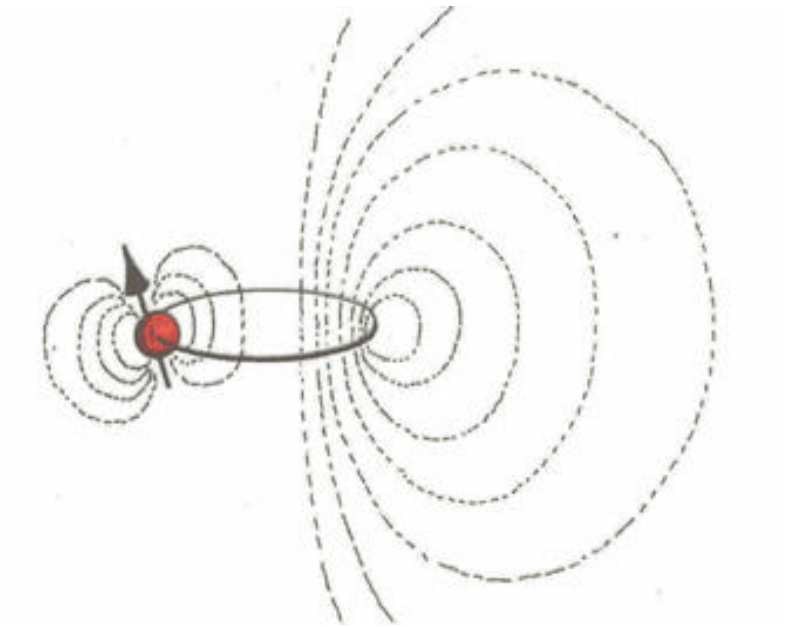
In organic molecule crystals the measured magnetic scattering is due mainly to unpaired spins aligned in the z direction:

The PND experiment



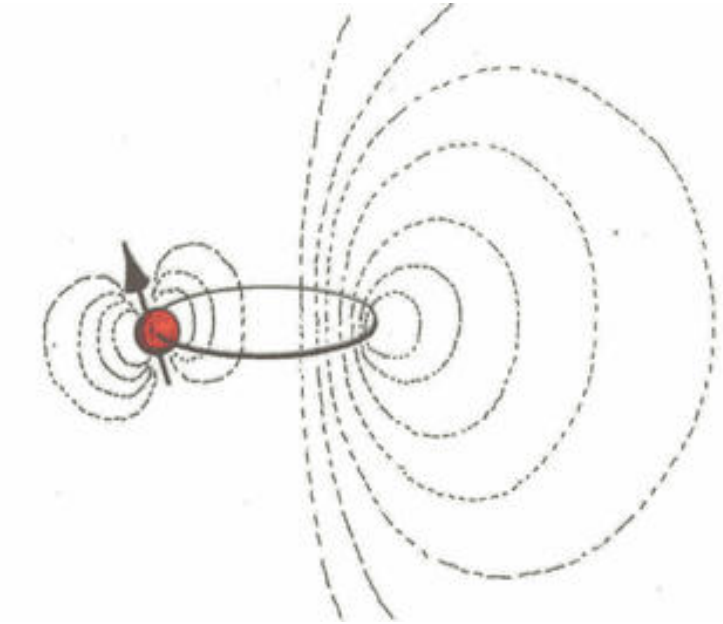
$$\bar{\boldsymbol{B}} \propto FT[\nabla \times J^S(\boldsymbol{r})]_z$$

The PND experiment



$$\bar{\boldsymbol{B}} \propto FT[\nabla \times \nabla \times S(\boldsymbol{r})]_z$$

The PND experiment



$$\bar{\boldsymbol{B}} \propto [\boldsymbol{k} \times S(\boldsymbol{k}) \times \boldsymbol{k}]_z$$

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In the PND experiment the spin density is not measured.

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We measure

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$$\bar{\boldsymbol{B}} \propto [\boldsymbol{k} \times S(\boldsymbol{k}) \times \boldsymbol{k}]_z$$

This is strictly not enough information to determine $\boldsymbol{S}$. However for systems with isotropic g tensor (e.g. most organic radicals) $\boldsymbol{S}$ can be assumed to lie in the z direction and then $\boldsymbol{S}$ can be determined.

PND constrained wavefunction

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We minimise the usual weighted sum :

$$E(\boldsymbol{c}) + \lambda\chi^2(\boldsymbol{c})$$

PND constrained wavefunction

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We must use a wavefunction which can model unpaired spins e.g. the UHF wavefunction or the UKS wavefunction.

PND constrained wavefunction

The final equations to solve[1] have the following form:

$$
\begin{aligned}
(\boldsymbol{F}^{\alpha} + \lambda \boldsymbol{v}^{N})\boldsymbol{c}^{\alpha} &= \boldsymbol{S}\boldsymbol{c}^{\alpha}\boldsymbol{\epsilon}^{\alpha} \\
(\boldsymbol{F}^{\beta} - \lambda \boldsymbol{v}^{N})\boldsymbol{c}^{\beta} &= \boldsymbol{S}\boldsymbol{c}^{\beta}\boldsymbol{\epsilon}^{\beta}
\end{aligned}
$$

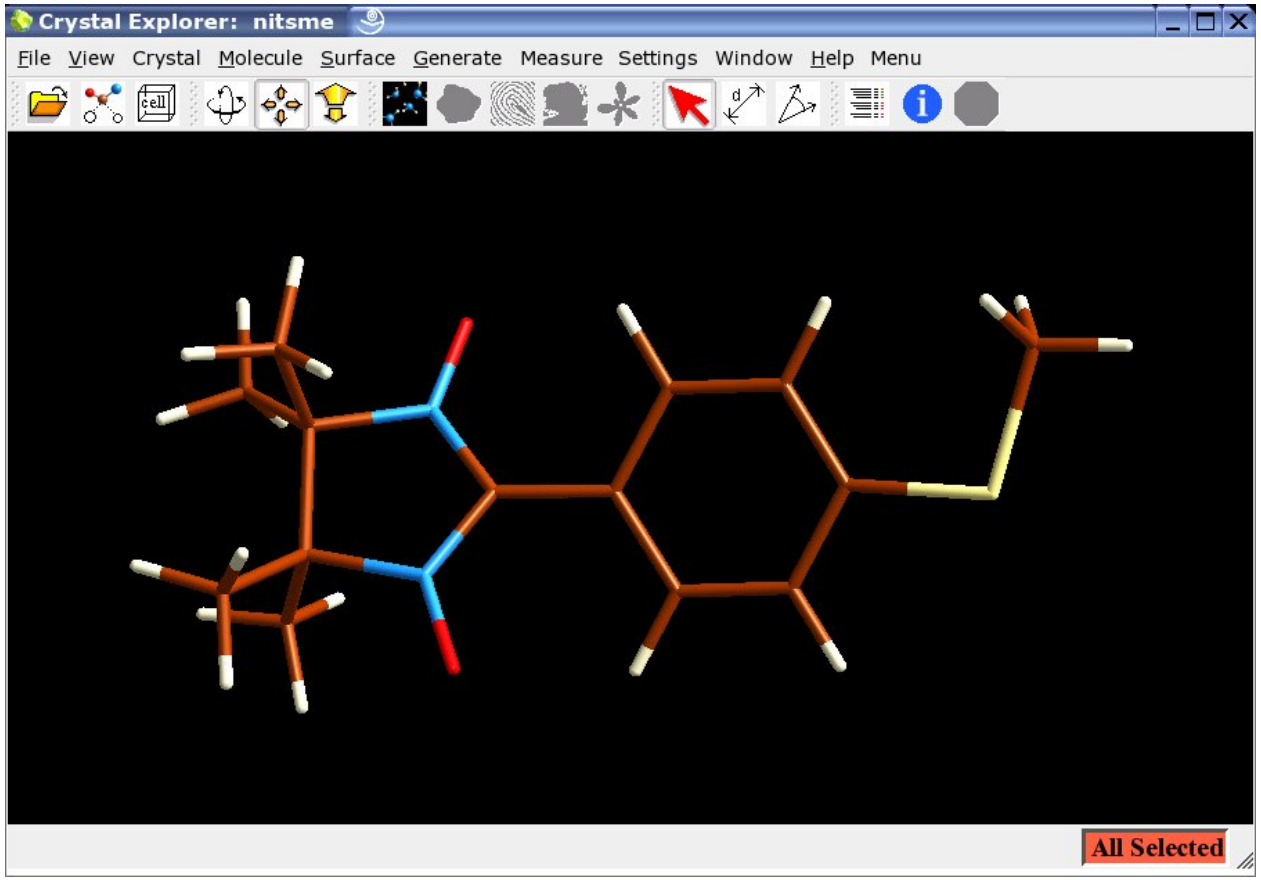
where

$$
\boldsymbol{v}^{N} = \frac{g_e}{2N_N} \sum_{\boldsymbol{k}}^{N_N} \frac{1}{(\sigma_{\boldsymbol{k}}^{N})^2} \left(F_{\boldsymbol{k}}^{N,exp} - |F_{\boldsymbol{k}}^{N}| \right) \boldsymbol{I}_{\boldsymbol{k}}
$$

[1] assuming a superposition of non-interacting molecular fragments

Preliminary results

PND constrained wavefunction for “NitSMe”



Preliminary results

PND constrained wavefunction for “NitSMe”

The situation until two months ago

	χ^2
X-ray χ^2, UHF	1.27
PND χ^2, UHF	125

Preliminary results

PND constrained wavefunction for “NitSMe”

The situation just after two months ago

	χ^2
X-ray χ^2, UHF	1.27
PND χ^2, UHF	125
PND χ^2, UBLYP	4.8

Conclusions

- We have derived and implemented a PND constrained wavefunction technique to recover spin densities in molecular crystals of organic radicals.

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- Density functional theory is essential to even get qualitatively correct spin densities
- Hartree-Fock results for the charge density of the radical are extremeley good, but are obtained from a wavefunction which is qualitatively wrong.

Non-linear optics and constrained wavefunctions

Non-linear optics and constrained wavefunctions

What is non-linear optics?

Non-linear optics and constrained wavefunctions

What is non-linear optics?

In linear optics, the bulk polarisation depends linearly on applied electric field:

$$\boldsymbol{P} = \epsilon_0 \chi E$$

Non-linear optics and constrained wavefunctions

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In linear optics, the bulk polarisation depends linearly on applied electric field:

$$\boldsymbol{P} = \epsilon_0 \chi E$$

Nonlinear optics:

$$\begin{aligned} \boldsymbol{P} &= \epsilon_0 (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3) \\ &= \epsilon_0 \chi^{eff}(E) E \end{aligned}$$

Why is non-linear optics important?

1. Control of refractive index by intensity of electric field

$$n^2 = 1 + \chi^{eff}$$

Why is non-linear optics important?

1. Control of refractive index by intensity of electric field

$$n^2 = 1 + \chi^{eff}$$

2. Make “doubled” frequencies of light

$$\begin{aligned} P &\approx \epsilon_0(\chi^{(1)}E + \chi^{(2)}E^2) \\ &\approx \epsilon_0(\chi^{(1)}E + \chi^{(2)}E_0^2 \sin^2 \omega t) \\ &\approx \epsilon_0(\chi^{(1)}E + \frac{1}{2}\chi^{(2)}E_0^2(1 - \cos 2\omega t) \end{aligned}$$

Non-linear optics and constrained wavefunctions

Non-linear optics on a molecular level

Non-linear optics and constrained wavefunctions

Non-linear optics on a molecular level

Analogue of the bulk equation is:

$$\langle \boldsymbol{\mu} \rangle = \boldsymbol{\mu}^0 + \alpha \boldsymbol{E} + \beta \boldsymbol{E}\boldsymbol{E} + \ldots$$

Non-linear optics and constrained wavefunctions

Non-linear optics on a molecular level

Analogue of the bulk equation is:

$$\langle \boldsymbol{\mu} \rangle = \boldsymbol{\mu}^0 + \boldsymbol{\alpha}\boldsymbol{E} + \boldsymbol{\beta}\boldsymbol{E}\boldsymbol{E} + \ldots$$

where

$$\begin{aligned} \alpha_{\alpha\beta} &= P_{\alpha\beta} \sum_{i \neq 0} \frac{\langle 0|\mu_\alpha|i\rangle\langle i|\mu_\beta|0\rangle}{E_0 - E_n} \\ &\approx \frac{2}{\Delta} \left[\langle 0|\mu_\alpha \mu_\beta|0\rangle - \langle 0|\mu_\alpha|0\rangle\langle 0|\mu_\beta|0\rangle \right] \end{aligned}$$

where in the last line we make the Unsöld approximation (Sylvian and Csizmadia; Spackman).

Non-linear optics and constrained wavefunctions

$$\alpha_{\alpha\beta} \approx \frac{2}{\Delta}\left[\langle 0|\mu_\alpha\mu_\beta|0\rangle - \langle 0|\mu_\alpha|0\rangle\langle 0|\mu_\beta|0\rangle\right]$$

Non-linear optics and constrained wavefunctions

$$\alpha_{\alpha\beta} \approx \frac{2}{\Delta}\left[\langle 0|\mu_\alpha\mu_\beta|0\rangle - \langle 0|\mu_\alpha|0\rangle\langle 0|\mu_\beta|0\rangle\right]$$

The polarisability is expressed only in terms on the ground state density matrix—can we use the constrained wavefunctions to develop models that fit the experimental data?

Non-linear optics and constrained wavefunctions

Results for α (linear polarizability)

		α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$
Benzene	X-ray constrained	6.78	13.02	13.37	11.05
	HF	7.18	12.77	12.77	10.91
	MP2	7.25	13.40	13.40	11.35
Urea	X-ray constrained	4.55	6.98	6.94	6.15
	HF	3.87	5.69	5.83	5.13
	MP2	4.40	6.79	6.87	6.02
MNA	X-ray constrained	9.59	18.10	25.51	17.73
	HF	10.0	18.47	23.19	17.22

Non-linear optics and constrained wavefunctions

Refractive index

		Expt	X-ray fitted	HF
Benzene	n_1	1.51	1.51	1.51
	n_2	1.61	1.66	1.66
	n_3	1.52	1.50	1.50
Urea	n_1	1.48	1.49	1.40
	n_2	1.58	1.61	1.50
MNA	n_1	1.95	2.07	1.94
	n_2	1.72	1.70	1.71
	n_3	1.43	1.32	1.34