- QCrOM 2020 -
N-REPRESENTABLE ONE-ELECTRON REDUCED DENSITY MATRICES RECONSTRUCTION AT NON-ZERO TEMPERATURES

Yoann Launay [1]

With the cooperation of :

Henri Durliat [1], Dimitri Gladkov [1], Virgin Durepaire [1], Humberto Borges [1], Lilian Seyve [1], Jean-Michel Gillet [2]

[1] *CentraleSupélec Engineering School at Paris Saclay University (FRA)*

[2] *SPMS lab, CentraleSupélec Engineering School at Paris Saclay University (FRA)*

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REVIEW OF FUNDAMENTALS : WHY 1RDMs & HOW ?

Spinless 1-electron reduced density matrix for a mixed state (N-électrons crystal)[1] :

$$\Gamma = \sum_k p_k \Gamma_k$$

$$\Gamma_k(\vec{r},\vec{r}') = \int \psi_k^*(\vec{r},\overrightarrow{r_2},\dots,\overrightarrow{r_N})\psi_k(\vec{r}',\overrightarrow{r_2},\dots,\overrightarrow{r_N})d^3\overrightarrow{r_2}\dots d^3\,\overrightarrow{r_N}$$

$n(\vec{p}) = \int \Gamma(\vec{r},\vec{r}')e^{-i\vec{p}\cdot(\vec{r}-\vec{r}')}d^3\vec{r}d^3\vec{r}'$
Densities in momentum space

& in position space
$\rho(\vec{r}) = \Gamma(\vec{r},\vec{r})$

Theoretical Structure factor & Compton profile :

$$F(\vec{Q}) = \int \rho(\vec{r})e^{-i\vec{Q}\cdot\vec{r}}d^3\vec{r}$$

$$J^{\vec{u}}(q) = \int n(\vec{p})\delta(\vec{p}\cdot\vec{u}-q)d^3\vec{p}$$

? $F_{exp}(\vec{Q})$ **&** $J^{\vec{u}}_{exp}(q)$

REVIEW OF PREVIOUS WORK: SDP programming [2]

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Model : $\Gamma(\vec{r},\vec{r}') = \sum_{ij} P_{ij}\phi_i^*(\vec{r})\phi_j(\vec{r}')$ (ϕ_i) orthogonalized basis set (AOs & GTOs)

Data : Crystal simulated F & J + Noise = **pseudo-experimental F_exp and J_exp**

Refinement [3] : $\min_P \chi^2 = \sum_\alpha \frac{|F_\alpha(P)-F_{exp,\alpha}|^2}{\sigma_\alpha^2} + \sum_\beta \frac{|J_\beta(P)-J_{exp,\beta}|^2}{\sigma_\beta^2}$

N-representability Constraints [4]: $tr(P) = N$, $\mathrm{Sp(P)C[0,2]}$

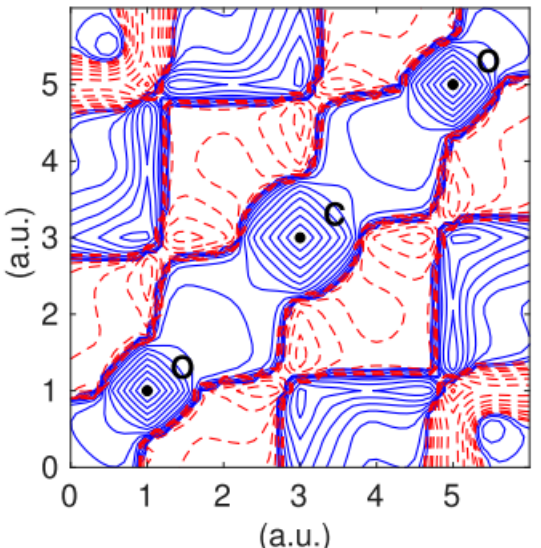
RESULTS : MOLECULAR CRYSTAL, DRY ICE AT OK

→**NEED OF FLEXIBLE MODEL:**
0K unreal?
Other crystals with interactions ?

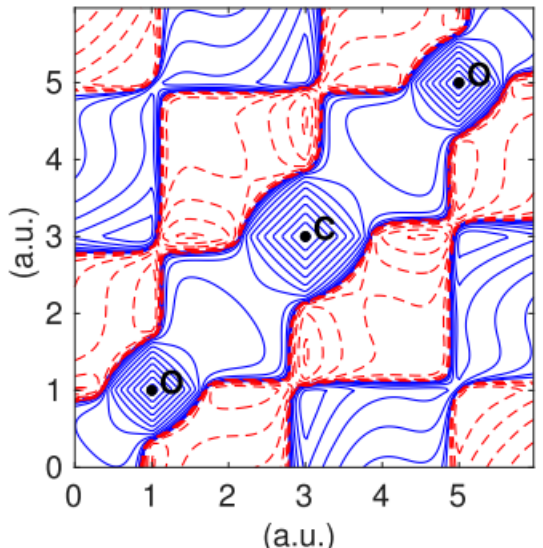
1-RDM along OCO bonding (+/- 0,01x 2^n contours)

Blue = non-negative & Red = non-positive

Inferred
(on 3 Compton profile directions, 1800 structure factors)



Pseudo-real & periodic (Crystal)



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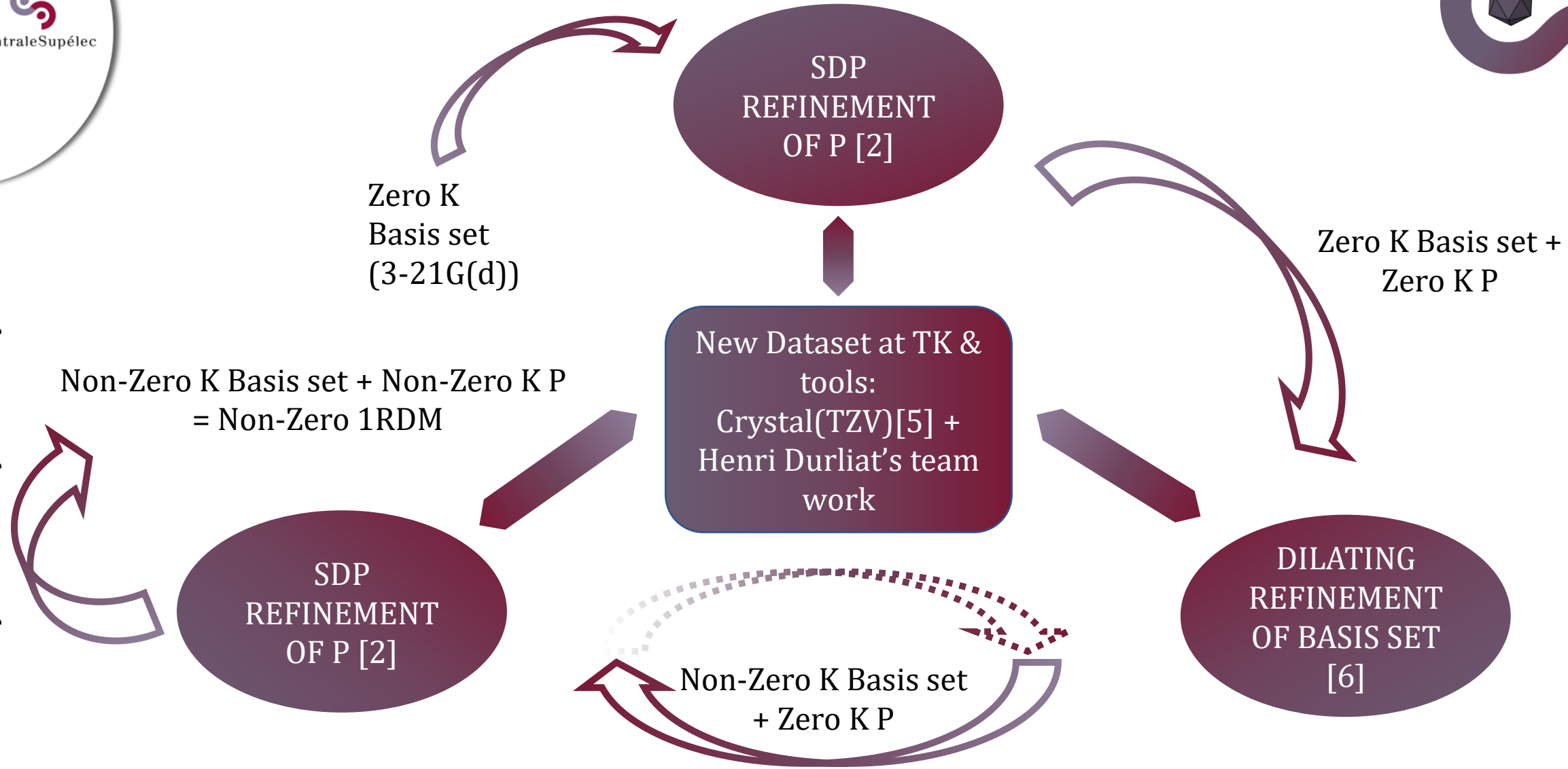
NEW PURPOSE AND METHODS: Road to non-zero K



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NEW PURPOSE AND METHOD: HOW TO DILATE ? 4 INVESTIGATIONS

1) **EXPLICIT ONE** : Crystal MSDs [8]
   + Dynamical Structure Factors refinement theory [9] (moving orbitals)
   + thermal non-sensitivity of Compton profiles

GTOs :

$$f(x,y,z)e^{-\alpha(\vec{r}-\vec{R})^2} \rightarrow f(x,y,z)e^{-\vec{\alpha}(\vec{r}-\vec{R})^2}$$

$$\alpha_X = \frac{\alpha}{1+2\alpha < R_X^2 >}$$ For Anisotropic Basis set

$$f(x,y,z)e^{-\alpha'(\vec{r}-\vec{R})^2}$$

$$\alpha' = \frac{\alpha}{1+2\alpha < R^2 >}$$ For Isotropic Basis set

2) « **Kappa** » : least squares refinement on data at T+ **Atomic** dilation of GTOs

$$f(x,y,z)e^{-\alpha(\vec{r}-\vec{R})^2} \rightarrow f(x,y,z)e^{-\alpha'(\vec{r}-\vec{R})^2}$$

3) « **Dzêta** » **:** least squares refinement on data at T+ Dilatation of **all Atomic Orbitals [6]**

4) « **Alphas** » **(general case)**: least squares refinement on data at T+ Dilatation of **all GTOs**

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CURRENT RESULTS

Dry ice at 100K

Blue = non-negative & Red = non-positive

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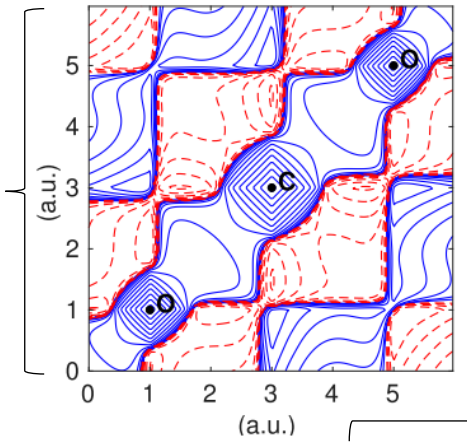
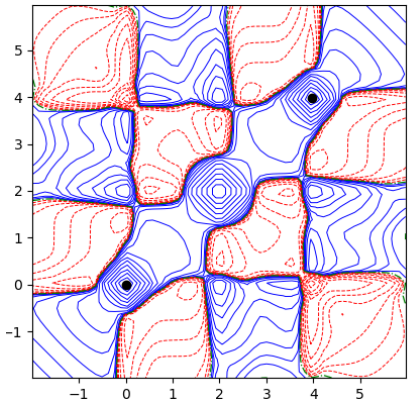
0K Theoretical 1RDM (Crystal)





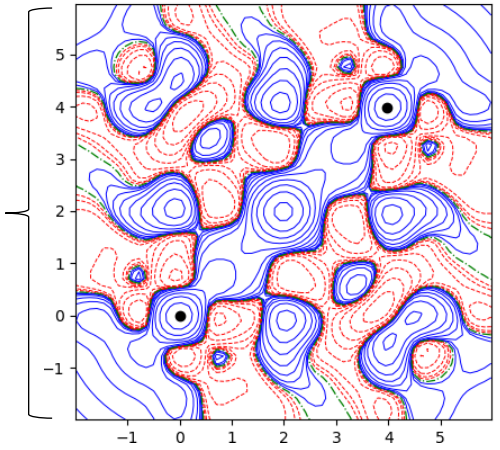
0K SDP-refined 1RDM

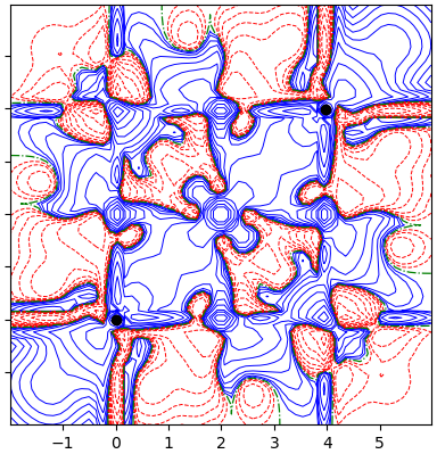
100K « Kappa » 1RDM

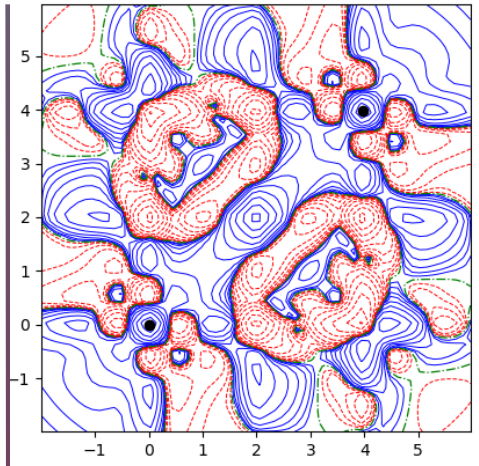
100K « Dzêta » 1RDM

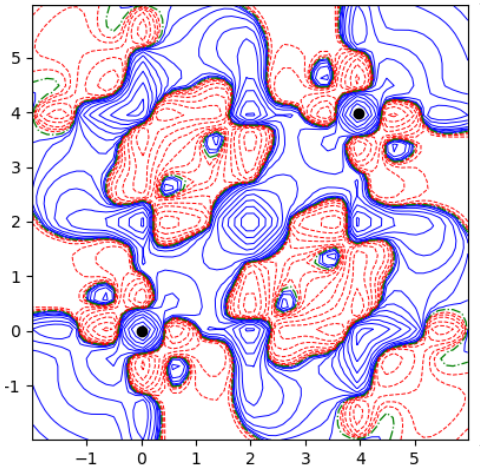
100K « Explicit » 1RDM

(+/- 0,01x 2^n contours)



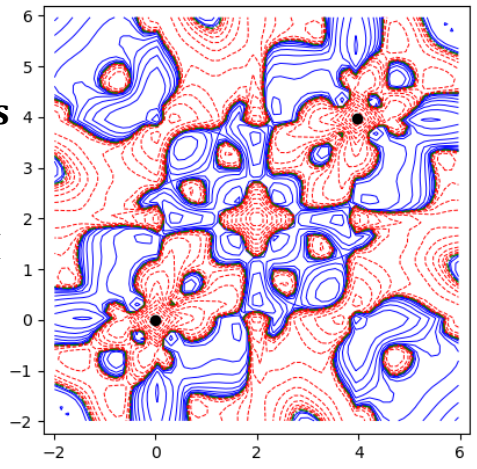


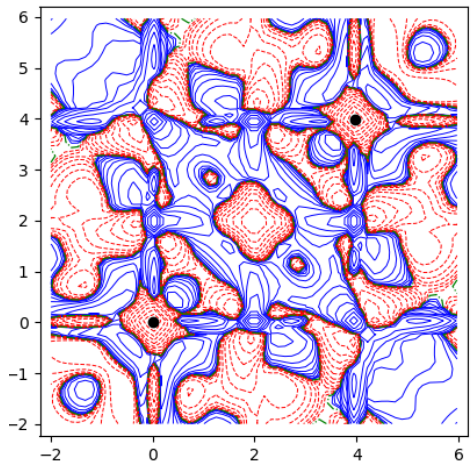


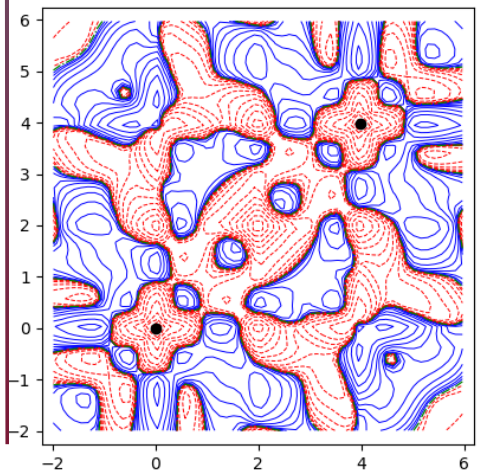


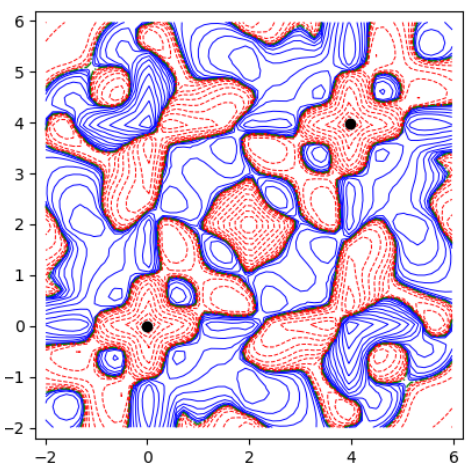
Déformations = 100K 1RDM - 0K SDP-refined 1RDM

(+/- 0,001x 2^n contours)









100K « Alphas » (10 iterations) 1RDM

Yoann Launay, Paris Saclay University Student

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CONCLUSION AND THANKS

TO DO: FIND COMPROMISES BETWEEN DATA AND PERFORMANCE OF REFINEMENTS

NEXT GOAL : POPULATION MATRICES REFINEMENT ON CLUSTERS

Crucial References

[1] Jean-Michel Gillet and Tibor Koritsanszky , *Past, Present and Future of Charge Density and Density Matrix Refinements*, Modern Charge-Density Analysis, Springer (2012), p181-211.

[2] Benjamin De Bruyne and Jean-Michel Gillet, *Inferring the one-electron reduced density matrix of molecular crystals from experimental data sets through semidefinite programming*, Acta Crystallographia Section A 76,1 (Jan. 2020), p1-6.

[3] Jean-Michel Gillet and Pierre Becker, *Position and momentum densities. Complementarity at work : Refining a quantum model from different data sets*, Journal of Physics and Chemistry of Solids 65.12 (2004), p. 2017-2023.

[4] A. J. Coleman, *Structure of Fermion Density Matrices,* Rev. Mod. Phys. **35**, 668 (July 1963).

[5] A. Erba, M. Ferrabone, R. Orlando and R. Dovesi, J. Comput. Chem., 34, 346 (2013). Accurate dynamical structure factors from ab initio lattice dynamics: The case of crystalline silicon.

[6] Saber Gueddida, Zeyin Yan and Jean-Michel Gillet, *Development of a joint refinement model for the spin-resolved one-electron reduced density matrix using different data sets*, Acta Crystallographica Section A 74,2 (March 2018), p131-142.

[7] MOSEK ApS. The MOSEK optimization toolbox for MATLAB manual. Version 9.0. 2019. url : http://docs.mosek. com.

[8] Madsen, Anders & Civalleri, Bartolomeo & Ferrabone, Matteo & Pascale, Fabien & Erba, Alessandro, *Anisotropic displacement parameters for molecular crystals from periodic Hartree–Fock and density functional theory calculations,* Acta Crystallographica Section A. 69 (2013).

[9] Patrick Azavant et al. , *A quantum chemical method for the calculation of dynamic structure factors : Applications to silicon, magnesium oxide and beryllium oxide*, Theoretica Chimica Acta 89.4 (1994), p. 213-226.

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Yoann Launay, Paris Saclay University Student

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