

## Deposited materials

### The experimental and theoretical QTAIMC study

#### of the atomic and molecular interactions in dinitrogen tetroxide

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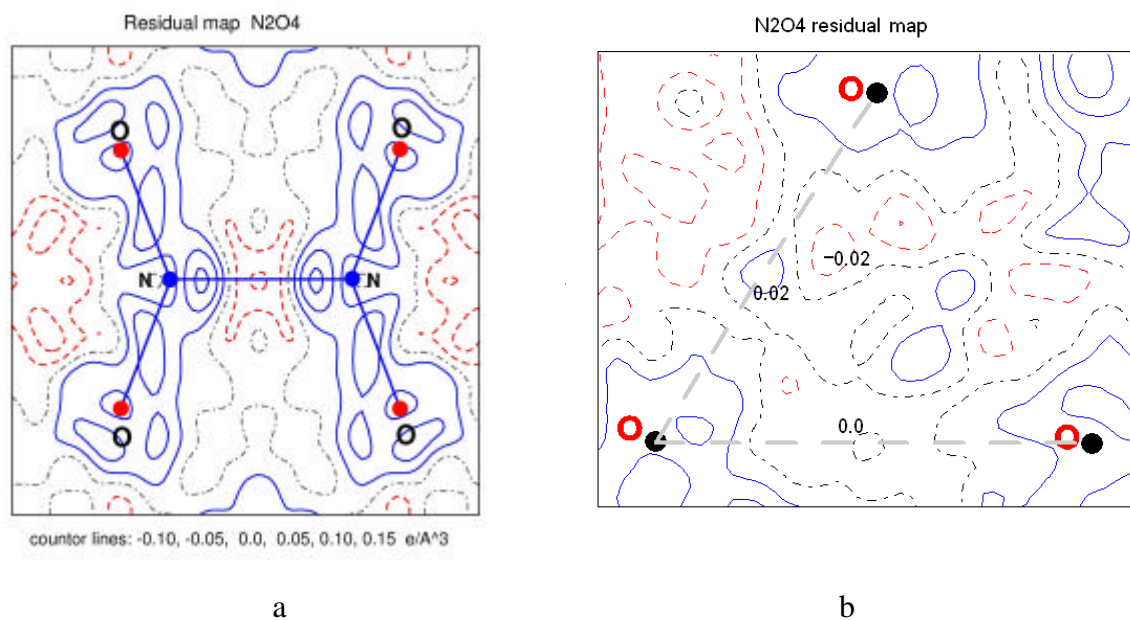


Fig 1D. The residual Fourier electron-density maps in crystalline  $N_2O_4$ : (a) in the (001) plane, (b) in the plane the containing O...O intermolecular bond paths.

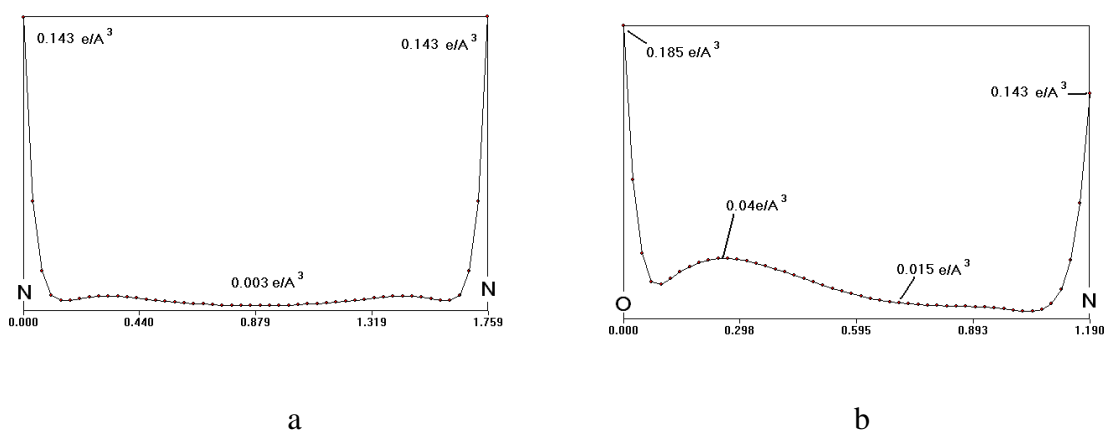
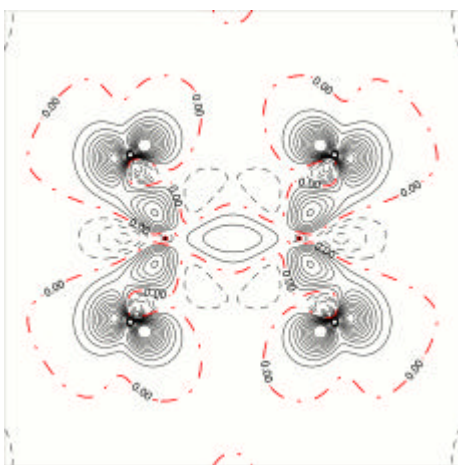
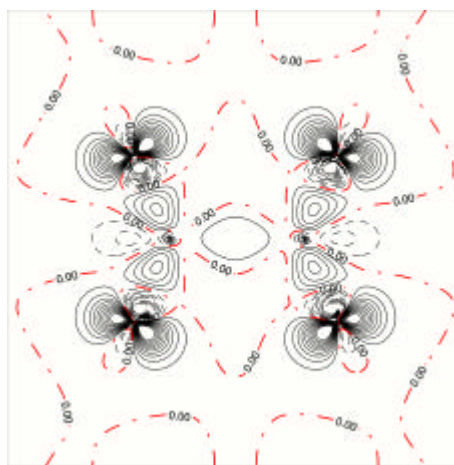


Fig 2D. The distribution of error in the experimental electron density along (a) the N-N and (b) N-O bonds.



a



b

Fig. 3D. Deformation electron density in the (001) plane of  $\text{N}_2\text{O}_4$ : (a) experiment, (b) theory. Line interval is  $0.1 \text{ e} \cdot \text{\AA}^{-3}$ .

## The main properties of the electrostatic (Coulomb) inner-crystal field

Consider the main properties of the electrostatic (Coulomb) inner-crystal field following to Pathak & Gadre (1990), Gadre et al. (1996), Zhurova et al. (2001), Leboeuf et al. (1999), Tsirelson & Ozerov, (1996), Tsirelson et al., (2000, 2001). The electrostatic potential (ESP),  $\phi(\mathbf{r})$ , is a scalar function which has the positive nuclear and negative electronic components. The ESP of isolated positively charged and neutral atoms is positive everywhere beyond the nuclear site and monotonically going to zero far from the nuclei (Weinstein et al., 1975). At the same time, the ESP of an isolated negatively charged atom monotonically falls, passes through zero and attains a unique negative minimum at some distance from nuclei (Sen & Politzer, 1989). Then, the ESP, being negative, approaches zero with increasing  $r$ . It is the superposition of the bounded-atom contributions that defines the features of the ESP in a crystal. Close to nuclei, the ESP goes to the infinity; the behavior of  $\phi(\mathbf{r})$  in these areas of a crystal is similar to that for true three-dimensional maxima. Also, the ESP exhibits in a crystal two- and one-dimensional maxima and local minima (Pathak & Gadre, 1990, Leboeuf et al., 1997, 1999, Tsirelson et al., 2000, Zhurova et al., 2001, 2002, Tsirelson et al., 2001, Balanarayan & Gadre, 2003, Bouhmaida et al., 2002, ? ata et al., 2007, Novakovic et al, 2007). These maxima, saddle points and minima in the ESP corresponding, respectively, to the nuclear positions, internuclear lines, atomic rings and cages in a crystal unit cell. Correspondingly, in the same way as electron density, the ESP can be characterized by the gradient vector field  $\nabla\phi(\mathbf{r})$  as well as by critical points,  $\mathbf{r}_c$ , points at which  $\nabla\phi(\mathbf{r}_c) = 0$ . The number of critical points in ESP obeys the Poincare-Hopf relationship in the form  $n_{-3} - n_{-1} + n_{+1} - n_{+3} = n_{\max} - n_{\min}$  (Leboeuf et al., 1999). Here  $n_S$  is the number of critical points with signature  $S$  (the algebraic sum of the signs of the ESP curvatures), while  $n_{\max}$  and  $n_{\min}$  denote the number of (asymptotic) ESP maxima and minima.

The physical meaning of the gradient lines of  $\phi(\mathbf{r})$  is well known: they define the classical electrostatic field  $\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r})$  as well as the value of the classical inner-crystal electrostatic force acting at a tangent to the gradient lines on the charge  $q$  at  $\mathbf{r}$ :  $\mathbf{F}(\mathbf{r}) = q \mathbf{E}(\mathbf{r})$ . The electric field  $\mathbf{E}(\mathbf{r})$  and electric-field force  $\mathbf{F}(\mathbf{r})$  vanish at the critical points in the ESP; at the nuclear positions at equilibrium, this agrees with the requirements of the Hellmann-Feynman theorem (Feynman, 1939, Hellmann, 1937).

Gradient lines are not allowed to cross. As in electron density, there are pairs of the gradient lines in the  $\nabla\phi(\mathbf{r})$  field originated at the (3,-1) critical point, which terminate at two neighbouring nuclei. They form the lines linking these nuclei, ESP is maximal along these lines with respect to any lateral shift. However, these lines do not correspond to any electrostatic

atomic interaction: the electric-field force  $\mathbf{F}(\mathbf{r})$  exerted on a point unit positive probe charge along these lines is directed to a (3,-1) critical point and changes its direction at this point. Correspondingly, the (3,-1) critical points in the  $\nabla\varphi(\mathbf{r})$  field are not the bond critical points.

Nuclei of neighbouring atoms in any crystal (as in a molecule) are separated in the electric field  $\mathbf{E}(\mathbf{r})$  and electrostatic force field  $\mathbf{F}(\mathbf{r})$  by surfaces  $P_i$ , satisfying the zero-flux condition

$$\mathbf{E}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = -\nabla\varphi(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = \mathbf{F}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0, \quad \forall \mathbf{r} \in P_i(\mathbf{r}),$$

where  $\mathbf{n}(\mathbf{r})$  is a unit vector normal to the surface  $P_i$  at  $\mathbf{r}$ . Each such surface defines the atomic  $\varphi$ -basin, inside of which the nuclear charge is completely screened by the electronic charge, i.e. *electrically neutral bonded* pseudoatom (Tsirelson et al., 2001). In other words, they define the regions in a crystal dominated by a charge of one or another nucleus: electron density within each  $\varphi$ -basin is attracted to the corresponding nucleus.

It is worth to mention that in a crystal,  $\varphi(\mathbf{r})$  does include the volume average value of the ESP,  $\varphi_0$ , which depends on crystal shape and crystal surface structure (Tsirelson & Ozerov, 1996), however the gradient field  $\nabla\varphi(\mathbf{r})$  does not depend on the  $\varphi_0$  value.

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Table 1D. N<sub>2</sub>O<sub>4</sub> multipole parameters obtained in this work in comparison with data by Messerschmidt et al (2002)

*harmonic approximation for atomic vibrations has been used*

Atom O

mutipole	This work	Messerschmidt et al (2002)
Pv	3.026(10)	2.97(2)
P1, 1	-0.049(5)	-0.03(1)
P1,-1	0.005(4)	-0.01(1)
P2, 0	-0.027(4)	-0.03(1)
P2, 2	-0.051(3)	-0.06(1)
P2,-2	-0.005(3)	-0.02(1)
P3, 1	-0.004(4)	0.00(1)
P3,-1	0.012(5)	0.01(1)
P3, 3	0.002(4)	0.01(1)
P3,-3	-0.012(4)	-0.02(1)

Atom N

mutipole	This work	Messerschmidt et al (2002)
Pv	1.224(10)	1.28(1)
P1, 0	-0.012(6)	0.00(0)
P2, 0	-0.011(5)	-0.02(0)
P2, 2	-0.074(5)	-0.06(1)
P3, 0	0.075(7)	0.05(1)
P3, 2	0.068(7)	0.03(1)

The refinement indices are:

This work:

$$R(F) = 0.015, wR = 0.023, S = 1.44.$$

Messerschmidt et al (2002):

$$R(F) = 0.021, wR = 0.053; S = 1.45.$$