Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Physics and Chemistry of Solids 65 (2004) 2025–2029

JOURNAL OF
PHYSICS AND CHEMISTRY
OF SOLIDS

www.elsevier.com/locate/jpcs

Phase transition in iodine: a chemical picture

A. Savin

Laboratoire de Chimie Théorique, CNRS et Université Paris VI, 4, place Jussieu, Paris F-75252, France

Abstract

The phase transition under pressure in iodine is analyzed using the electron localization function (ELF), explaining that the increase of the *c*/*a* ratio under compression is due to the presence of the lone pairs.

A probabilistic interpretation is given for ELF.

Keywords: D. Phase transitions

1. Introduction

The iodine molecular crystal undergoes a metal–insulator transition at high pressure [1–3]. Under pressure, iodine loses its diatomic molecular character. In this phase, each iodine atom has a nearly isotropic environment in one plane while a significant anisotropy exists in the direction perpendicular to it [4,5]. In spite of the reduction of volume with pressure, the *c*/*a* ratio is significantly increased.

The aim of the present paper, based upon a density functional calculation, is not to analyze the band structure of iodine in different phases, but to describe them 'chemi-chemically'. The tool used for doing it is the electron localization function (ELF), introduced by Becke and Edgecombe [6]. This function detects the arrangement of electron pairs in molecules and crystals. Starting with [7], many systematic tests have been performed. (For a review, see [8].)

Before discussing the results, the present paper will first introduce ELF by presenting a new interpretation, based upon the probability of finding a pair of electrons with opposite spins in a given vanishingly small region of space. It should be mentioned that several other interpretations of ELF exist, cf., e.g. Refs. [6,8], the one based on the fluctuations being the closest [9].

2. The significance of the electron localization function (ELF)

It has been soon recognized in quantum chemistry that a bridge between chemical concepts and quantum mechanics can be constructed by considering the probabilities of having a given number of electrons in a region of space [10, 11]. Of course, these probabilities depend on the region. When the volume of this region becomes very small, one can introduce local descriptions, functions of the spatial coordinates. It will be discussed below, how a probabilistic description for small regions is related to a function which had been used with success in analyzing chemical bonding, electron localization function (ELF).

The probability to find an electron in an infinitesimal region is given $\int_\Omega \rho(r)\mathrm{d}^3r$, or by the product of the electron density, ρ, which is practically constant within the region, and the volume of the region, $V_\Omega = \int_\Omega \mathrm{d}^3r$. One might be tempted to extend this image to larger regions. The belief that the probability of finding one electron in a given region Ω, $p(1;\Omega)$, is given by the population of this region, or the average number of electrons in Ω, $\langle N_\Omega \rangle = \int_\Omega \rho(r)\mathrm{d}^3r$, is wrong, however, when the total number of electrons in the system, $N > 1$. This can be seen most easily when considering the case when Ω corresponds to the whole space yielding $\int \rho(r)\mathrm{d}^3r = N$; this is impossible as the probability must lie between 0 and 1. The error stems from ignoring the fact that with the increase of V_Ω, it starts to be

---

E-mail address: savin@lct.jussieu.fr

0022-3697/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2004.08.015

probable to have more than one electron in Ω, and this contributes to the average, $\langle N_\Omega\rangle$.

ELF is a local measure of the probability of having more than one electron in a small region Ω. It can be quantified by the difference between $\langle N_\Omega\rangle$ and $p(1;\Omega)$: one explores space with a small sphere having constant $\langle N_\Omega\rangle$, and analyzes how $p(1;\Omega)$ changes in space, with respect to $\langle N_\Omega\rangle$. (A derivation is given below.)

It should be mentioned that ELF has been defined originally [6] for a single closed-shell Slater determinant. With this restriction, many other interpretations of ELF can be given, the preceding being just one among many (see, e.g. [8], and references therein). For example, for a closed shell single determinant, the probability of finding two electrons with antiparallel spin in a small region Ω, is proportional to $\langle N_\Omega\rangle^2$ (see below), and thus invariant all over space. ELF can be thus seen as a measure of the intrusion of electrons with same spin, or of how the probability of finding two electrons with same spin changes through space, when the probability to find a pair electrons of opposite spin, in the same small region Ω is given in of the position of the sphere. (This explains the observations made in Ref. [12], and shows that the 'modified' ELF function given there will yield ELF for sufficiently small volumes.) It is important to notice that several ELF definitions differ for correlated (or even open-shell) functions. It is not yet clear how important these differences will be, although a preliminary study seems to indicate that they are not so large as one would be inclined to expect [13].

ELF is a function of r, $\eta(r)$, defined to lie between 0 and 1. For a one- or two-electron system (the latter described by a single closed-shell Slater determinant) $\eta=1$. In a region where the intrusion of other electrons is feeble, $\eta \lesssim 1$. These are the regions where electron pairs are formed (e.g. bonding regions). Between these regions, η drops down to small values. When analyzing ELF, it should be kept in mind that quantum mechanics allows several pairs to occupy the same region of space, simply by keeping orbitals orthogonal. This makes the value of η to decrease. Examples are the uniform electron gas (where $\eta=1/2$, by the definition of ELF), or the atomic shells, where η decreases from ≈ 1 (s^2 shells), to ≈ 0.8 (shells made of s and p orbitals), ≈ 0.6 (shells made of s, p and d orbitals), etc.

It is also possible to define regions Ω such that the probability of finding a pair of electrons in Ω is maximal [14,15]. In many (but not all) cases these regions are similar to those defined by the 'basins' of ELF [16], the spatial domains attached to a given maximum in ELF. (For each point contained in a basin of ELF, following the gradient of η leads to the same maximum of η.)

We will now start with the deviation of formulas. (The reader not interested in the derivation may skip the remaining part of this section.) Let us consider first the average number of electrons in a given region, Ω, its population. It is given by

$$\langle \hat{N}_\Omega\rangle = \int_\Omega \rho(r)\mathrm{d}^3r = \sum_{\nu=0,N} \nu p(\nu;\Omega)$$
$$= 0p(0;\Omega) + 1p(1;\Omega) + 2p(2;\Omega) + \cdots \qquad (1)$$

where $\hat{N}_\Omega$ counts the electrons in Ω. ($\hat{N}_\Omega$ can be written as $\hat{N}_\Omega = \sum_{i=1,N} \hat{\theta}_\Omega(r_i)$, where the one-particle operator $\hat{\theta}_\Omega(r_i)=1$, if r_i is in Ω, and $\hat{\theta}_\Omega(r_i)=0$ otherwise.) Furthermore, $p(\nu;\Omega)$ is the probability of finding exactly ν electrons in Ω.

For vanishingly small Ω, $1 \approx p(0;\Omega) \gg p(1;\Omega) \gg p(2;\Omega) \gg \cdots$ and $\int_\Omega \rho(r)\mathrm{d}^3r \approx \rho(r)\int_\Omega \mathrm{d}^3r = \rho(r)V_\Omega$, where V_Ω is the volume of the region Ω; Eq. (1) yields the usual interpretation of the electron density:

$$\langle \hat{N}_\Omega\rangle \approx \rho(r)V_\Omega \approx p(1;\Omega), \quad \text{for } V_\Omega \to 0. \qquad (2)$$

As V_Ω increases, $\langle \hat{N}_\Omega\rangle$ starts to differ from $p(1,\Omega)$, as the term containing $p(2;\Omega)$ starts to interfere (cf. Eq. (1)). As it was convenient to use the electron density ρ to describe the first term appearing in the description of $p(1;\Omega)$, we will use the pair density, $P_2(r_1,r_2)$, normalized to $N(N-1)$, to obtain the dominant term for small V_Ω and thus replace $p(2;\Omega)$. To get the relationship between $p(2;\Omega)$ and P_2, we may, e.g. consider $\langle \hat{N}_\Omega^2\rangle$, where

$$\hat{N}_\Omega^2 = \left(\sum_{i=1,N} \hat{\theta}_\Omega(r_i)\right)^2$$
$$= 2\sum_{i\neq j} \hat{\theta}_\Omega(r_i)\hat{\theta}_\Omega(r_j) + \sum_{i=1,N} \hat{\theta}_\Omega(r_i)^2$$
$$= 2\sum_{i<j} \hat{\theta}_\Omega(r_i)\hat{\theta}_\Omega(r_j) + \hat{N}_\Omega \qquad (3)$$

as $\hat{\theta}_\Omega(r_i)^2 = \hat{\theta}_\Omega(r_i)$. As $\sum_{i\neq j} \hat{\theta}_\Omega(r_i)\hat{\theta}_\Omega(r_j)$ is a two-particle operator:

$$\langle \hat{N}_\Omega\rangle = \frac{1}{2}\int_\Omega\int_\Omega P_2(r_1,r_2)\mathrm{d}^3r_1\mathrm{d}^3r_2 + \langle \hat{N}_\Omega\rangle$$
$$= \sum_{\nu=0,N} \nu^2 p(\nu;\Omega)$$
$$= 0p(0;\Omega) + 1p(1;\Omega) + 2^2p(2;\Omega) + \cdots \qquad (4)$$

Subtracting Eq. (1) from Eq. (4) gives:

$$p(2;\Omega) = \frac{1}{2}\int_\Omega\int_\Omega P_2(r_1,r_2)\mathrm{d}^3r_1\mathrm{d}^3r_2 + \cdots \qquad (5)$$

It is noted in passing that for infinitesimal volumes around the position r, $p(2;\Omega) \approx \frac{1}{2}(P_2(r,r)V_\Omega^2)$, a relationship analogous to Eq. (2). (The factor 1/2 appears due to the normalization of P_2 to $N(N-1)$; $N(N-1)/2$ is the total number of electron pairs.)

From Eqs. (1) and (5), we now obtain an expression of the probability of finding one electron in Ω:

$$p(1;\Omega) = \langle \hat{N}_\Omega \rangle - \int_\Omega \int_\Omega P_2(r_1, r_2) + \cdots \tag{6}$$

Eq. (6) shows how to eliminate the contributions of the intrusion of other particles to the population of Ω, in order to obtain $p(1;\Omega)$, for small V_Ω.

To introduce a local function, we will now analyze the change of the probability of finding one electron, in a sphere centered on r, of radius R, of small volume $V_\Omega = 4\pi/3R^3$, having a constant population, for different positions r of this sphere. (This construct has been already used for defining ELF, cf. [8,17].) Thus, from now on, we will consider that $\langle \hat{N}_\Omega \rangle$ is a given small number. As Eq. (2) shows, the population $\langle \hat{N}_\Omega \rangle$ is constant, but, as the density ρ changes with r, the radius of the sphere, R, has also to change with r, $R = R(r)$:

$$R(r) \approx \left(\frac{3}{4\pi}\right)^{1/3} \langle \hat{N}_\Omega \rangle^{1/3} \rho(r)^{1/3}, \quad \text{for } V_\Omega \to 0. \tag{7}$$

Although the first term on the r.h.s. of Eq. (6), $\langle \hat{N}_\Omega \rangle$, is, by construction, invariant with r, the second may not be. As we are in the limit of small V_Ω, as for Eq. (2), it is enough to use a Taylor expansion of r_1 and r_2 around the center of the sphere, r, and consider the first r-dependent term appearing in the expansion in R.

As we want to recover the definition of ELF, as given in Ref. [6], we will now consider in our derivation the case of a closed shell Slater determinant, although we could continue it without this assumption. P_2 can be decomposed

$$P_2(r_1, r_2) = \frac{1}{2}\rho(r_1)\rho(r_2) + P_2^{\parallel}(r_1, r_2), \tag{8}$$

where the first term on the r.h.s. comes from the electrons of opposite spin, while $P_2^{\parallel}$ gives the contribution of electrons with the same spin. Double integration over Ω, as needed in Eq. (6) produces for the first term on the r.h.s. of Eq. (8) a constant

$$\int_\Omega \int_\Omega \rho(r_1)\rho(r_2)\mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 = \langle \hat{N}_\Omega \rangle^2 / 2 \tag{9}$$

The second term, however, yields a function dependent on r (cf. Ref. [18]):

$$\int_\Omega \int_\Omega P_2^{\parallel}(r_1, r_2) = \frac{32\pi^2}{45} \rho(r) \left[\tau(r) - \frac{1}{8} |\nabla \rho(r)|^2 / \rho(r)\right] R(r)^8 + \cdots, \tag{10}$$

where $\tau(r) = \sum_{i=1,N/2} |\nabla \varphi_i|^2$, ϕ_i are the orbitals, and N is the number of electrons. Eq. (10) will not be derived, but can be shortly explained. As Ω is small, a Taylor expansion of r_1 and r_2 around the center of the sphere, r, can be made. $P_2^{\parallel}(r, r) = 0$, due to the Pauli principle, and the first terms arising are quadratic ('no cusp for exchange'). The coefficient of the quadratic term of the expansion is the part containing $\rho(r)$ and $\tau(r)$ in Eq. (10). The three-dimensional integration over r_1 and over r_2, together with the term quadratic in r_1 and r_2, yields R^8. Eliminating the dependence on R in favor of $\rho(r)$, Eq. (7), and introducing Eqs. (9) and (10), into Eq. (6), one obtains

$$p(1;\Omega) = \langle \hat{N}_\Omega \rangle - \frac{1}{2}\langle \hat{N}_\Omega \rangle^2 - \frac{32\pi^2}{45}\left(\frac{3}{4\pi}\right)^{8/3} \left[\tau(r) - \frac{1}{8}|\nabla \rho(r)|^2/\rho(r)\right] \rho(r)^{-5/3} + \cdots \tag{11}$$

which shows that, up to some constants, arbitrary by the choice of the small constant $\langle \hat{N}_\Omega \rangle$, the effect of the interference of higher number of electrons into a small volume Ω is described by a function

$$y(r) = \left[\tau(r) - \frac{1}{8}|\nabla \rho(r)|^2/\rho(r)\right] \rho(r)^{-5/3} + \cdots \tag{12}$$

ELF, $\eta(r)$, as defined in Ref. [6], is recovered by scaling $y(r)$:

$$\eta(r) = [1 + c y(r)^2]^{-1}. \tag{13}$$

Please notice that this scaling does not affect the topology of the function: the critical points of η are those of y ($\nabla y(r_c) = 0 \Leftrightarrow \nabla \eta(r_c) = 0$). The choice of the constant c is just a matter of convenience: it does not affect the positions in space where $\eta(r)$ is maximal. In Ref. [6], it is chosen to have $\eta = 1/2$ for the uniform electron gas; this can be done as for a uniform electron gas of density ρ, τ is proportional to $\rho^{5/3}$, $\nabla \rho = 0$, and thus y is just a constant, independent of ρ. Of course, the choice of the scaling function affects the values of the functions, but not their meaning.

3. Technical details

Density functional calculations have been performed with the LMTO-ASA program [19–22].

Being a function of the 3D coordinates, η is still difficult to assimilate. This can be made easier, by choosing different isosurfaces of η, e.g. at medium and at high ELF values, and plotting them. As ELF does not provide a transferable scale, no specific values will be given for 'high' and 'medium' η. The plots were produced with the program SciAn [23].

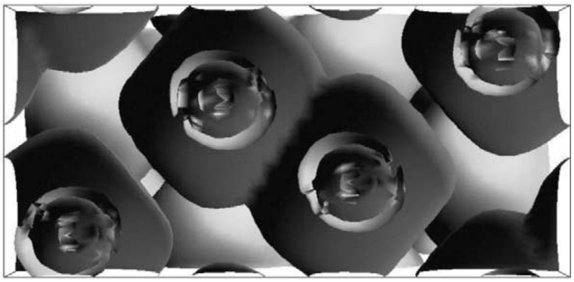

Fig. 1. Iodine crystal at 1 bar. Isosurfaces at low ELF value, showing the molecular character of the crystal.

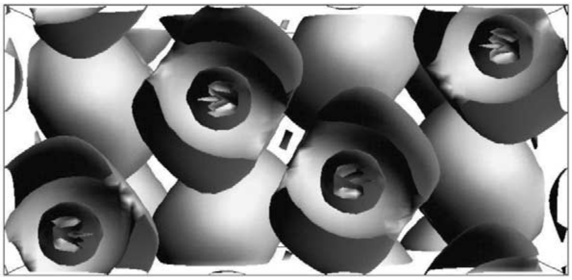

Fig. 2. Iodine crystal at 1 bar. Isosurface at high ELF value, showing the cores, bond, and lone pairs in the iodine molecule.

4. The electron localization function in iodine

Fig. 1 shows isosurfaces of ELF, for medium η values, for the iodine crystal at normal pressure. One easily recognizes the shape of the molecules in the crystal. Increasing the value of η (Fig. 2), one can distinguish spatial characteristics reflecting the electronic structure features: around the nuclei one can see nearly spherical core regions, around them toroidal regions corresponding to the three lone pairs. (As ELF reflects the symmetry, and iodine practically retains the diatomic character in the crystal, the three lone pairs appear together as a torus, just as a sphere appears for an atomic shell.) More interestingly, one can distinguish in the center of the figure, between two cores, a region of higher η: this corresponds to the I–I bond. For the pressure of 206 kbar, close to the transition to the metallic phase, the ELF plot shows a close resemblance to Fig. 2. There is, however, a noticeable difference: the maximum of ELF, showing the molecular bond, has disappeared. In the metallic phase, the 'atomic' character becomes evident (cf. Fig. 3 which shows simultaneously the contours of Figs. 1 and 2). Taking a different perspective, one notices the significant elongation along the c-axis (cf. Fig. 4, the lower of the two η values). It is interesting to notice that in the 001 plane the 'medium' value of ELF produces an isosurface joining all the atoms in the plane, a pattern indicating a metallic character. At this point, however, it is still not understood why the atoms are elongated, i.e. why the c/a ratio was increased by pressure. This is clarified by looking at higher η values, which shows that the lone pairs did not

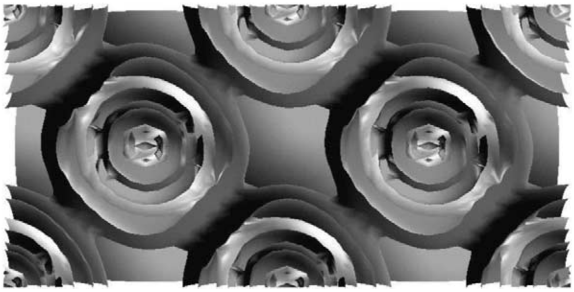

Fig. 3. Iodine crystal at high pressure (metallic phase); same orientation as for molecular crystal. Low and high ELF isosurfaces, showing the 'atomic' character.

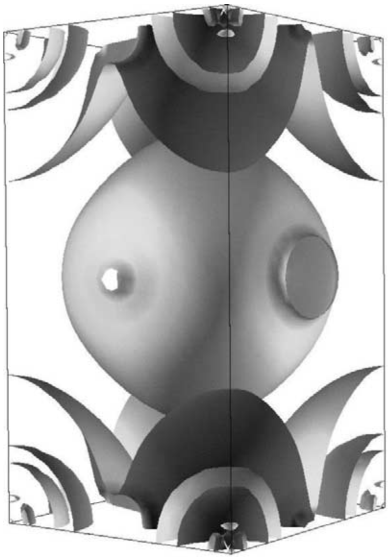

Fig. 4. Iodine crystal at high pressure (metallic phase). Low ELF value; the openings in the middle horizontal plane connect to the next atoms, indicating a metallic character in this plane.

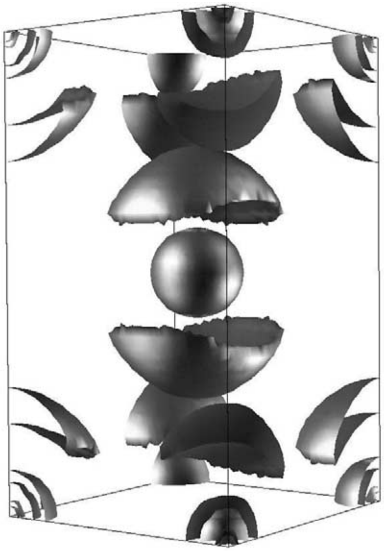

Fig. 5. Iodine crystal at high pressure (metallic phase). High ELF value, besides the spherical surfaces around the nuclei (cores) regions describing the lone pairs (above and below the cores) can be identified.

disappear: they show up, above and below the conduction plane, explaining the deformation (Fig. 5).

Acknowledgements

I would like to thank Prof. H. Preuss (Universität Stuttgart, Germany), and Prof. H.-G. von Schnering (Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany), for stimulating discussions and support. I would also like to thank Prof. E. Cancès (Ecole Nationale des Ponts et Chaussées, Marne-la-Vallée, France) for the discussions about the probabilities, and Dr A. Congeduti (Université Pierre et Marie Curie, Paris, France) for informing me about recent developments in the study of the phase transition in iodine.

References

[1] A.S. Balchan, H.G. Dirkamer, J. Chem. Phys. 34 (1961) 1948.
[2] M. Riggleman, H.G. Dirkamer, J. Chem. Phys. 37 (1962) 446.
[3] M. Riggleman, H.G. Dirkamer, J. Chem. Phys. 38 (1963) 2721.
[4] K. Takemura, S. Minomura, O. Shimomura, Y. Fuji, Phys. Rev. Lett. 45 (1980) 1881.
[5] K. Takemura, S. Minomura, O. Shimomura, Y. Fuji, Phys. Rev. Lett. 45 (1980) 1881.
[6] A.D. Becke, K.E. Edgecombe, J. Chem. Phys. 92 (1990) 5397.
[7] A. Savin, A.D. Becke, J. Flad, R. Nesper, H. Preuss, H.G. von Schnering, Angew. Chem. 103 (1991) 421; A. Savin, A.D. Becke, J. Flad, R. Nesper, H. Preuss, H.G. von Schnering, Angew. Chem. Int. Ed. Engl. 30 (1991) 409.
[8] A. Savin, R. Nesper, S. Wengert, Th.F. Fässler, Angew. Chem. 109 (1997) 1893; A. Savin, R. Nesper, S. Wengert, Th.F. Fässler, Angew. Chem. Int. Ed. Engl. 36 (1997) 1809.
[9] P. Ayers, McMaster University, Hamilton, Ontario, Canada, unpublished.
[10] R. Daudel, C.R. Acad. Sci. (Paris) 237 (1953) 601.
[11] C. Aslangul, R. Constanciel, R. Daudel, P. Kottis, Adv. Quantum Chem. 6 (1972) 93.
[12] B. Silvi, J. Phys. Chem. A 107 (2003) 3081.
[13] M. Kohout, K. Pernal, F. Wagner, Y. Grin, Theor. Chem. Acc., submitted for publication.
[14] A. Savin, in: K.D. Sen (Ed.), Reviews of modern quantum Chemistry: a Celebration of the Contributions of Robert G. Parr, World Scientific, Singapore, 2002, p. 43.
[15] E. Cancès, R. Keriven, F. Lodier, A. Savin, Theor. Chem. Acc 111. (2004) 373.
[16] B. Silvi, A. Savin, Nature 371 (1994) 683.
[17] M. Kohout, Int. J. Quantum Chem. 97 (2004) 651.
[18] J.F. Dobson, J. Chem. Phys. 94 (1991) 4328.
[19] O.K. Andersen, Phys. Rev. B 12 (1975) 3060.
[20] O.K. Andersen, O. Jepsen, Phys. Rev. Lett. 53 (1984) 2571.
[21] O.K. Andersen, O. Jepsen, D. Gloetzel, in: F. Bassani, F. Fumi, M.P. Tosi (Eds.), Highlights of Condensed-Matter Theory, North Holland, New York, 1985.
[22] http://www/docs/Andersen/docs/lmto_program.html.
[23] E. Pepke, J. Lyons, SciAn User's Guide, Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida, 1993.