

Direct Visualization of Covalent Chemical Bonds in Crystalline Silicon

Kucherov O. P.

Institute of Structural Information Technology, Kyiv, Ukraine

ABSTRACT: *The covalent chemical bonds structure have been calculated within the Schrödinger equation due to the electron beam shifting effect. An experimental method of electron cloud densitometry obtained a number of photos of crystalline silicon atoms in the state of symmetric and anti-symmetric covalent bonds. The form of covalent bonds of silicon atoms was separated from the general photograph of atoms by methods of electron cloud geometry developed in the work.*

KEYWORDS: *Electronic band structure, Crystalline silicon, Electron cloud densitometry, Covalent chemical bonds, Visual chemistry, Electron beam shifting effect.*

Date of Submission: 25-05-2021

Date of acceptance: 07-06-2021

I. INTRODUCTION

Chemical bonds are the result of the interaction of electrons and atomic nuclei and are described by quantum mechanics. A single covalent chemical bond is created by a binding electron pair. In all current theories (the theory of valence bonds, the molecular orbital theory, the density functional theory, the density perturbation functional theory [1], the theory of repulsion of valence electron pairs, the Bohr model of chemical bonding [2]), the binding electron pair is located in the space between the atoms of the molecule.

In 1927, Heitler and London, [3] attempted to quantitatively mechanically calculate the ground steady state of the H_2 molecule. The success of this attempt became the basis for all further development of quantum chemistry.

II. QUANTUM THEORY OF COVALENT BONDS FOR ANY ATOMS

The advent of visual chemistry [5] makes it possible to create a general theory of the covalent bond of any identical atoms of the periodic table. Usually the term "exact solution" in physics is understood as "accurate to the error of the experiment."

Let's explain it.

Here we solve this problem for covalent bonds in a system consisting of two atoms A and B , which have bonding electrons 1 and 2, which belong to both atoms at the same time. Since the difference between the masses of nuclei and electrons is large, it can be argued that the relative motion of nuclei is thousands of times slower than the motion of electrons. The relative location of these force centers, ie atomic nuclei, determines the spatial configuration of two atoms.

Quantum chemistry is based on the Schrödinger equation. Let the exchange electron 1 be described by the wave function $\varphi_a(1)$ and the exchange electron 2 be described by the wave function $\varphi_b(2)$. In addition, the atom A with the rest of its electrons are characterized by a wave function φ_A , and the atom B with the rest of its electrons are characterized by a wave function φ_B .

According to the principle of superposition, the wave function of a system of two bound electrons is the product of their wave functions $\Psi_1 = \varphi_a(1) \times \varphi_b(2)$.

However, the function Ψ_1 is not unique for the system of two atoms. Although the electron is numbered, it is not really possible to do so.

But in quantum mechanics there is the principle according to which identical particles cannot be distinguished. Therefore, nothing will change, as the exchange electrons change places. The function $\Psi_2 = \varphi_a(2) \times \varphi_b(1)$ with rearranged electrons is also the solution of the problem in the zero approximation. In this case, an arbitrary linear combination of the functions Ψ_1 and Ψ_2 is also the solution of the wave equation. Thus, the solution of the

Schrödinger equation can be given in a form $\Psi(1,2) = C_1\Psi_1 + C_2\Psi_2$, where C_1 and C_2 are arbitrary coefficients that satisfy the physical condition of the problem.

In fact, the square of the function characterizes the probability density of the simultaneous presence of the first and second electrons at certain distances from the nuclei. Since it is impossible to distinguish electrons, the condition must be true $\Psi^2(1,2) = \Psi^2(2,1)$, that is, the square of the function $\Psi(1,2)$ should not change its value when the electrons are rearranged. Obviously, this is true only when $C_1 = C_2$, ie Ψ can have only two values: $\Psi_+(1,2) = C(\Psi_1 + \Psi_2)$ and $\Psi_-(1,2) = C(\Psi_1 - \Psi_2)$.

The function $\Psi_+(1,2)$ is symmetric, it retains its value when the electrons are rearranged. The function $\Psi_-(1,2)$ is anti-symmetric; when the electrons are rearranged, it changes sign.

Therefore, instead of the initial functions Ψ_1 and Ψ_2 , we obtained the functions Ψ_+ and Ψ_- , which determine the covalent chemical bond that arises due to the hybridization of electron clouds.

Given the above, the total wave function of two atoms bonded by a covalent bond takes the following form:

$$\Psi(q) = \varphi_A(q) + \varphi_B(q) + \Psi_{\pm}(q).$$

III. ELECTRON CLOUD DENSITOMETRY

A direct image of an electron cloud can be obtained due to the electron beam shifting effect by passing a plane wave of electrons through atoms. The quantum theory of the electron beam shifting effect was elaborated by the O.P. Kucherov and others [4,5].

Using the theory of electron beam shifting effect, we find how a plane electron wave interacts with covalently bound atoms.

As is known, the wave function of a beam of electron rays propagating along the z axis is a plane wave:

$$\Psi(z) = \sqrt{j} \exp(ikz),$$

where j is the electron beam density; k is a constant for a plane wave.

Based on the principle of superposition, the wave function of a system of two atoms plus the beam of electron rays is the product of their functions:

$$\Psi(q, z) = \sqrt{j} \exp(ikz) \{ \varphi_A(q) + \varphi_B(q) + \Psi_{\pm}(q) \}.$$

The probability density is the square of the modulus of this function. Let's find him.

$$\Psi^2(q, z) = j \exp(2+ikz) \{ \varphi_A(q) + \varphi_B(q) + \Psi_{\pm}(q) \}^2$$

$$= j \exp(2+ikz) \{ \varphi_A^2(q) + \varphi_B^2(q) + \Psi_{\pm}^2(q) + \varphi_A(q)\varphi_B(q) + \varphi_A(q)\Psi_{\pm}(q) + \varphi_B(q)\varphi_A(q) + \varphi_B(q)\Psi_{\pm}(q) + \Psi_{\pm}(q)\varphi_A(q) + \Psi_{\pm}(q)\varphi_B(q) \}.$$

According to the Pauli principle, the functions $\varphi_A(q)$, $\varphi_B(q)$ and $\Psi_{\pm}(q)$ are at different energy levels, ie if at some point in the space q one of these functions is nonzero, the other function will necessarily be equal to zero.

Therefore, the last expression takes the form:

$$\Psi^2(q, z) = j \exp(2+ikz) \{ \varphi_A^2(q) + \varphi_B^2(q) + \Psi_{\pm}^2(q) \}.$$

Take the integral of this expression over the variable z from the lower surface of the sample z_0 to the upper z_{max} , and for electron cloud densitometry we finally get:

$$\rho(x, y) = j \{ \rho_A(x, y) + \rho_B(x, y) + \rho_{\pm}(x, y) \}.$$

That is, the intensity of the electron beam passing through the atom is directly proportional to the thickness (path length) of the electron cloud of the atom at the point of transmission of the rays.

IV. EXPERIMENTAL PHOTO OF COVALENT BONDS

The silicon layer was grown at 650 ° C for 45 s. The height of an island is 6 nm, the width of the base - 12 nm. In part, the problem of high defect of silicon layers on sapphire, which occurs in the initial stages of growth, was removed by using UTSi technology (Peregrine corp.) [6]. Obtaining a cross section was carried out using special equipment (Gatan 601.07000 TEM Specimen Preparation Kit), developed by Gatan, USA.

Electron cloud density technology was used to directly visualize chemical bonds. Images of silicon atoms together with their symmetrical and anti-symmetric covalent bonds were obtained.

Direct images of crystalline silicon atoms with chemical bonds were studied using a transmission electron microscope JEM2100F (JEOL, Japan).

An experimental method [7] of electron cloud densitometry which based on the electron beam shifting effect [4,5] with resolution of 10 picometers was used.

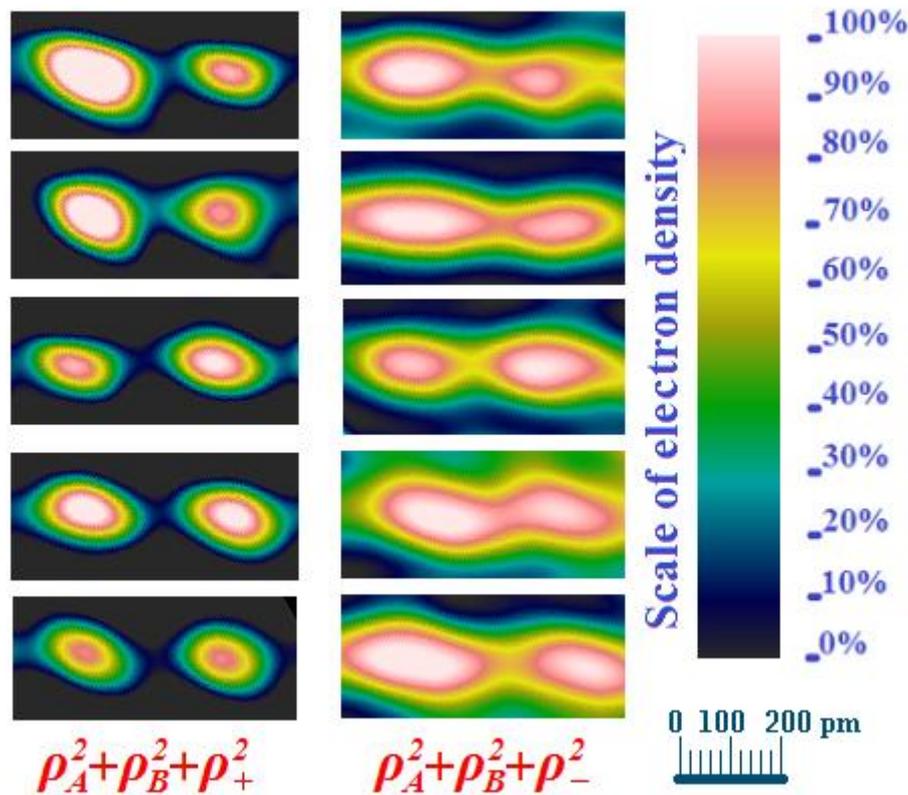


Figure 1: Photos of electron clouds of silicon atoms symmetric $\rho_A(x,y)+\rho_B(x,y)+\rho_+(x,y)$ and anti-symmetric $\rho_A(x,y)+\rho_B(x,y)+\rho_-(x,y)$ covalent bonds. The electron clouds of the inner electrons $\rho_A(x,y)$ and $\rho_B(x,y)$ are pink. Valence electrons are green - symmetric $\rho_+(x,y)$ on the left, anti-symmetric $\rho_-(x,y)$ - on the right.

Fig. 1 shows photos of five electron clouds of silicon atoms symmetric $\rho_A(x,y)+\rho_B(x,y)+\rho_+(x,y)$ and anti-symmetric $\rho_A(x,y)+\rho_B(x,y)+\rho_-(x,y)$ covalent bonds. The electron clouds of the inner electrons $\rho_A(x,y)$ and $\rho_B(x,y)$ are pink. Valence electrons are green - symmetric $\rho_+(x,y)$ on the left, anti-symmetric $\rho_-(x,y)$ - on the right. The scale of electron cloud density and length scale are given next to it.

V. GEOMETRY OF ELECTRON CLOUDS

Fig. 1 shows the photos of the total contribution of bonding and remaining electrons. Schematically, these two clouds are presented in Fig. 2a. The cloud of remaining electrons is a sphere of radius OB , and the bonding electron is a shell with a thickness of BA . According to the electron beam shifting effect, in the center of the atom with coordinates $x = y = 0$ (see Fig. 2a), all electrons make the same contribution to the total intensity (100%).

Thus, the contribution of all 14 silicon electrons is characterized by a segment OA , which consists of one bonding electron (segment BA) and remaining electrons (segment OB). Therefore, from the ratio $100\% / x = 14/1$ for the contribution of the bonding electron we find $x = 7\%$.

The contribution of the binding electron at any distance from the center OE can be found from the following relation.

The intensity of the electron density of the clouds will be equal to $EC-ED$, and EC is from the experiment, and ED - from two right triangles: OCE and ODE . The following conditions allow to solve this problem: $OD = OB$ and $OC = OA$.

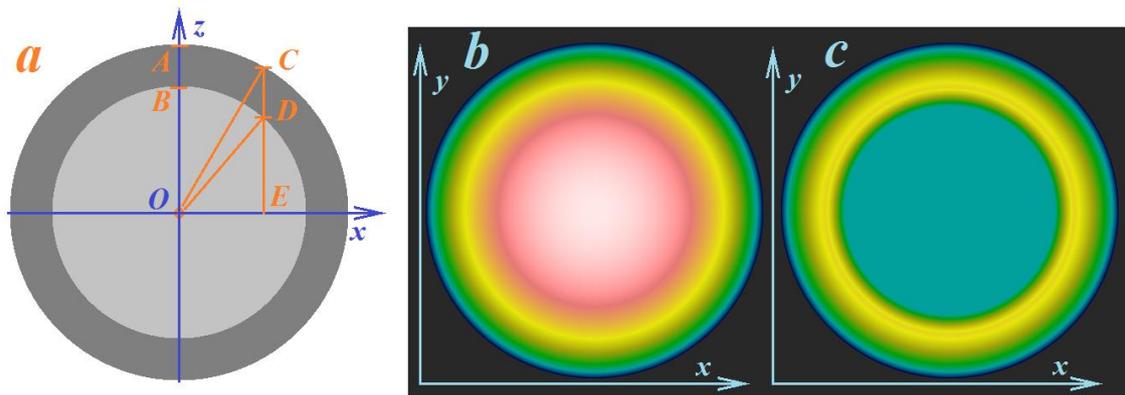


Figure 2: Technology of separation of an individual electron cloud from an atom: a) geometry of the thickness of electron clouds of bonding and remaining electrons, side view; b) model of the atom $\rho_A(x,y)+\rho_B(x,y)+\rho_+(x,y)$; c) model of the separated bonding electron cloud $\rho_+(x,y)$, top view.

To illustrate this, a model of the silicon atom was made in accordance with the Fermi-Thomas model (E. Fermi, L. Thomas, 1927), which works for atoms of any complexity. The method uses a quasi-classical approximation: each atom of the periodic table has a certain radius r (Bohr radius), so at the distance $a < r$ the electron density is large and almost the same, and at the distance $a > r$ the electron density is small and decreases exponentially.

Fig. 2b shows the model of the atom with all electron clouds $\rho_A(x,y)+\rho_B(x,y)+\rho_+(x,y)$. Fig. 2c shows the model of the electron cloud of the separated bonding electron cloud $\rho_+(x,y)$. Using the technology of electron cloud geometry, from the photo of five electron clouds of silicon atoms, Fig. 1, the contribution of the remaining electrons $\rho_A(x,y)+\rho_B(x,y)$ was subtracted.

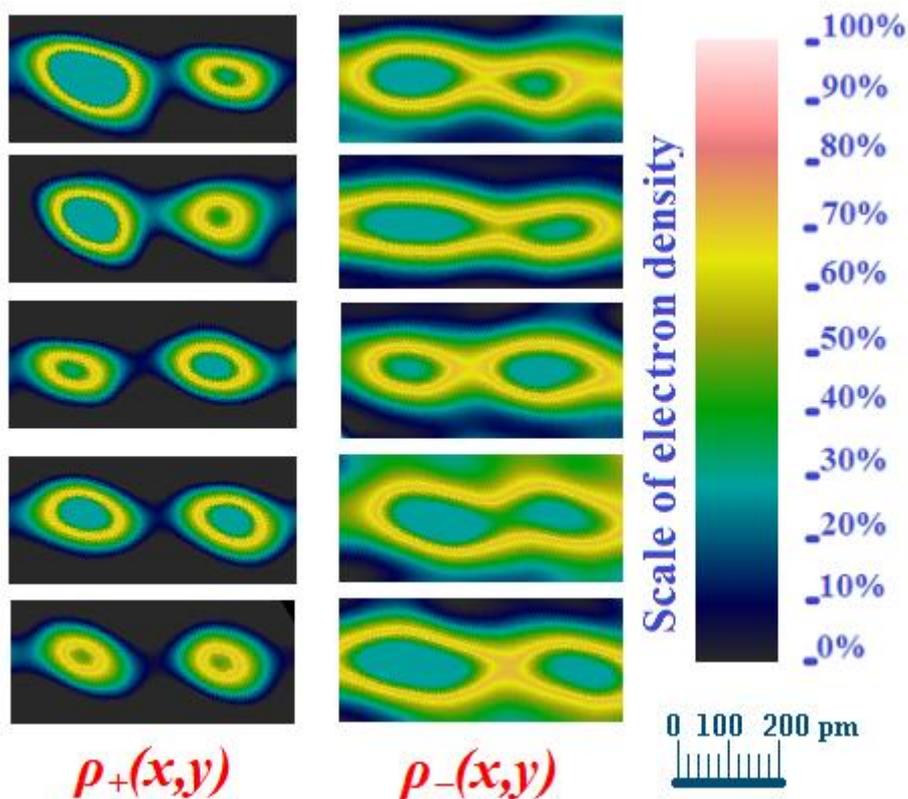


Figure 3: Electron cloud density distribution of non-hybridized $\rho_+(x,y)$ and hybridized $\rho_-(x,y)$ covalent bonds obtained by subtracting the electron cloud density of remaining electrons $\rho_A(x,y)+\rho_B(x,y)$.

Fig. 3 shows the electron clouds of pairs of silicon atoms not hybridized $\rho_+(x,y)$ and hybridized $\rho(x,y)$ by covalent bond.

As a result, we see that during hybridization, the electron clouds of binding electrons do not overlap, but form a single cocoon stretched in the middle.

VI. CONCLUSION

The advent of electron density densitometry makes every atom visible in molecules with a wide range of chemical bonds. The method of electron density densitometry not only makes it possible to see the molecular structure of already known molecular crystals, but also to discover new ones with extraordinary technological properties. For example, a two-layer diamond gubanite [5] and superdense two-layer diamond-like carbon allotrope, rudenite [4].

In this work, quantum-mechanical calculations of the covalent bond were developed for the general case of any identical atoms of the periodic table. The solution of the Schrödinger equation due to the electron beam shifting effect is found. A number of photos of silicon atoms in the state of symmetric and anti-symmetric covalent bonds were obtained by densitometry of electron cloud density. The geometry of the electron cloud developed in this paper separates the form of pure covalent bonds of silicon atoms from the general photo of atoms.

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Kucherov O. P. "Direct Visualization of Covalent Chemical Bonds in Crystalline Silicon." *American Journal of Engineering Research (AJER)*, vol. 10(6), 2021, pp. 54-58.