The Coulombic Nature of the van der Waals Bond Connecting Conducting Graphene Layers in Graphite

Raji Heyrovska*

Private Research Scientist, Na Stahlavce 6, 160 00 Praha 6, Czech Republic.

Email: rheyrovs@hotmail.com

Abstract

Carbon forms a variety of compounds with single, double, triple and the intermediate resonance bonds with atoms of its own or other kinds. This paper is concerned with graphite, a very useful material, which is a stack of electrically conducting graphene layers held together by weak van der Waals (vdW) bonds. It crystallizes in hexagonal and rhombohedral forms, in which the hexagon inter-planar bond distance is 0.34 nm. Here a new and simple approach accounts for this bond length and shows the coulombic nature of the vdW bond.

Key words: Carbon, Graphite, Graphene, van der Waals bond, Bond length, Golden ratio based ionic radii

*Academy of Sciences of the Czech Republic (former).

1. Introduction.

Carbon [1a] is a wonder element of Nature. One of its forms, graphite [1b,2], crystallizes in hexagonal and rhombohedral forms. It is a solid stack of layers of graphene [1c,3] with the inter-planar spacing of 0.34 nm in both forms [1,2], held by weak van der Waals bonds [4a,b]. This article provides *for the first time* a new and simple interpretation of the length and nature of this bond.

2. Atomic structure of graphene.

Graphene is a two-dimensional network of regular hexagons of identical carbon atoms, with equal inter-atomic spacing of $d(CC)_{res}$ = 0.142 nm [1-3,5-7]. It is usually represented like a wire mesh in the ball and stick model [3]. Its electrical conductivity as an atomically thin material makes it very useful in many ways, see e.g., [8]. Its structure at the atomic level was worked out by the author [5-7], in which all the details can be found. The Fig. 4 in [7a] shows the alternately charged cations and anions, which are the ionic resonance forms (as for the H_2 molecule [2]) of the adjacent C atoms bound by covalent bonds, responsible for electrical conduction in graphene. This is shown in Fig. 1a here. The sum of the radii of the cation R(+) and anion R(-) is equal to the covalent bond length, d(CC), [7,9]. The atomic and ionic radii in Fig. 1a are related by the Golden ratio, $\phi = (1+5^{1/2})/2$ as explained in [7,9] and in the legend for Fig.1. The covalent radius, $R_{Cres} = (\phi - 1/2)a_B = d(CC)_{res}/2$ = 0.71 nm, where $(\phi - 1/2) = 5^{1/2}/2 = 1.118$ and a_B is the Bohr radius obtained from the first ionization potential [10].

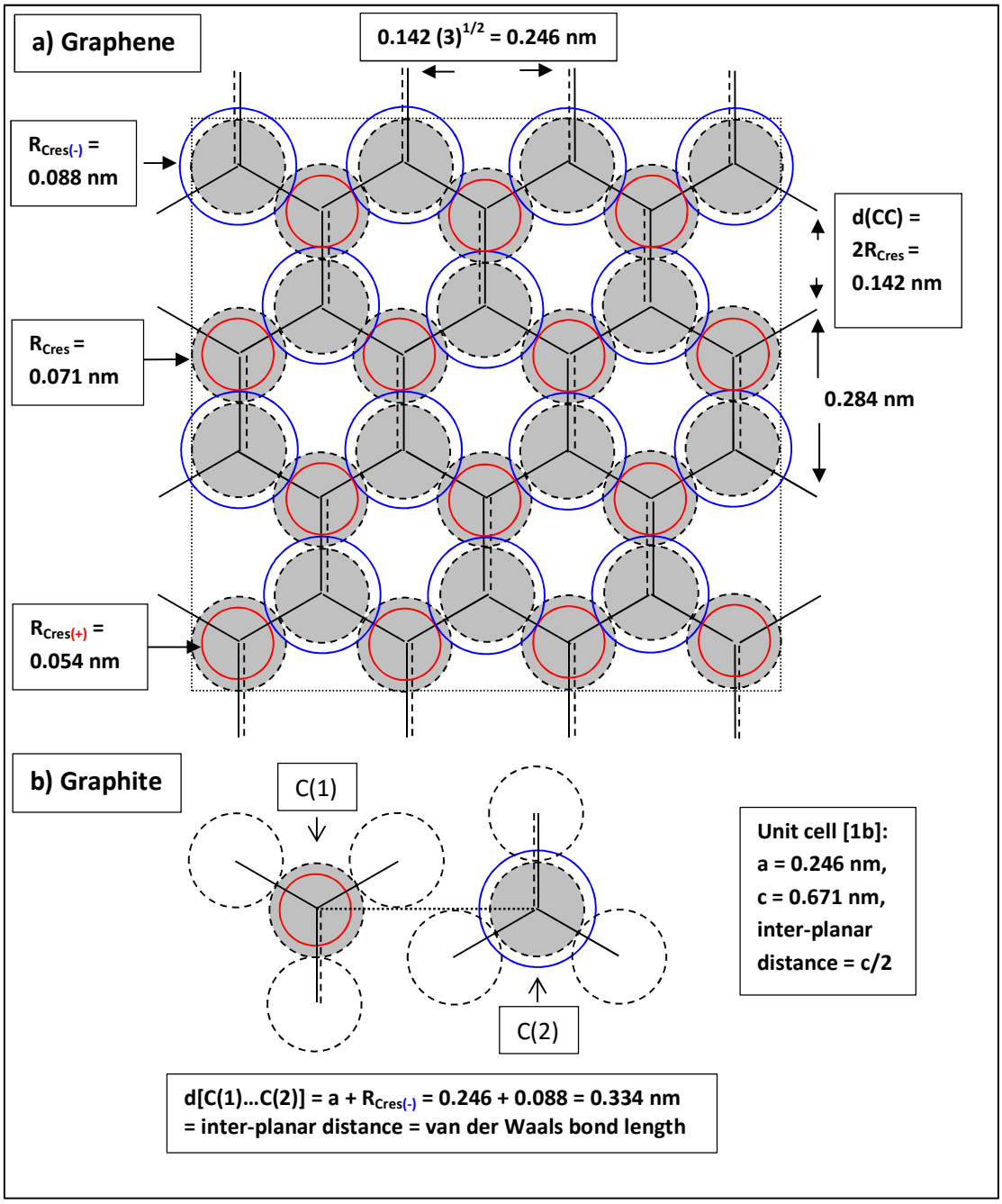

Figure 1. a) Graphene, [7a]. Bond length d(CC) = $2R_{Cres}$ = 0.142 nm. The alternate red and blue circles are cations and anions (responsible for conduction) of radii, $R_{Cres(+)} = d(CC)/\phi^2$ and $R_{Cres(-)} = d(CC)/\phi$ and $d(CC) = R_{Cres(+)} + R_{Cres(-)}$, where ϕ is the Golden ratio (see [7a] for details); b) Graphite. Atoms C(1) and C(2) are in adjacent graphene layers connected by the van der Waals bond as shown by the dotted line.

3. Atomic structure of graphite.

In graphite [1,2], the graphene layers are connected by weak van der Waals bonds. Van der Waals bonds exist in a variety of molecules [11]. These bonds are, in general, longer than the covalent bonds. Pauling [2] describes van der Waals bonds as arising out of the attractive and repulsive forces, and defines the van der Waals radius as half the corresponding bond length. In the case of carbon, the reported value of van der Waals radius is around 0.17nm [4b,10,11]. The unit cell of graphite [1b] has the lattice constants, a = 0.246 nm and c = 0.670 nm. The inter-planar spacing in (both hexagonal and rhombohedral) graphite is c/2 = 0.335 nm, which is the length of the van der Waals bond. Half of this is the van der Waals radius, 0.17 nm.

4. The van der Waals bond in graphite.

In Fig. 1b are shown two carbon atoms, C(1) and C(2) in two adjacent graphene layers (1) and (2) connected by the van der Waals bond of length $d(C..C)_{vdW}$ = 0.335 nm (= c/2). On examining this distance, it was astonishing to find that it is actually the sum of the width of the graphene hexagon (0.246 nm, see Fig. 1a) and the anionic radius, $R_{C(-)}$ = 0.088 nm of carbon,

$$d(C..C)_{vdW} = 0.142[(3^{1/2} + 1/\phi] = 0.246 + 0.088 = 0.334 \text{ nm} \qquad (1)$$

where, $d(CC)_{res} = 0.142 = 5^{1/2}a_B$, $0.246 = 0.142(3^{1/2})$ and $R_{C(-)} = 0.142/\phi = 0.088$ nm. It can be seen that all the distances are related to the Golden ratio, ϕ [7,9,12].

This shows, *for the first time*, that the van der Waals bond in graphite is a long range coulombic bond between the positively charged carbon cation , C(1)(+) on graphene layer (1) and the negatively charged carbon anion , C(2)(-) in layer (2).

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