The Potential Power of Graphene

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[Abstract] Graphene’s many unique physical properties have also contributed to its popularity. Physics is highly dependent on the number of available dimensions. Since graphene is a single atomic layer of crystallized carbon, electrons that travel through the material only have two free dimensions to move. This gives us a readily available two-dimensional system to test how physics changes with the number of dimensions. In addition to the 2D nature of graphene, the carbon atoms in graphene form a hexagonal (honeycomb) lattice. The overall structure of graphene (its 2D nature and its honeycomb lattice) gives rise to many interesting properties. First, even at room temperature, electron transport through graphene is ballistic, making it a material with one of the highest electron mobilities. Second, the band structure of graphene causes electrons to no longer follow simple quantum mechanics, but actual behave like relativistic quantum particles.


1] Introduction

Graphene is a single atomic layer of crystalline graphite. It was previously thought that two dimensional crystals, such as graphene, could not exist. Two dimensional crystals were thought to be thermodynamically unstable and would melt when isolated. However, in 2004, Andrew Geim and Konstantin Novoselov successfully isolated a single layer of graphite, and due to its stability (it is now believed that graphene is stable up to several thousand degrees) they were able to perform measurements to explore many of its unique properties. For their work with the newly found material, they were awarded the 2010 Nobel prize. As its name indicates, graphene is extracted from graphite, the material used in pencils. Like graphite, graphene is entirely composed of carbon atoms and 1mm of graphite contains some 3 million layers of graphene. Whereas graphite is a three-dimensional crystalline arrangement, graphene is a two-dimensional crystal only an atom thick. The carbons are perfectly distributed in a hexagonal honeycomb formation only 0.3 nanometres thick, with just 0.1 nanometres between each atom. Graphene conducts electricity better than copper. It is 200 times stronger than steel but six times lighter. It is almost perfectly transparent since it only absorbs 2% of light. It impermeable to gases, even those as light as hydrogen or helium, and, if that were not enough, chemical components can be added to its surface to alter its properties. This study is for the purpose of demonstrating the potential of graphene.


Carbon is one of the most important materials and especially essential for organic connections, because all organic structures include carbon.
Carbon atoms can contribute to many different crystal structures which reveal also very different properties. A carbon atom contains six electrons which occupy the following electron configuration: \(1s^22s^22p^2\). In the ground state there are two unpaired electrons in the outer shell, so that one could assume the ability to bind only two additional molecules. The reason is the small energy difference between the \(2s\)- and the \(2p\)-state, so that it is easily possible to excite one electron from the \(2s\) state into the \(2p\)-state[1].

In order to fulfill the octet rule, carbon must use its 4 valence electrons when bonding to other atoms. However, only unpaired electrons can bond. That means that the two paired electrons occupying the \(2s\) orbital must become unpaired before they can bond. Since the energy gap between the \(2s\) and \(2p\) orbitals is very small, one of the \(2s\) electrons can be promoted to the empty \(2p\) orbital, leading to the following situation: Now the four electrons appear to be ready for bonding, but there is a problem. The \(2p\) orbitals are known to be at right angles to each other. If bonding occurs in this state, the 3 equivalent \(p\) electrons in the second shell are the valence electrons. Valence electrons are important because they help determine if an element is able to participate in a chemical reaction. Carbon exists in nature as graphite and diamonds, but it often combines with other elements, such as hydrogen and oxygen, in forming compounds that are necessary for life. The valence of carbon allows it to combine in many different forms. Carbon atoms often join with other carbon atoms to form long chains and rings. If we look at the valence shell configuration of carbon, we find two paired electrons in the \(2s\) orbital, and two unpaired electrons in the \(2p_X\) and \(2p_Y\) orbitals, one in each as below.
would form 3 equivalent bonds oriented at 90° to each other, and the s electron would form a bond of a different type and orientation from the other three. No such compound exists. The shapes and relative positions of the valence orbitals in atomic carbon do not explain the shapes and relative positions of the bonds in carbon compounds.

The electronic configuration of carbon is 1s^22s^22p^2, i.e. with four valence electrons spread in the s and p orbitals. In order to create covalent bonds in diamond, the s orbital mixes with the three p orbitals to form sp^3 hybridization. The four valence electrons are thus equally distributed among the sp^3 orbitals, while each orbital points to one of the four corners of a tetrahedron. The tetrahedral structure, together with the highly directed charge density, give strength and stability to the bonds. Consequently, all the bonds in diamond are of the same length (1.54 Å), with the same bond angle (109.47°). Going back to the carbon model with four unpaired electrons in the valence shell, we can take it as a point of departure for formation of hybrid orbitals. The first step is to take either 2, 3, or all four of those orbitals and equalize their energies. Let’s say that we take all four of them and form 4 equivalent new orbitals. These orbitals are now of the same energy, which is intermediate between those of the original 2s and 2p orbitals. At the same time, we cannot name the new orbitals s or p, for they’re neither. We have to find a new name that reflects the fact that they were created from one s orbital and three p orbitals. We will call them sp^3 orbitals. The process that leads to their formation is called sp^3 hybridization[2]. Diamond is very special owing to its exceptionally strong sp 3 bonds (formed by the hybridization of one s and three p orbitals), which are responsible for its unique physical and chemical properties. The stable bonding configuration of carbon at normal temperature and pressure is not diamond but graphite, in which the C atoms are sp 2 bonded (here one s and two p orbitals enter into the hybridization), leaving delocalized electrons available for electrical conduction. The great versatility of carbon materials arises from the strong dependence of their physical properties on the ratio of sp2 (graphite-like) to sp3 (diamond-like) bonds[3]. The most common chemical bonds, in amorphous and nanocrystalline carbon are sp3 and sp2 hybridizations. In the sp3 configuration, a carbon atom forms four sp3 orbitals making a strong σ bond to the adjacent atom[4]. In the sp2 configuration, a carbon atom forms three sp2 orbitals forming three σ bonds and the remaining p orbital forms a π bond. The π orbital geometrically lies normal to the σ bond plane and is the weaker bond so that it is closer to the Fermi level, E_f. The three σ bonds and π bond usually constitute a ring plane in sp2 clusters[4].


the C ≡ C bond is stronger than the C = C bond. In turn, the C = C bond is stronger than the C – C bond. See diagram below.

![Figure 4 Carbon Bond 1](image-url)
As the number of electrons in the same space increases, there would be more repulsion between the electrons (since like charges repel), resulting in a lower than proportionate increase in the bond strength as the number of bonds increases.

According to Valence Bond, a triple bond is essentially made up of one sigma bond and two pi bonds. In the same manner, a double bond has one sigma and one pi bond while a single bond has just one sigma bond. The C-C triple bond has one sigma bond which is a head-on overlap of the s-orbitals and two pi bonds which are side-way overlaps of two p-orbitals. This side-way overlap makes the C-C triple bond weaker. Carbon has a few unique bonding properties - the most important of which is its ability to form long chains of carbon. No other elements can do this. Silicon has the ability to theoretically do this, but silicon-oxygen bonds are so strong that silicon would much prefer to make Si - O - Si bonds than silicon-silicon bonds. The reason carbon can do this is that carbon-carbon bonds are extremely strong. This allows carbon to make up many of the basic building blocks of life (fats, sugars, etc). Also, because carbon makes four bonds, it is able to exist in two or more different forms, known as allotropes of that element. In each different allotrope, the element’s atoms are bonded together in a different manner. Allotropes are different structural modifications of an element. Carbon is an element that exhibits allotropy. Some of its allotropes are shown below:

[Figure 5] Carbon Bond 2

a) diamond; b) graphite; c) lonsdaleite; d-f) buckyballs (C60, C540, C70); g) amorphous carbon; h) carbon nanotube.

[Figure 6] Allotropes of Carbon

[4] Diamond and Graphite

[Figure 7] Diamond (Cubic):
4-coordinate, sp³ tetrahedral carbon coordination
An electrical insulator, and 3D-lattice crystal structure. This is the hardest known substance (this is because it is made up of very strong C-C covalent bonds). Each C atom forms four bonds, tetrahedrally arranged, to other C atoms, resulting in an open, but strongly bonded, 3D-structure.

**[Figure 8]** Graphite (hexagonal):

3-coordinate, sp² planar carbon coordination. the lines show that the carbon atoms in every other layer are in line, and not those in adjacent layers.

An electrical conductor, and layered lattice crystal structure. This is slippery and used as a lubricant (this is a property of its layered structure, with the lubricating effect coming from the ability of the layers to slide over one another, as they are only weakly held together by van der Waals forces). Here, each C atom forms three covalent σ-bonds to further C atoms. These σ-bonds are made up of sp² hybrid orbitals. The remaining p-orbitals, which are perpendicular to the plane of the σ-bonds, overlap to form a delocalized π-system. The planes are widely separated as they are held together only by the weak van der Waals forces. Both diamond and graphite are made entirely out of carbon. The way the carbon atoms are arranged in space, however, is different for the three materials, making them allotropes of carbon. The differing properties of carbon and diamond arise from their distinct crystal structures. In a diamond, the carbon atoms are arranged tetrahedrally. Each carbon atom is attached to four other carbon atoms 1.544 x 10^-10 meter away with a C-C-C bond angle of 109.5 degrees. It is a strong, rigid three-dimensional structure that results in an infinite network of atoms. This accounts for diamond’s hardness, extraordinary strength and durability and gives diamond a higher density than graphite (3.514 grams per cubic centimeter). The carbon atoms in graphite are also arranged in an infinite array, but they are layered. These atoms have two types of interactions with one another. In the first, each carbon atom is bonded to three other carbon atoms and arranged at the corners of a network of regular hexagons with a 120-degree C-C-C bond angle. These planar arrangements extend in two dimensions to form a horizontal, hexagonal "chicken-wire" array. In addition, these planar arrays are held together by weaker forces known as stacking interactions. Unlike diamond, graphite can be used as a lubricant or in pencils because the layers cleave readily. It is soft and slippery, and its hardness is less than one on the Mohs scale. Graphite also has a lower density (2.266 grams per cubic centimeter) than diamond. The planar structure of graphite allows electrons to move easily within the planes. This permits graphite to conduct electricity and heat as well as absorb light and, unlike diamond, appear black in color.

**[5] Weak bonds on Graphite.**

Each carbon atom in graphite forms three σ bonds, one to each of its nearest neighbors, by means of sp²-hybrid orbitals. The unhybridized p orbital on each carbon atom will overlap unhybridized orbitals on adjacent carbon atoms in the same layer to form π bonds. Many resonance forms are necessary to describe the electronic structure of a
The below Figure illustrates two of these forms.

![Figure 9] Electronic structure of a graphite layer

(a) Carbon atoms in graphite have unhybridized p orbitals. Each p orbital is perpendicular to the plane of carbon atoms.

(b) These are two of the many resonance forms of graphite necessary to describe its electronic structure as a resonance hybrid.

The structure of graphite consists of many flat layers of hexagons. The layers are called graphene sheets. Each carbon atom in the layer is joined by strong covalent bonds to only three other carbon atoms. Compare this with the structure of diamond. Each graphene sheet is itself a giant molecule. Carbon is in group 4 of the periodic table and so it has four electrons in its outer shell. Three of these electrons are used for covalent bonding in the graphene sheet.

![Figure 10] The structure of graphite.

There are no covalent bonds between the layers and so the layers can easily slide over each other making graphite soft and slippery and an excellent lubricant (like oil). The fourth electron between the layers is delocalised. It is a free electron and these free electrons between the layers allows graphite to conduct electricity and heat. Atoms within a graphite layer are bonded together tightly by the σ and π bonds; however, the forces between layers are weak. London dispersion forces hold the layers together. The weak forces between layers give graphite the soft, flaky character that makes it useful as the so-called “lead” in pencils and the slippery character that makes it useful as a lubricant. The loosely held electrons in the resonating π bonds can move throughout the solid and are responsible for the electrical conductivity of graphite. Graphite may be viewed as a stacking of graphene sheets that stick together due to the van der Waals interaction, which is much weaker than the inplane covalent bonds. This physical property explains the graphic utility of the material: when one writes with a piece of graphite, i.e. when it is scratched over a sufficiently rough surface, such as a piece of paper, thin stacks of graphene sheets are exfoliated from bulk graphite and now stick to the surface. This is possible due to the above-mentioned weak van der Waals interaction between the graphene sheets.

The potential power of graphene

[Figure 11] : The carbon atomic $\sigma$ and $\pi$ orbitals in the $sp^2$ honeycomb lattice/ Schematic view of the $sp^2$ hybridisation

In the atomic ground state, the 6 electrons are in the configuration $1s^2\ 2s^2\ 2p^2$, i.e. 2 electrons fill the inner shell $1s$, which is close to the nucleus and which is irrelevant for chemical reactions, whereas 4 electrons occupy the outer shell of $2s$ and $2p$ orbitals. Because the $2p$ orbitals ($2px$, $2py$, and $2pz$) are roughly 4 eV higher than the $2s$ orbital, it is energetically favourable to put 2 electrons in the $2s$ orbital and only 2 of them in the $2p$ orbitals. It turns out, however, that in the presence of other atoms, such as e.g. H, O, or other C atoms, it is favourable to excite one electron from the $2s$ to the third $2p$ orbital, in order to form covalent bonds with the other atoms. The gain in energy from the covalent bond is indeed larger than the 4 eV invested in the electronic excitation. In the excited state, we therefore have four equivalent quantum-mechanical states, $2s$, $2px$, $2py$, and $2pz$. A quantum-mechanical superposition of the state $2s$ with $n\ 2p$ states is called $sp^n$ hybridisation, which play an essential role in covalent carbon bonds. The $sp^2$ hybridization in carbon atoms is of great importance. The hybridization between one $s$ orbital and two $p$ orbitals forms a $\sigma$ band which makes the lattice structure robust, and leads to a hexagonal planar structure. These bands have a filled shell due to the Pauli principle. The other $p$ orbital is perpendicular to the planar. This $p$ orbitals can bind with the neighboring carbon atoms, which forms a $\pi$ band. It is half-filled because this $p$ orbital has one extra electron[6]. Graphene consists of carbon atoms arrayed in a hexagonal pattern in a large sheet. Layers of graphene constitute graphite, the familiar "lead" in pencils. The electrons in each carbon atom are arranged in different orbitals. Two electrons occupy the inner spherical $1S$ shell. Then $2S$ and $2P$ accommodate the remaining four electrons. In a molecule, $2S$ and $2P$ are modified to create a hybridized SP2 bonding orbital. This has three equal lobes pointing outwards in a a plane and connecting to adjacent carbon atoms. The fourth electron in this outer shell occupies a $\pi$ orbital that projects above and below the molecular plane. This $\pi$ orbital merges with adjacent $\pi$ orbitals creating a huge orbital which allows easy movement of electrons across the plane of the molecule. This is what gives graphene its remarkable electrical conductivity.


Graphene is an excellent candidate for the next generation of electronic materials due to the strict two-dimensionality of its electronic structure as well as an extremely high carrier mobility[16]. Graphene also has the highest current density (a million times that of copper) at room temperature; the highest intrinsic mobility (100 times more than in silicon); and conducts electricity in the limit of no electrons’. Which means it can carry more electricity more efficiency, faster and with more precision than any other material[7]. Graphene owes its amazing electronic properties to its honeycomb lattice carbon network, in which $2s$, $2px$, and $2py$ orbitals hybridize such that each carbon atom is bonded to its three neighbors by strong “$sp^2$” or “sigma” bonds[5]. The remaining $pz$ or “$\pi$” orbital determines the low-energy electronic structure of graphene. The unit cell of graphene contains two $\pi$ orbitals, which disperse to form two $\pi$ bands that may be thought of as bonding (the lower energy valence band) and anti-bonding (the higher energy conduction band).
in nature[5], one orbital remained, the pz orbital with one electron. Is orbital is perpendicular to the plane formed by the carbon atoms. As in the case of the 2s, 2px and 2py orbitals, the pz orbitals of different atoms combine to form the pi-bonds. Each pz orbital contributes with one electron, and therefore graphene is a system with one electron per lattice site (the carbon atoms define the sites in the lattice) is called a half filled system[13]. First it is clear that the valence and the conduction bands touch each other at a number of finite momentum values. The momentum values at which the two bands touch are termed Dirac points (there are two in the Brillouin zone). As a consequence, graphene’s spectrum does not have an energy gap. On the other hand, since the bands only touch at two momentum points the density of states is zero at the corresponding energy. Therefore, graphene is sometimes termed a zero-gap semiconductor with vanishing density of states at the Fermi energy[13]. Even more interesting is the form of the valence and the conduction bands close to the Dirac points. They show a conical shape, with negative (valence) and positive (conduction) energy values. In fact, the energy spectrum of graphene close to the Dirac point is well represented. As a consequence of the interaction between the lattice and the pi-electrons, an effective theory emerges where the electrons (or better: the quasi-particles) are massless Dirac electrons[13]. The electronic structure of epitaxial graphene is twodimensional by nature. It is a zero-gap semiconductor, i.e., a semimetal, with a conically shaped valence and conduction band reminiscent of relativistic Dirac cones for massless particles[16]. This latter property is a direct consequence of the massless Dirac nature of the pi-electrons in graphene. When the Fermi level is tuned below the Dirac point the valence band is filled with holes; when the Fermi level is tuned above the Dirac point the conduction band is filled with electrons. These two possibilities give graphene its ambipolar (electron and hole) nature, with the Hall effect measurements giving direct evidence on the charge of the carriers. Graphene, a material that consists of a lattice of carbon atoms, one atom thick, is widely touted as being the most electrically conductive material ever studied[8]. A single 2-D sheet of graphene is a hexagonal structure with each atom forming 3 bonds with each of its nearest neighbors. These are known as the σ bonds oriented towards these neighboring atoms and formed from 3 of the valence electrons. These covalent carbon-carbon bonds are nearly equivalent to the bonds holding diamond together giving graphene similar mechanical and thermal properties as diamond. The fourth valence electron does not participate in covalent bonding. It is in the 2pz state oriented perpendicular to the sheet of graphite and forms a conducting π band[9]. The electronic wave functions from different atoms on the hexagonal lattice overlap. However, any such overlap between the pz(π) and the s or px and py orbitals is strictly zero by symmetry. Consequently, the px electrons, which form the π-bonds, can be treated independently from the other valence electrons[7]. With one px electron per atom in the \( \pi-\pi' \) model (the three other s, px, py electrons fill the low-lying σ-band), the (−) band (negative energy branch) in equation is fully occupied, whereas the (+) branch is totally empty. These occupied and unoccupied bands touch at the K points. The Fermi level \( E_F \) is the zero-energy reference, and the Fermi surface is defined by K and \( K' \)[11].
The linear dispersion relation of electrons in graphene at the ends of the 1st Brillouin Zone. This conical shape is the same at K and K' points.

(a) When the Fermi level is above the Dirac point the carriers are electron-like
(b) When the Fermi level is below the Dirac point, the carriers are hole-like.

The Fermi level lies at E = 0 and bisects the two bands, running through just the points K and K'. The bonding-anti-bonding gap closes at the corners of the Brillouin zone, or the K points. As a result, the π-band dispersion is approximately linear around the K points. The Fermi surface (just a curve for this two-dimensional example) is that part of the energy band surface that intersects the Fermi energy; the Fermi “surface” is just a square that surrounds the k = 0 (point) in the BZ (Brillouin zone)[11]. Graphene is a 2-dimensional solid, with honeycomb sp2-carbon nets that are layered upon one another with separations of 3.35 Å. The π-electronic structure is very strongly controlled by hexagonal translational symmetry of the 2-dimensional graphene sheets. The conducting properties of graphene are determined by the π-bands. In valence bands, the s orbitals of carbon are the dominant contributors at lower energies while the p orbitals of carbon are more pronounced contributors at higher energies just below the Fermi level (E_F). In building up the sp2 hybrids, the s orbital of carbon participates to form low-lying σ bands while the pz orbitals of carbon form the higher-lying π bands[14]. The most notable feature about the early work on graphene transistors was the ability to continuously tune the charge carriers from holes to electrons[9].

Electrons in graphene thus behave like photons or other ultra-relativistic particles (such as neutrinos), with an energy-independent velocity v_F that is approximately 300 times smaller than the speed of light[5]. This is the Dirac equation for massless relativistic particles. The positive energy conduction band and the negative energy valence band touch at the K point, just as electron and positron bands touch at zero momentum in the zero mass limit of the relativistic Dirac equation[17]. Graphene has sp2 hybridization: 2s orbital overlaps with 2px and 2py orbitals and generates three new inplane sp2 orbitals each having one electron. The 2pz orbital remains unaltered and becomes singly occupied. Due to overlap of sp2 orbitals of adjacent carbon atoms strong σ (bonding) and σ* (antibonding) bonds are formed. The bonding σ bonds, lying in a plane, make an angle of 120° with each other and is at the root of hexagonal planar structure of graphene. pz orbitals being perpendicular to the plane overlap in a sidewise fashion and give π (bonding) and π* (antibonding) bonds. sp2 orbitals with a lower binding energy compared to 1s (core level) are designated as semi-core levels and pz orbitals having lowest binding energy are the valence levels. Overlapping of pz energy levels gives the valence band (bonding π band) and conduction
band (antibonding π∗ band) in graphene. Thus, we see that while the structure of graphene owes to σ bonds, π band is responsible for the electronic properties of graphene and hence as far as electronic properties of graphene are concerned, concentration is given only on π bands. Since the pz orbitals overlap in a sidewise manner, the corresponding coupling is weaker compared to that of σ bonds (where sp2 orbitals overlap face to face). So the pz orbitals almost retain their atomic character[12]. Since there are two atoms in each unit cell and each carbon atom has one electron in pz state, the valence band is completely filled and hence, the fermi level lies at the top of the valence band at zero energy which appears at K and K′ points of the brillouin zone in energy momentum space. The resulting shape of the Fermi surface is a triangle centred at the K points in the Brillouin zone[15]. The Dirac point is located at the K point, which lies in the corner of the hexagonal Brillouin zone[16]. The point \( \mathbf{k} \mathbf{d}=0 \), referred to as the "Dirac point," is a convenient choice for the reference of energy; thus, \( E(\mathbf{k})=0 \) eV. Each \( \mathbf{k} \) point is twofold spin degenerate \( (g_s=2) \), and there are two valleys in the first BZ (the K and K* valleys), \( g v=2 \)[18],[19]. The semimetallic character induced by the close proximity of valence and conduction band as well as the conical shape of the bands results from a delicate balance between the electrons and the lattice[16],[20].

[8] Conclusion.
The "super material" isn't ready yet, but it's going to make future technologies so awesome. Graphene, the pure carbon material that's just one atom thick and nearly transparent when laid out in sheets, manages to be roughly 200 times stronger than steel, even though it's 60,000 times thinner than Saran Wrap. Graphene is also an excellent conductor of energy, can be synthesized from unique carbon sources, it has thousands of possible applications. How is it possible for one material to have so many ideal characteristics? The most common picture you'll see on web is a molecular lattice that resembles a honeycomb, or chicken wire. In reality, this depiction of graphene is perhaps the best way to understand its incredible properties: The structure is remarkably strong and efficient — even self-repairing — but it is essentially two-dimensional. As such, graphene is the most chemically reactive form of carbon, which also makes the material highly conductive and flexible, as well as strong. Graphene still has a long way to go before it reaches commercialization..
The Potential Power of Graphene

[REFERENCE]


(2) David Saada et al, Transformation of Diamond (sp3) to Graphite (sp2) bonds by ion-impact. 1997, worldscientific, Volume 09, Issue 01.


(17) Lin Miao et al, Quasiparticle dynamics in reshaped helical Dirac cone of topological insulators, PNAS, 2013, vol. 110, no. 8 : 2758–2762


(19) S. Samaddar et al, Charge Puddles in Graphene Near the Dirac Point, Physical Review Letters, American
(20) J. Huang et al, Physics of a disordered Dirac point in epitaxial graphene from temperature-dependent magnetotransport measurements, *PHYSICAL REVIEW B* 92, 075407 (2015)