Carbon-based (organic) materials.

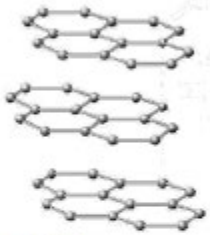
PH 673

Nanoscience and nanotechnology

October 29, 2025

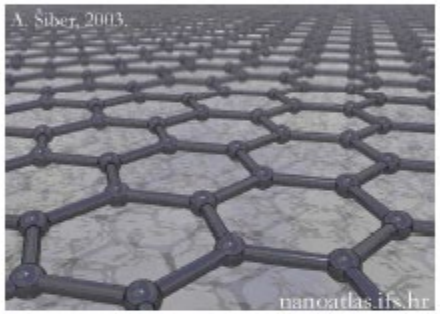
Carbon

3d



Graphite

2d



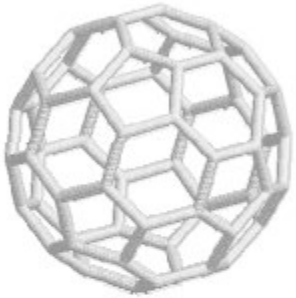
Graphene

1d

Nanotube

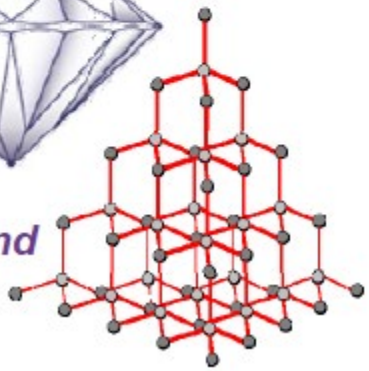
"Multi-wall" 1991
"Single-wall" 1993

0d



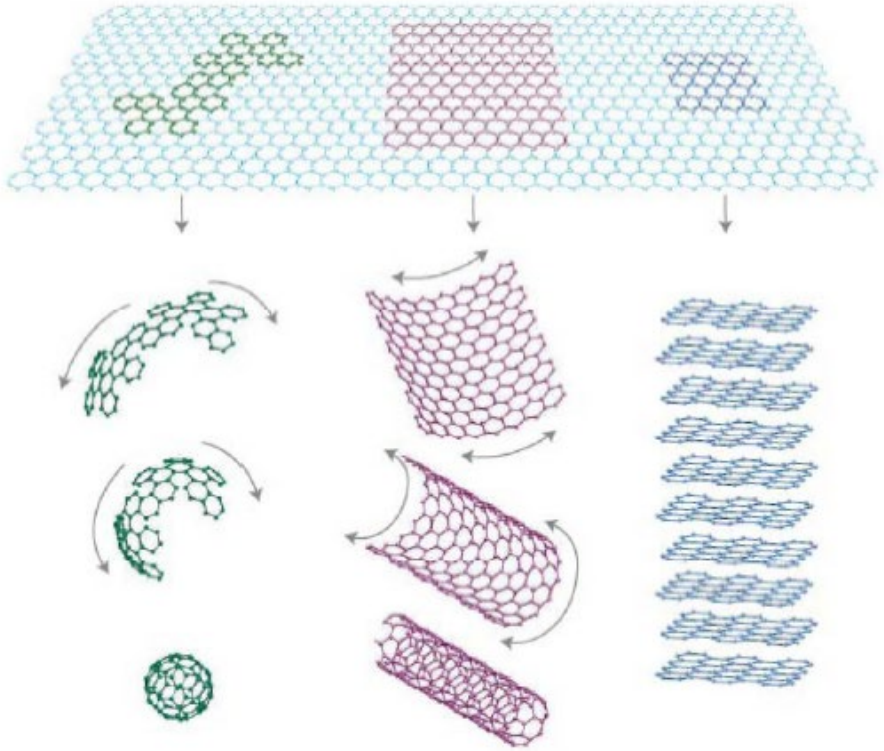
Fullerene

1985

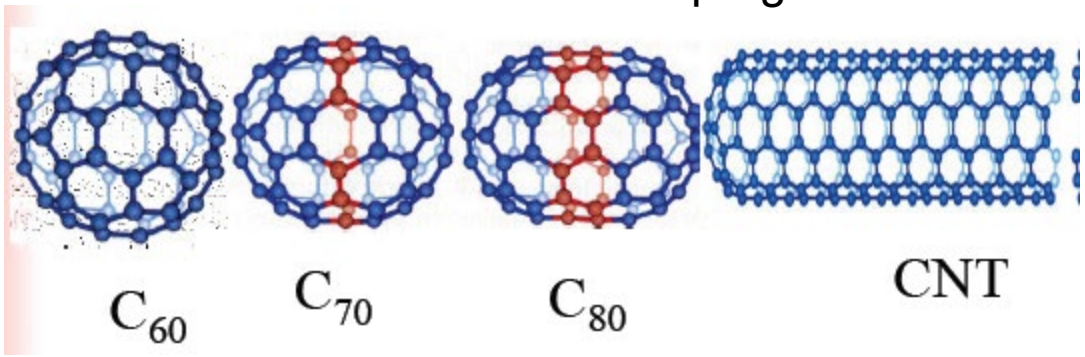


Diamond

graphene, fullerenes, nanotubes and graphite

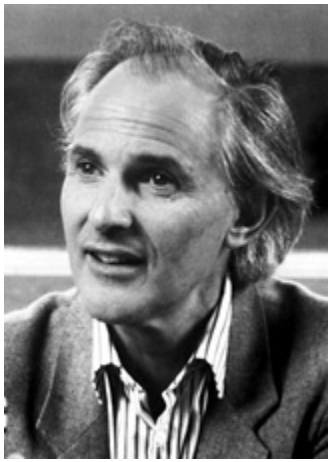
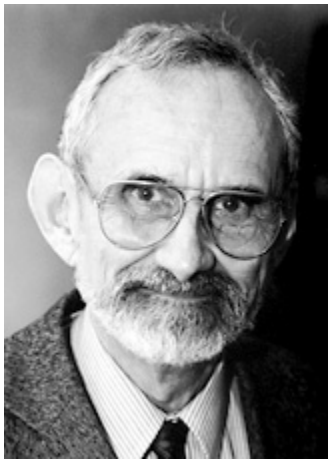
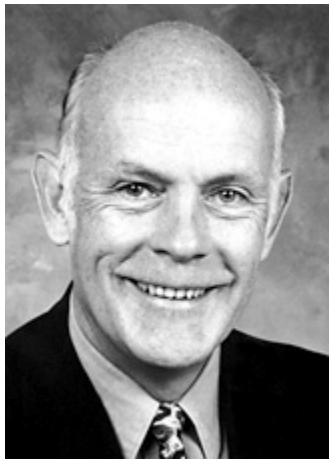


Or… fullerene progression



Nobel prize in Chemistry 1996

Fullerenes

Robert F. Curl Jr. (Rice U, USA), Sir Harold W. Kroto (U of Sussex, UK) and Richard E. Smalley (Rice U, USA) *"for their discovery of fullerenes"*.

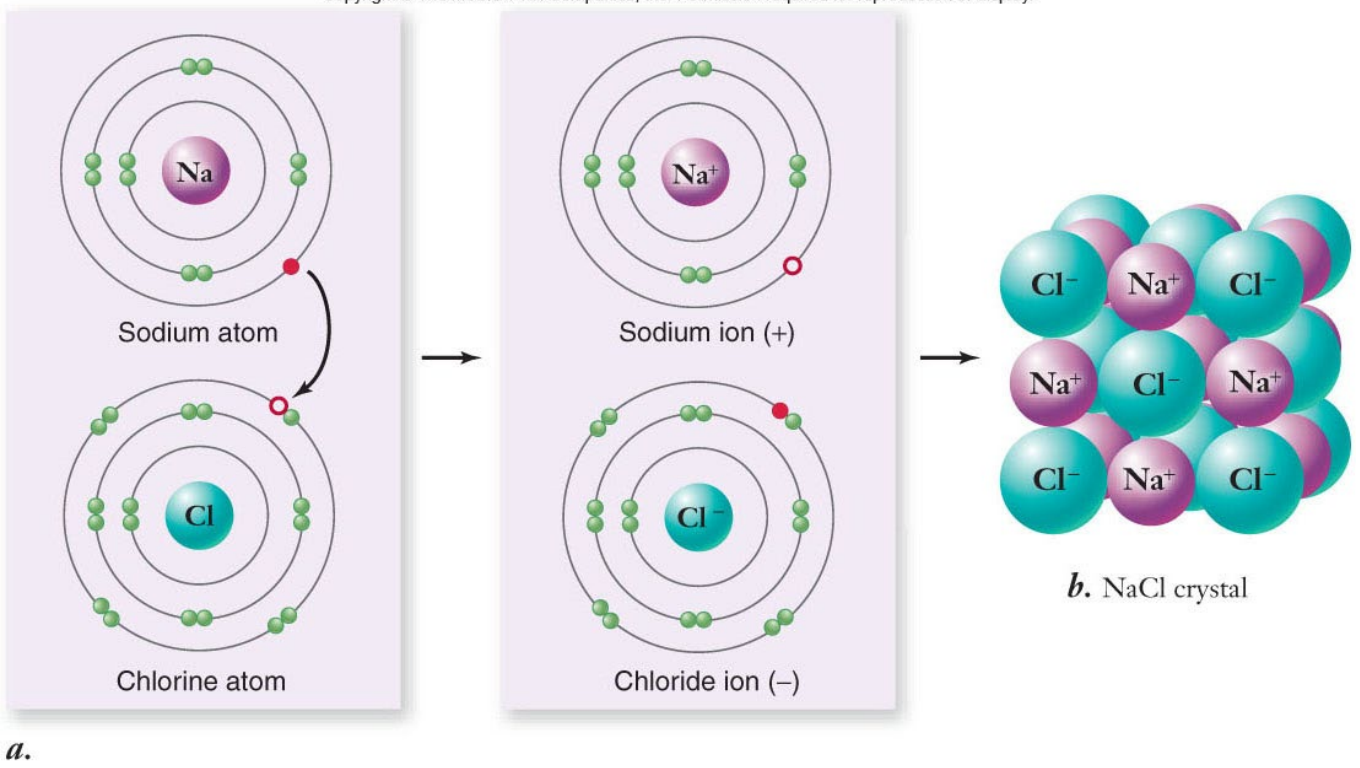
Nobel prize in Physics 2010

Graphene


Andre Geim and Konstantin Novoselov (U of Manchester, UK) *"for groundbreaking experiments regarding the two-dimensional material graphene"*

Chemical Bonds

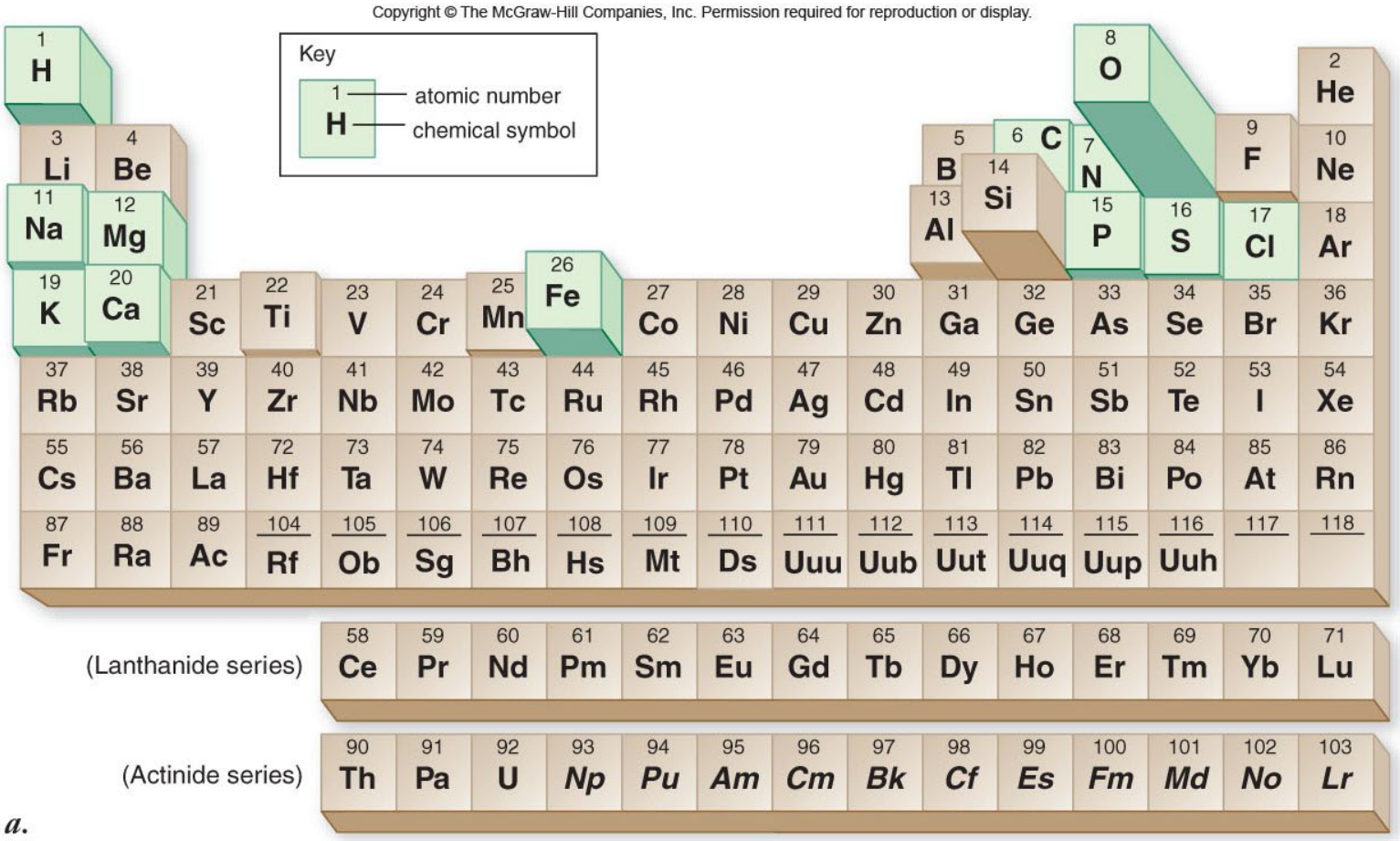
Ionic bonds are formed by the attraction of oppositely charged ions.



a.

b. NaCl crystal

Periodic Table of the Elements



Chemical Bonds

Covalent bonds form when atoms share 2 or more valence electrons.

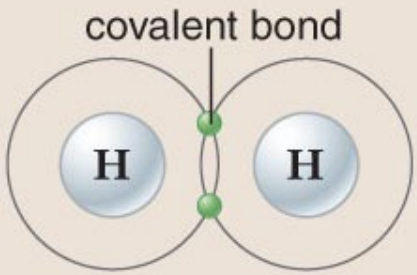
Covalent bond strength depends on the number of electron pairs shared by the atoms.

single bond < double bond < triple bond

Chemical Bonds

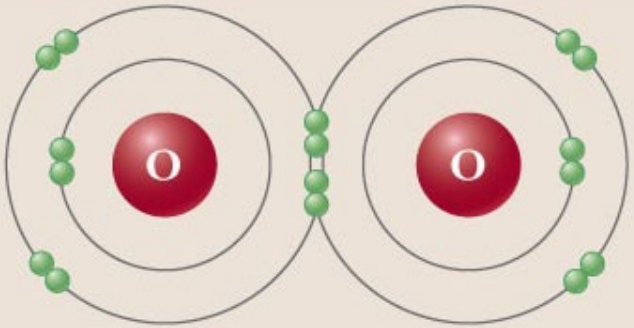
Single covalent bond
hydrogen gas

H—H H_2



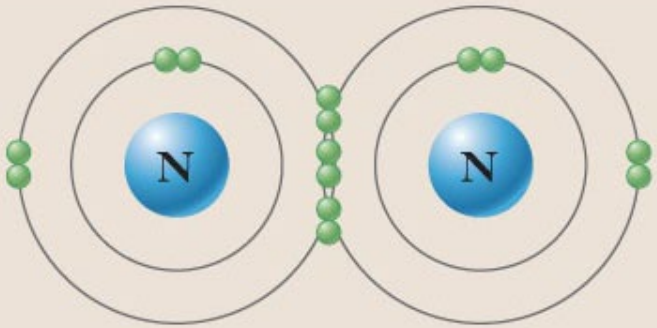
Double covalent bond
oxygen gas

O=O O_2



Triple covalent bond
nitrogen gas

N≡N N_2



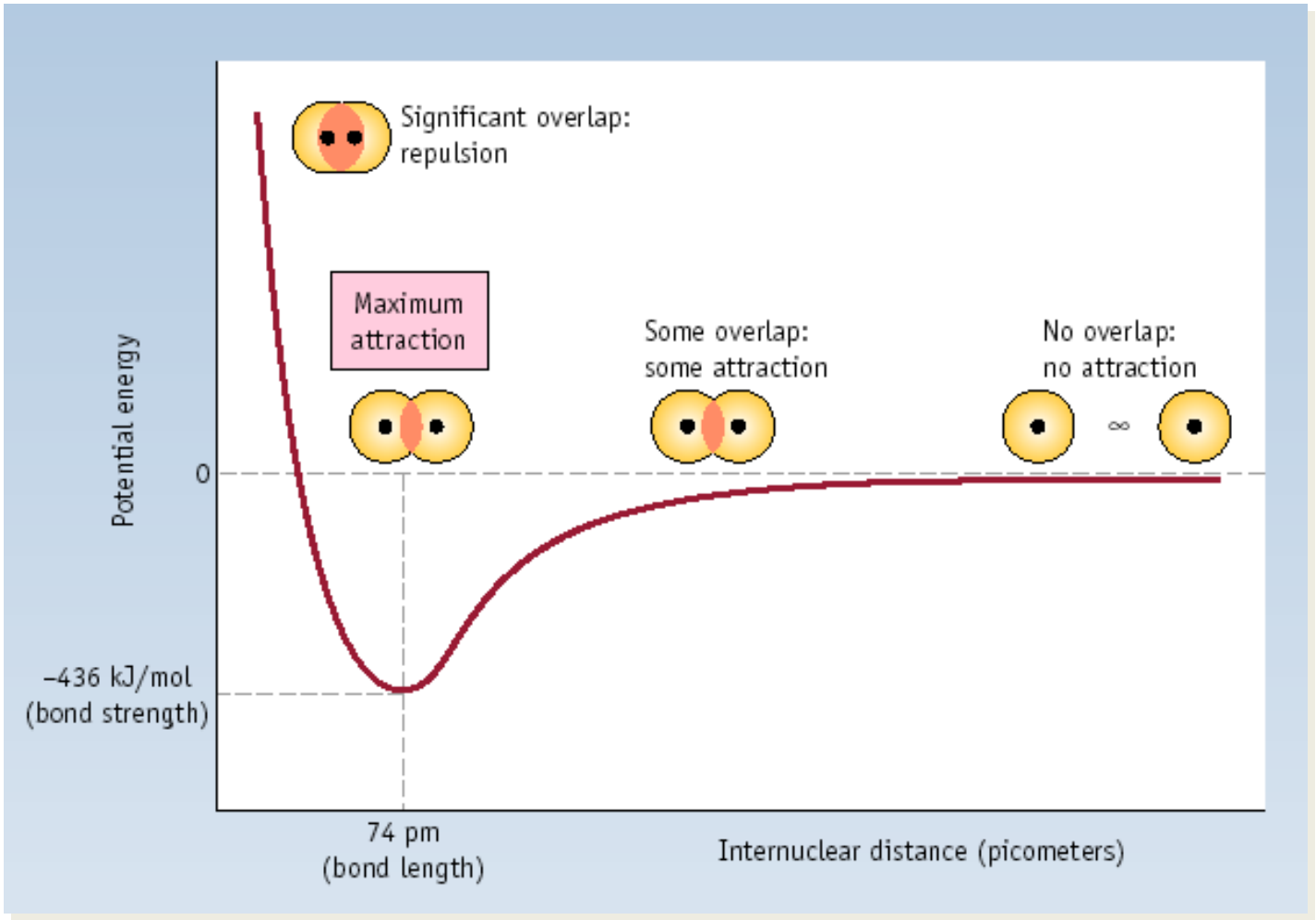
Chemical Bonds

Electronegativity is an atom's affinity for electrons.

Differences in electronegativity dictate how electrons are distributed in covalent bonds.

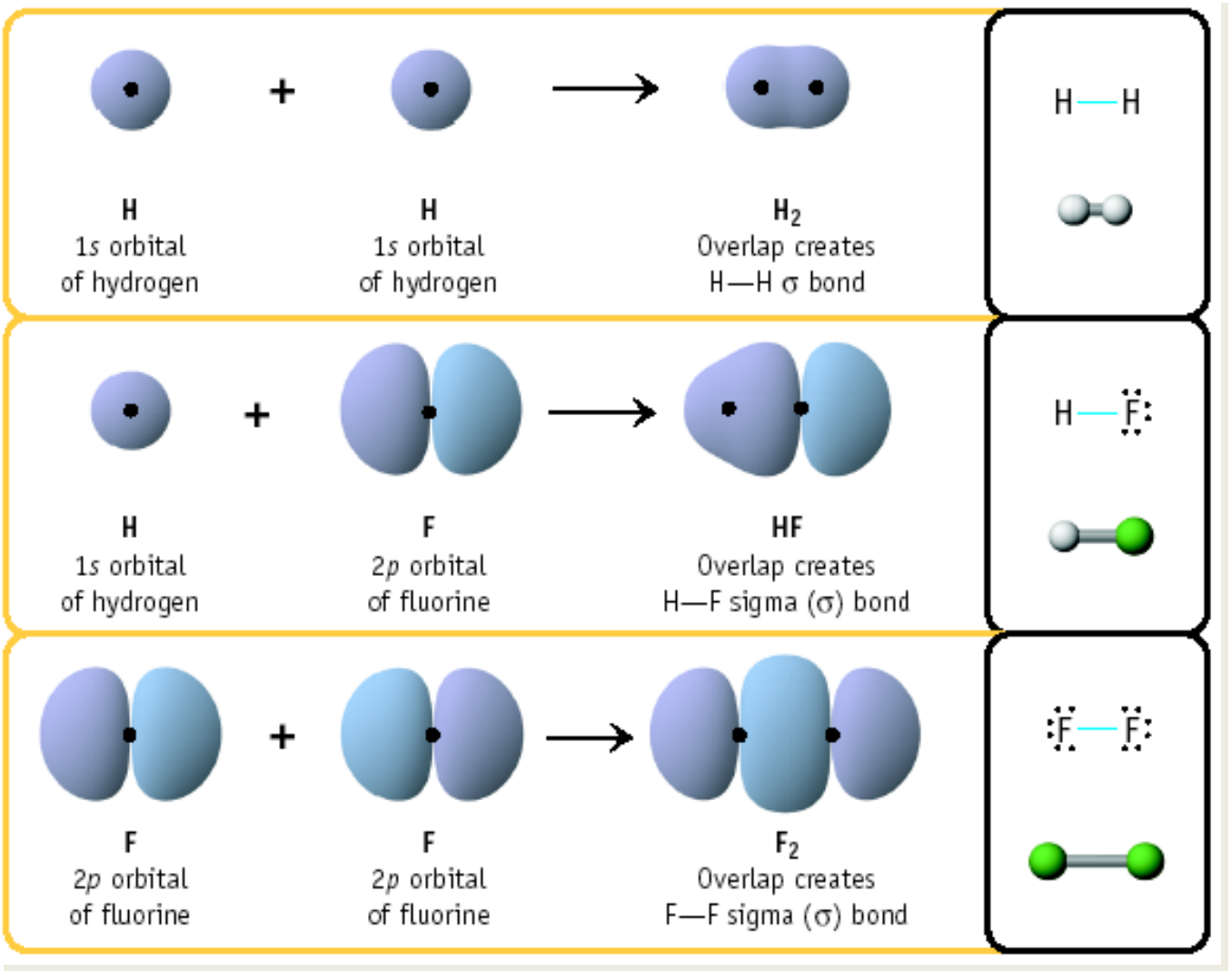
- **nonpolar covalent bonds** = equal sharing of electrons
- **polar covalent bonds** = unequal sharing of electrons

Energy Diagram of Sigma Bond Formation by Orbital Overlap



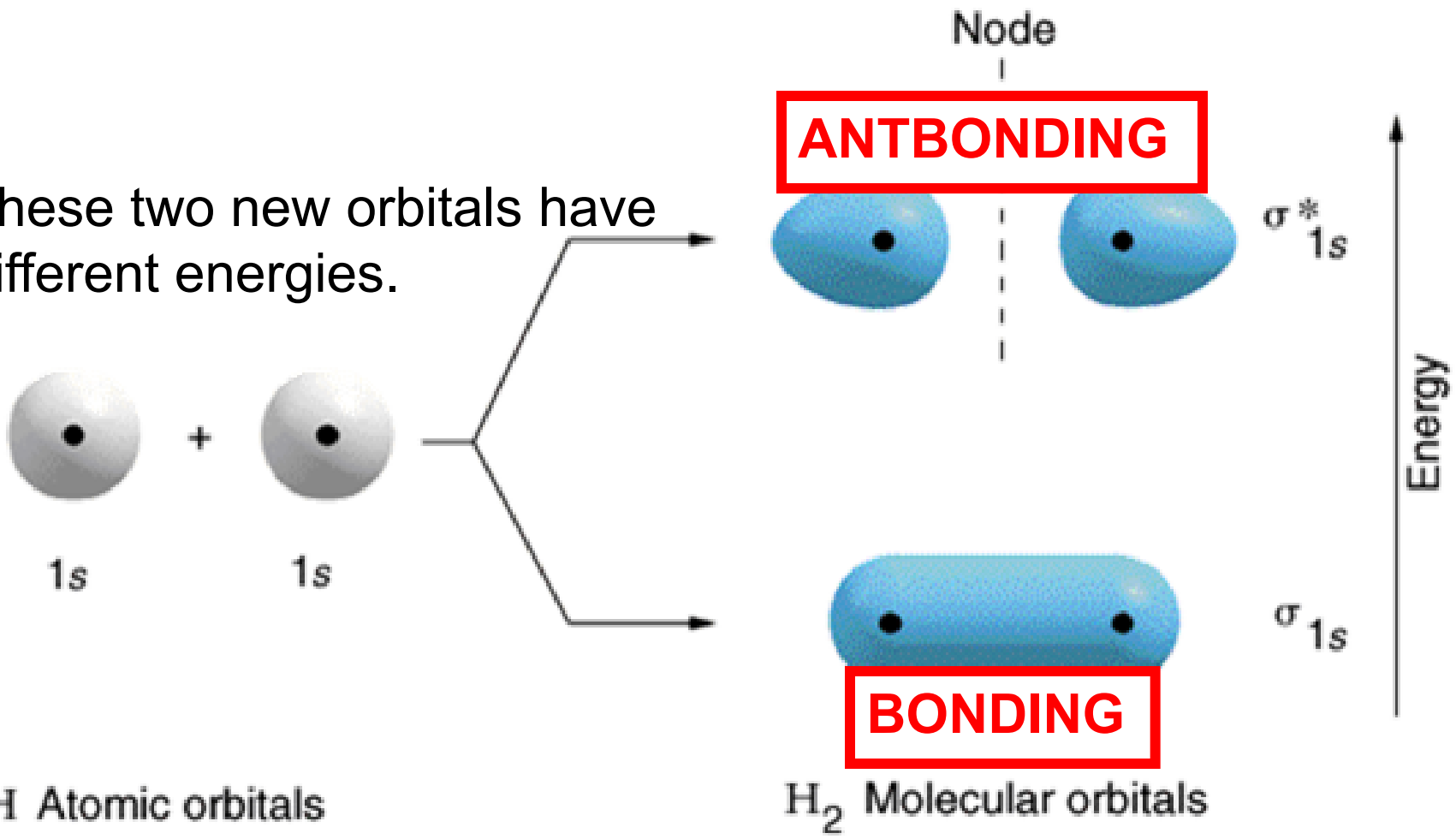
Examples of Sigma Bond Formation

Sigma bond (σ) → *A bond where the line of electron density is concentrated symmetrically along the line connecting the two atoms.*



Moleculuar Orbital (MO) Theory

These two new orbitals have different energies.

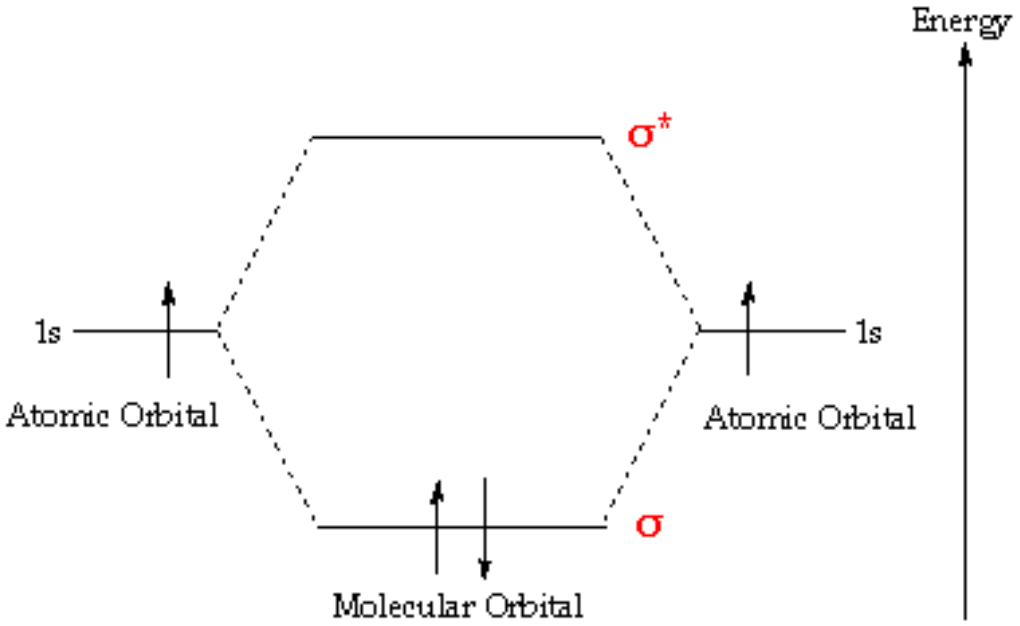


The one that is lower in energy is called the **bonding orbital**,

The one higher in energy is called an **antibonding orbital**.

Atomic and Molecular Orbitals

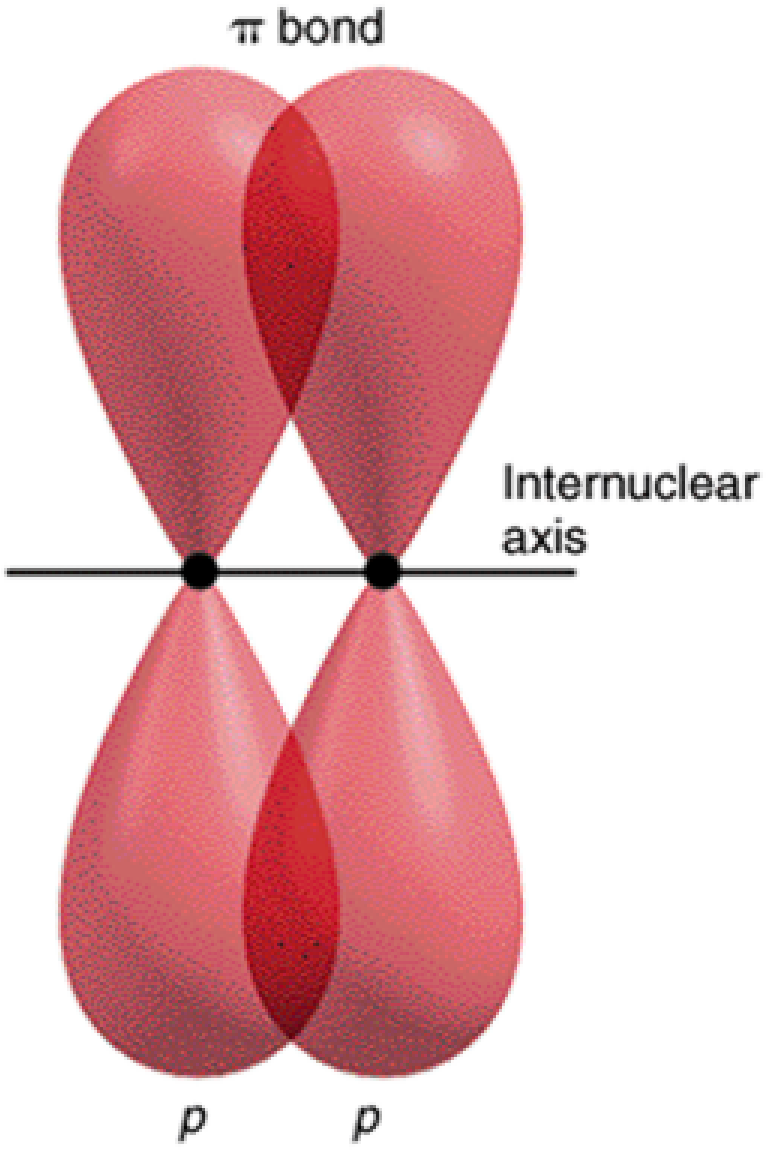
- In atoms, electrons occupy **atomic orbitals**, but in molecules they occupy similar **molecular orbitals** which surround the molecule.
- The two 1s atomic orbitals combine to form two molecular orbitals, one bonding (σ) and one antibonding (σ*).



http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/main.html

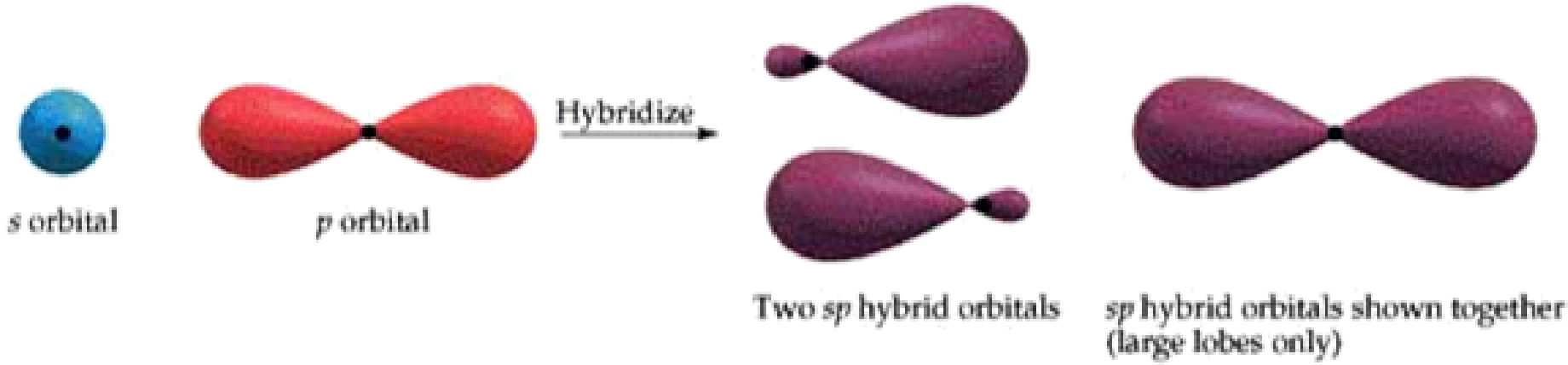
- This is an illustration of molecular orbital diagram of H_2.
- Notice that one electron from each atom is being "shared" to form a covalent bond. This is an example of orbital mixing.

Pi bond (π) $\rightarrow$ *A* bond where the overlapping regions exist above and below the internuclear axis (with a nodal plane along the internuclear axis).



Formation of sp hybrid orbitals

The combination of an **s orbital and a p orbital produces 2 new orbitals called sp orbitals.**

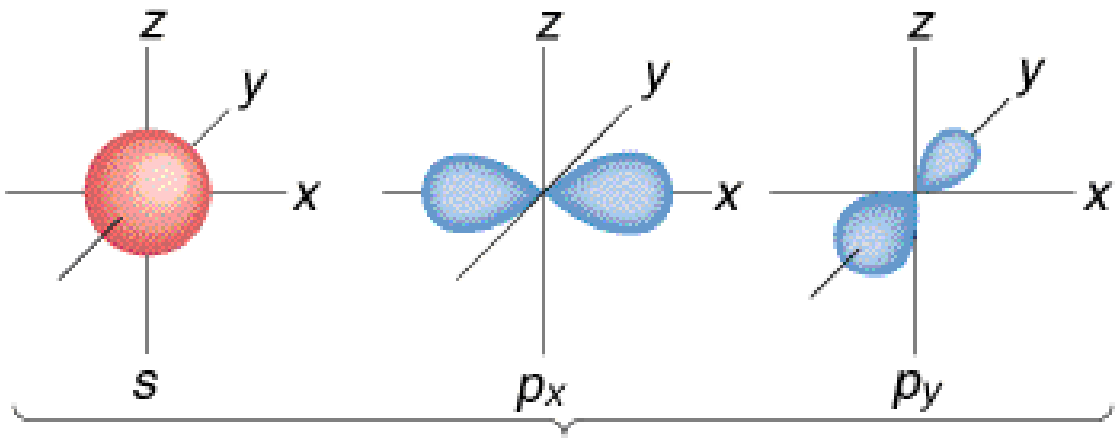


These new orbitals are called **hybrid orbitals**

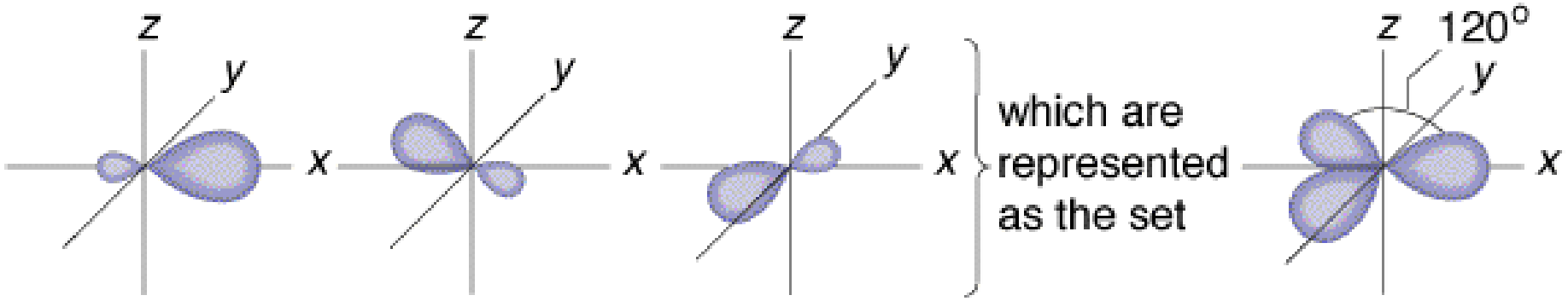
The process is called **hybridization**

What this means is that both s and p orbitals are involved in bonding to the connecting atoms

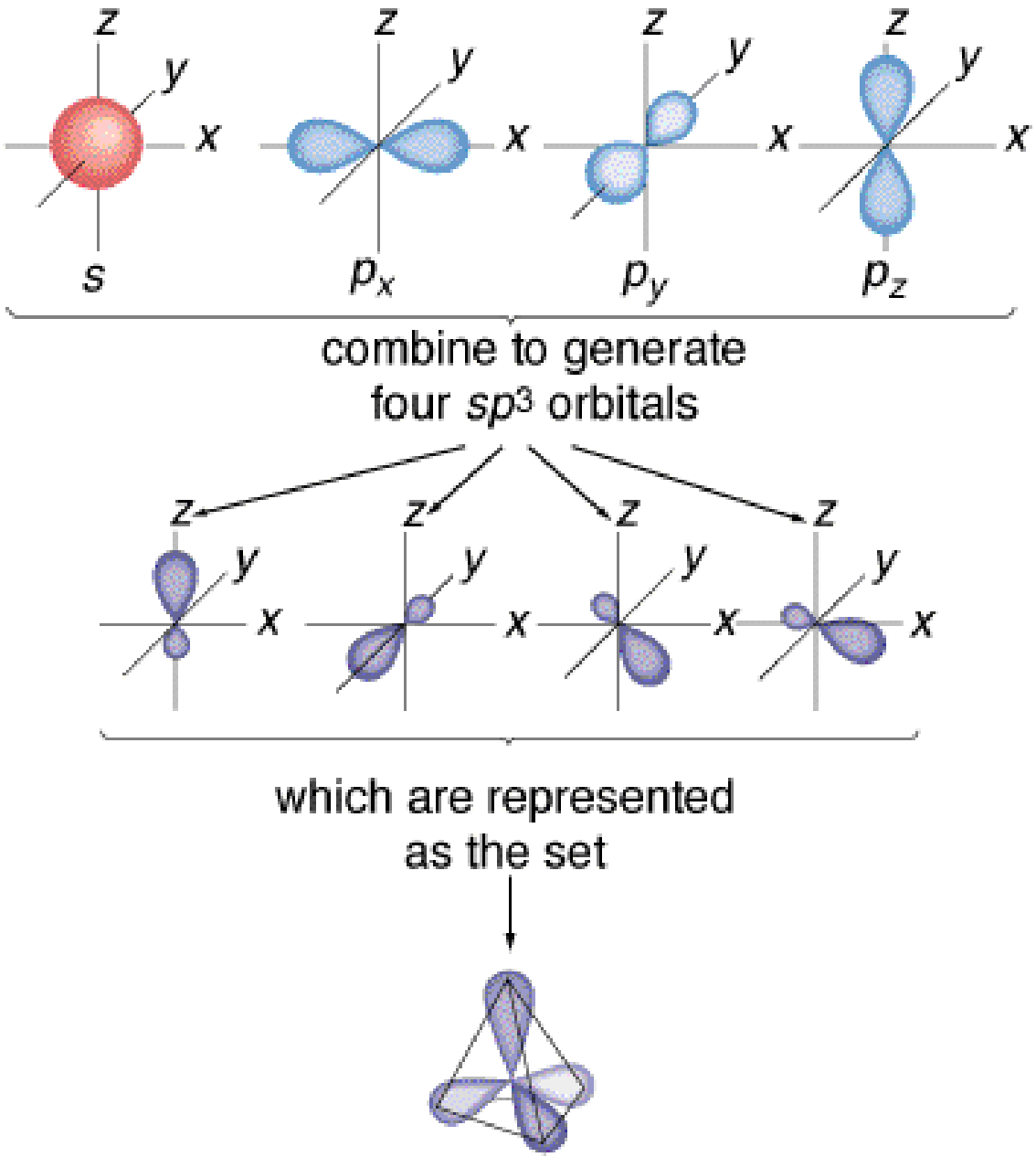
Formation of sp^2 hybrid orbitals



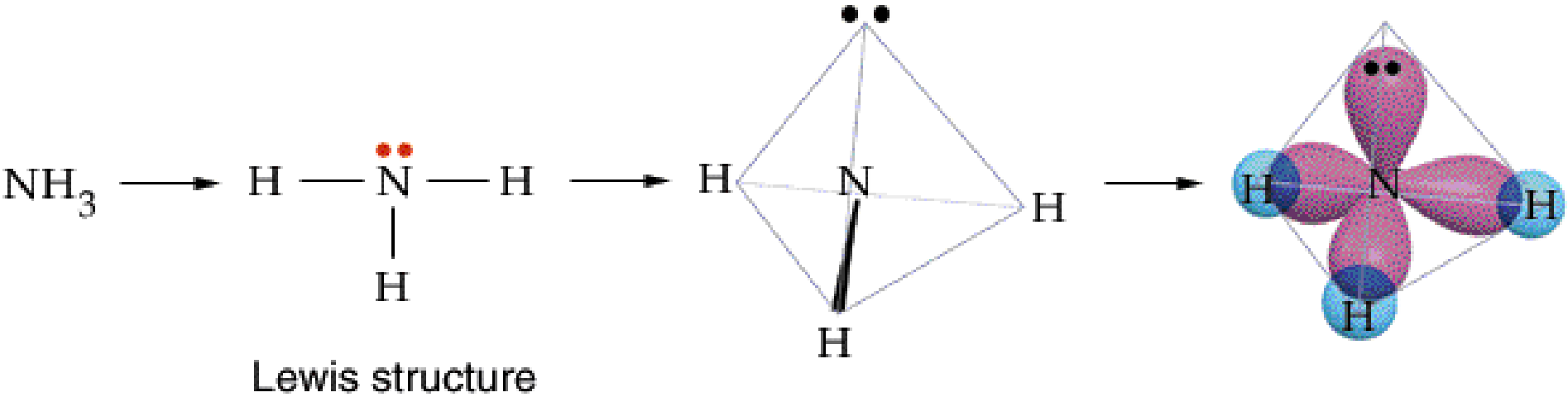
combine to generate
three sp^2 orbitals



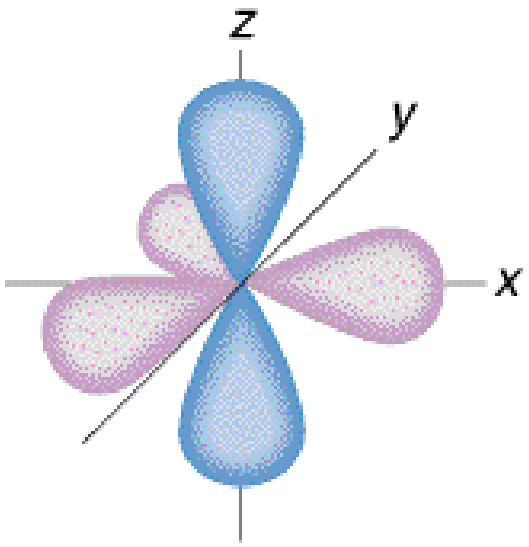
Formation of sp^3 hybrid orbitals



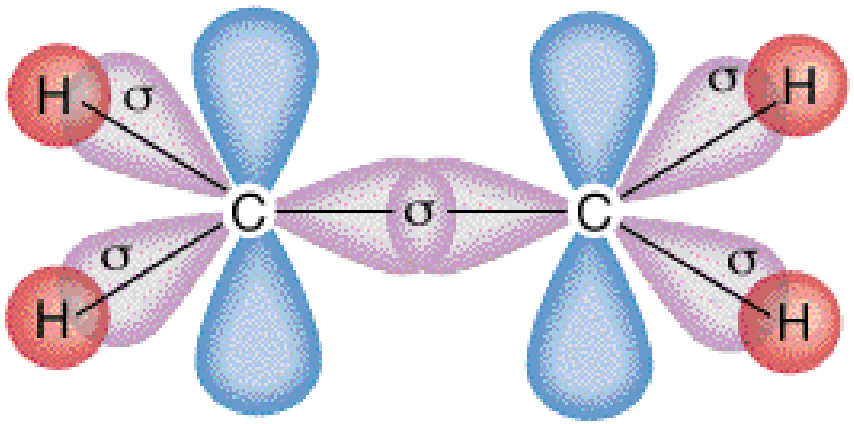
Hybrid orbitals can be used to explain bonding and molecular geometry



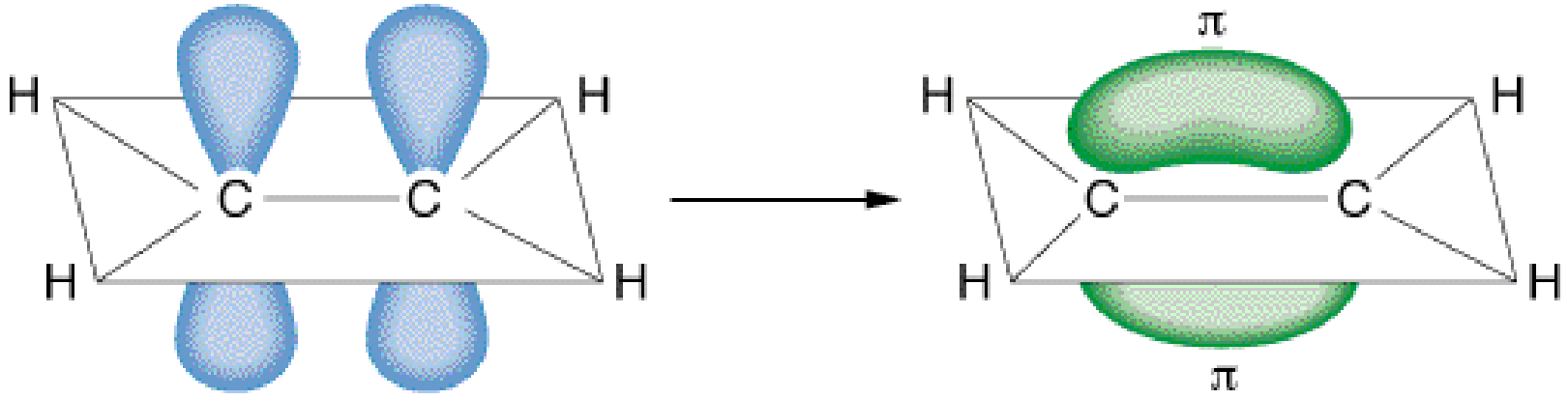
Example: $H_2C=CH_2$



the set of orbitals $sp^2 + p$

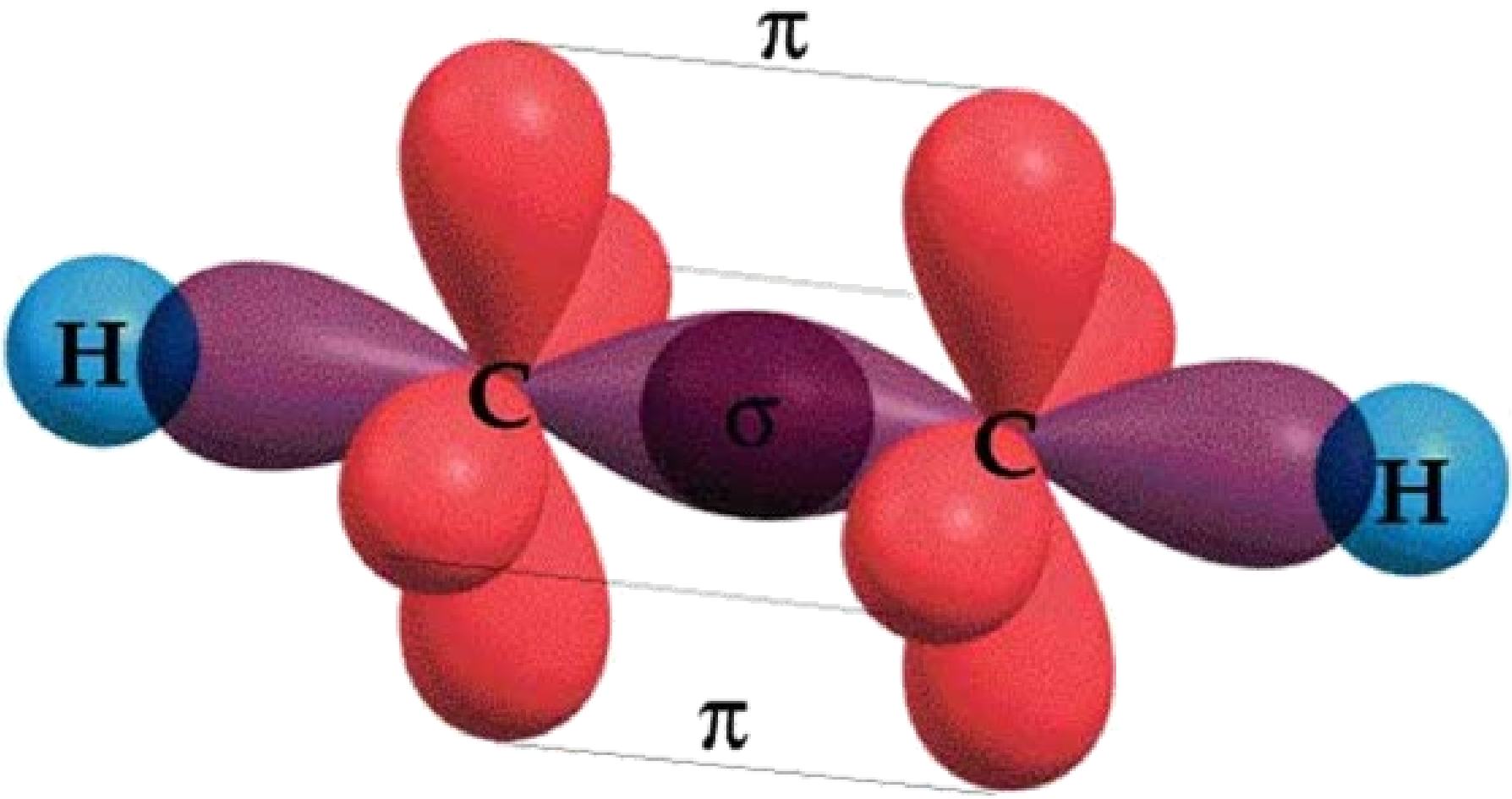


sigma (σ) bonds



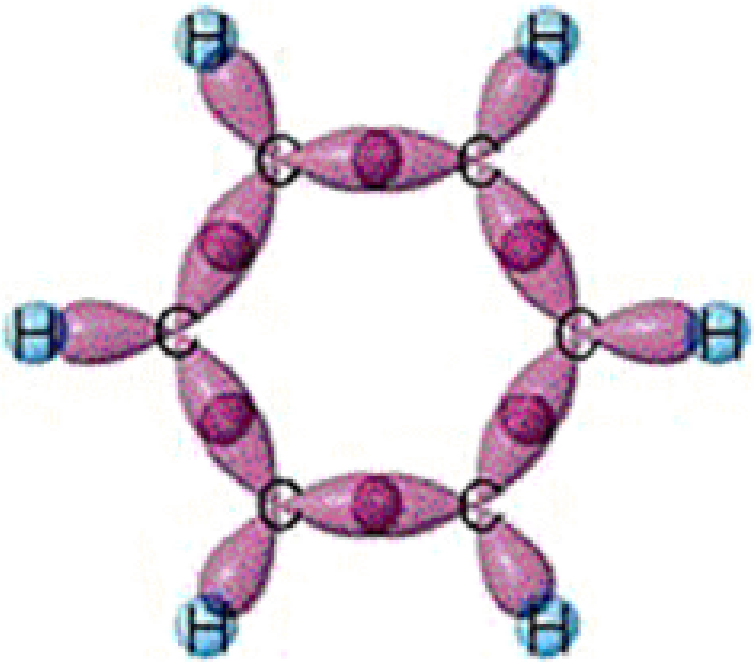
overlap of *p* orbitals leading to pi (π) bond

Example: HC≡CH

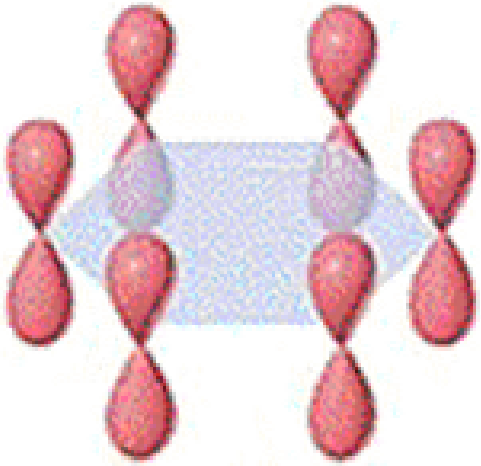


Delocalized π bonds

The pi electrons can be delocalized over all the atoms that have pi bond overlap.



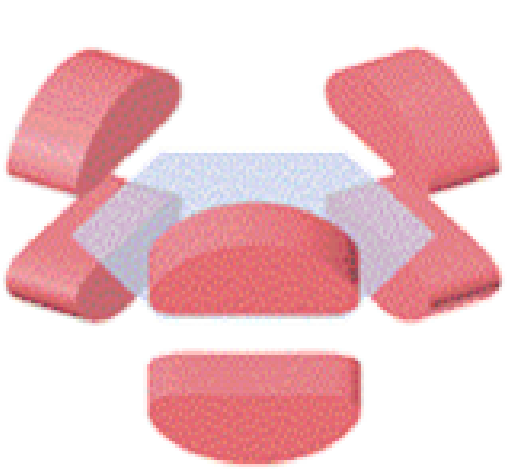
(a) σ bonds



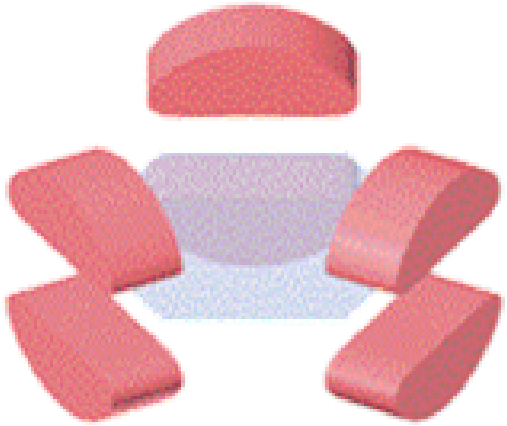
(b) 2p atomic orbitals

Example: C_6H_6 benzene

Benzene is an excellent example. For benzene the π orbitals all overlap leading to a very delocalized electron system



(a) Localized π bonds

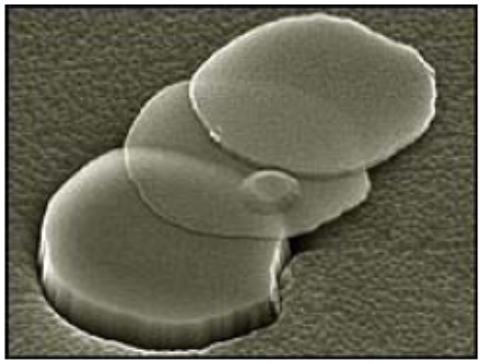


(b) Localized π bonds

(c) Delocalized π bonds

Graphene discovery

Graphene, the world's first 2-dimensional fabric
Posted Oct 26, 2004, 3:30 PM ET

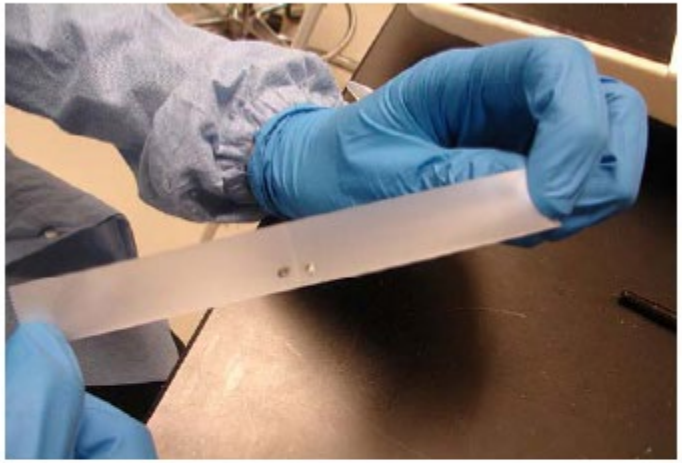


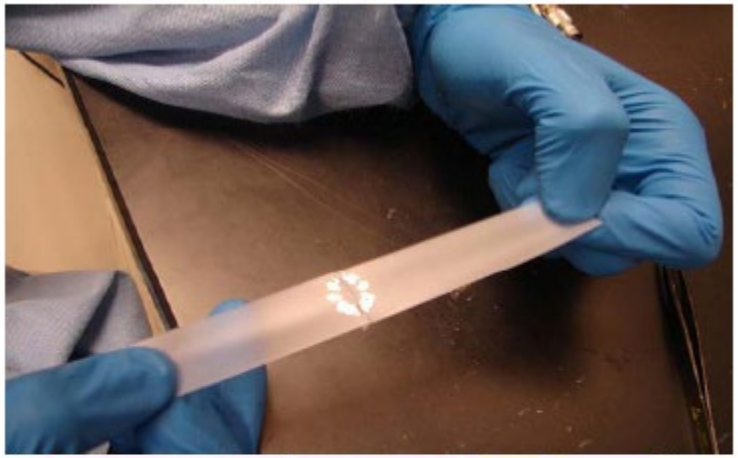
Researchers at The University of Manchester and Chernogolovka, Russia have created the first-ever single-atom-thick substance, a fabric they call "graphene". The substance is stable, flexible, and highly conductive, and researchers believe it could be used to create computers made from a single molecule. Professor Andre Geim at The University of Manchester was able to extract a single plane of graphite crystal, resulting in the new fabric. The hope is that the fabric will be used in the future to create nanotubes, transistors for microscopic computers, that could result in some seriously small electronic gadgetry.

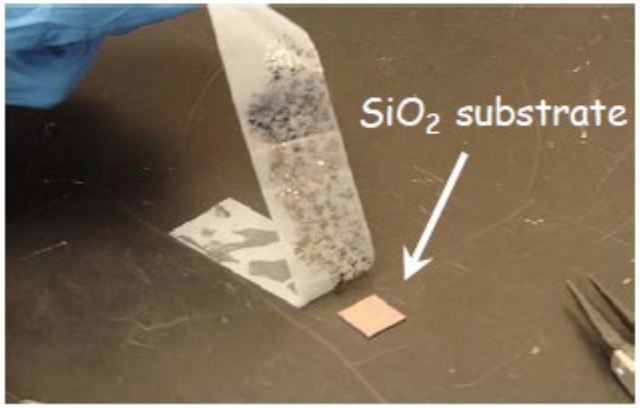
- high mobility (up to ~200,000 $cm^2/(Vs)$)
- transparent
- most importantly: opportunities for new effects and for bench-top experiments in quantum field theory

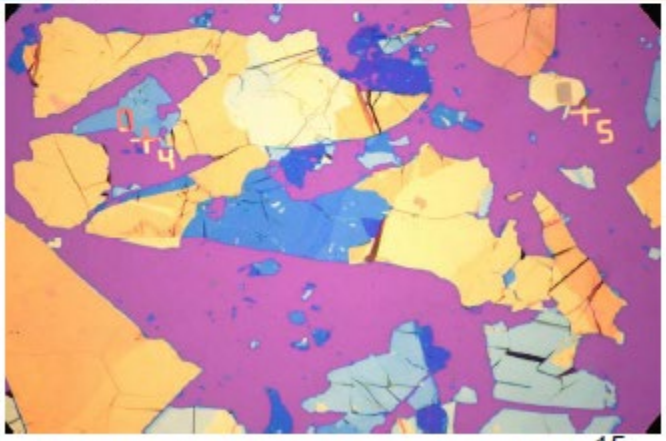
The Scotch trick

Novoselov et al., Science 2004







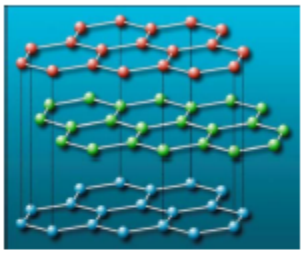


http://www.sciam.com/article.cfm?id=diy-graphene-how-to-make-carbon-layers-with-sticky-tape

Short history

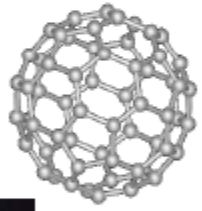
1564 Discovery of graphite (plumbago)

1779 Graphite is carbon



1789 Named from greek γραφειν

Graphite: pencils, light bulbs, nuclear moderator,..



1962 HOPG (graphite monocrystal)

1960-1980 Graphite intercalation compounds

1985 Fullerenes [Kroto, Curl, Smalley]

1991-1993 Carbon nanotubes [Iijima]

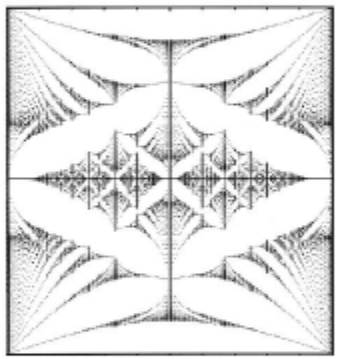
1992-1993 few layers graphite on metal substrate

History: theory

1947 Graphene band structure [Wallace]

1956 Graphene Landau levels [McClure]

1985 Hofstadter butterfly [Rammal]



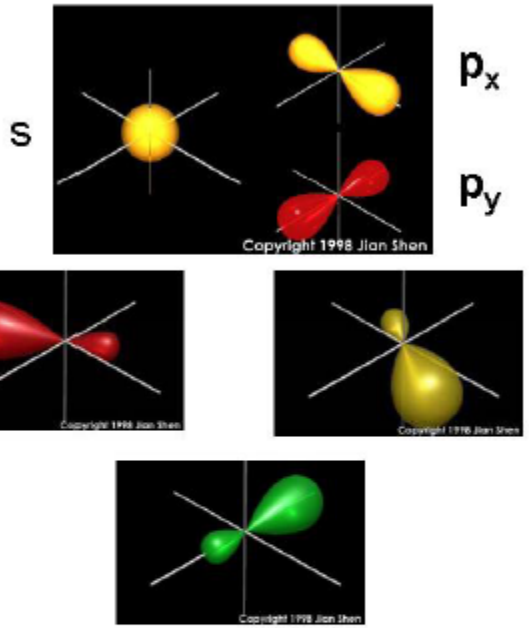
1984-1988 Connection to 2+1 field theory [Semenoff, DiVincenzo & Mele, Fradkin, Haldane, etc.]

~90's Theory of carbon nanotubes
[Dresselhauss, Saito, Ando, etc.

Graphene electronic structure

Graphene = 2D honeycomb carbon crystal

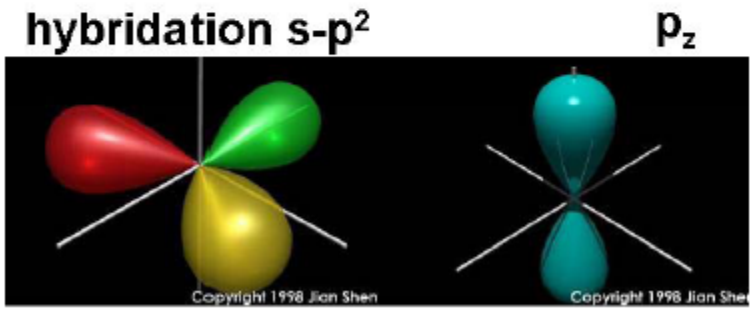
Carbon: 6 electrons $1s^2$, $2s^2$ $2p^2$
hybridation: 1 orbital 2s and 2 orbitals 2p
→ 3 orbitals sp^2
-3 coplanar σ bonds, angle 120°:
→honeycomb structure
→covalent bonding



+ 1 orbital $2p_z$ perpendicular to the plane

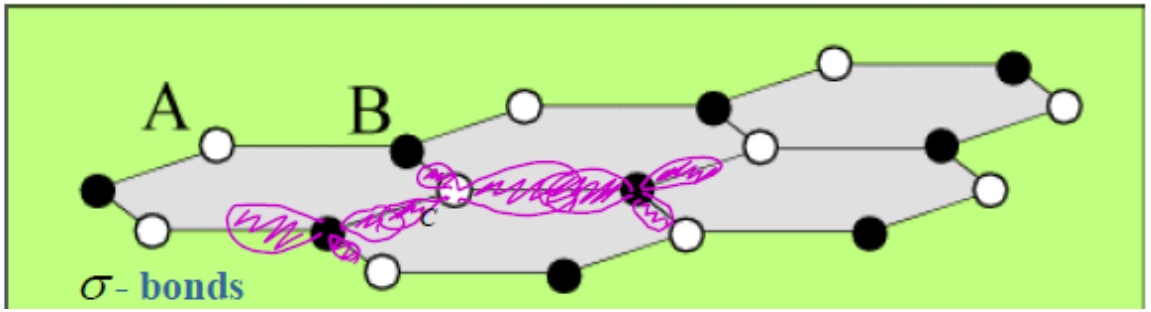
→ 1 conduction e per C

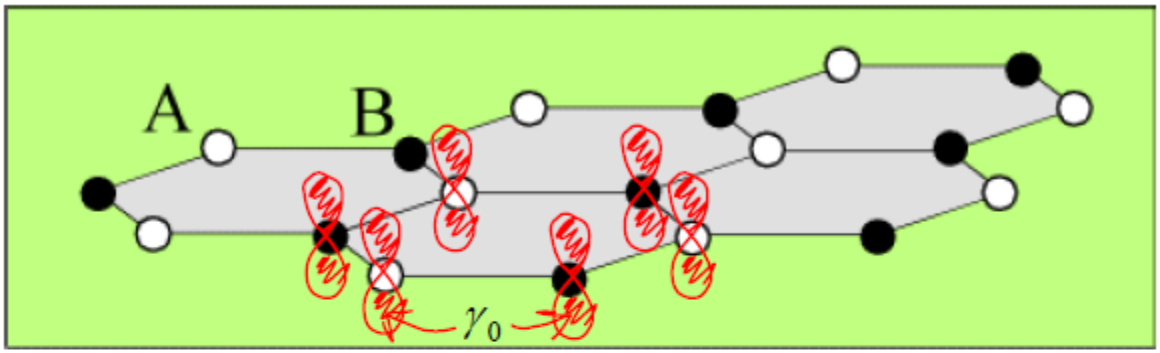
→ Half-filled band



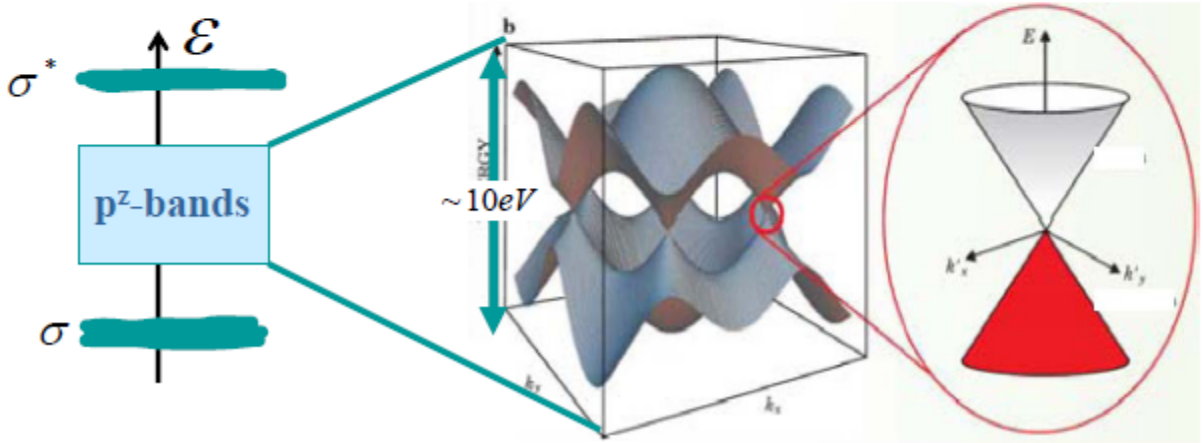
Carbon has 4 electrons in the outer s-p shell

sp^2 hybridisation forms strong directed bonds which determine a honeycomb lattice structure.



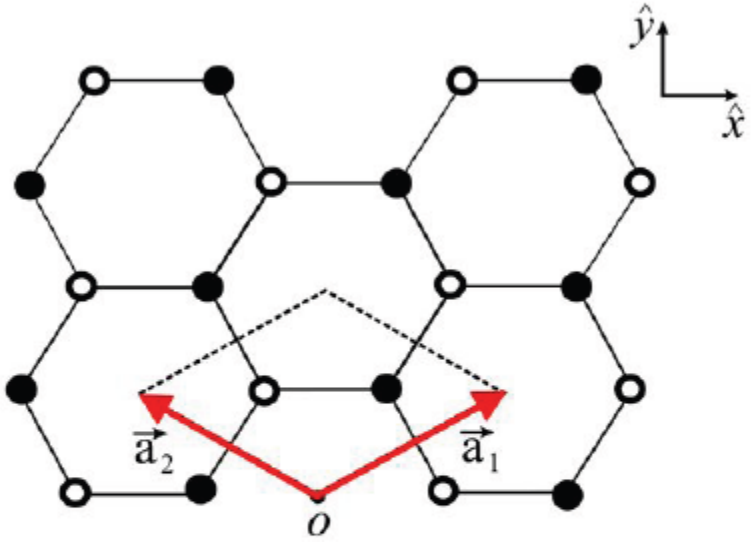


$p^z(\pi)$ orbitals determine conduction properties of graphite

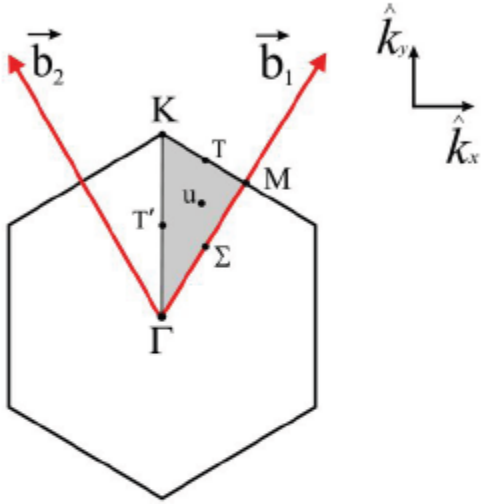


2D Graphite (Graphene) unit cells

Direct lattice



First Brillouin zone (BZ)



$$\vec{a}_1 = \frac{a}{2}\left(\sqrt{3}\,\hat{x} + \hat{y}\right)$$

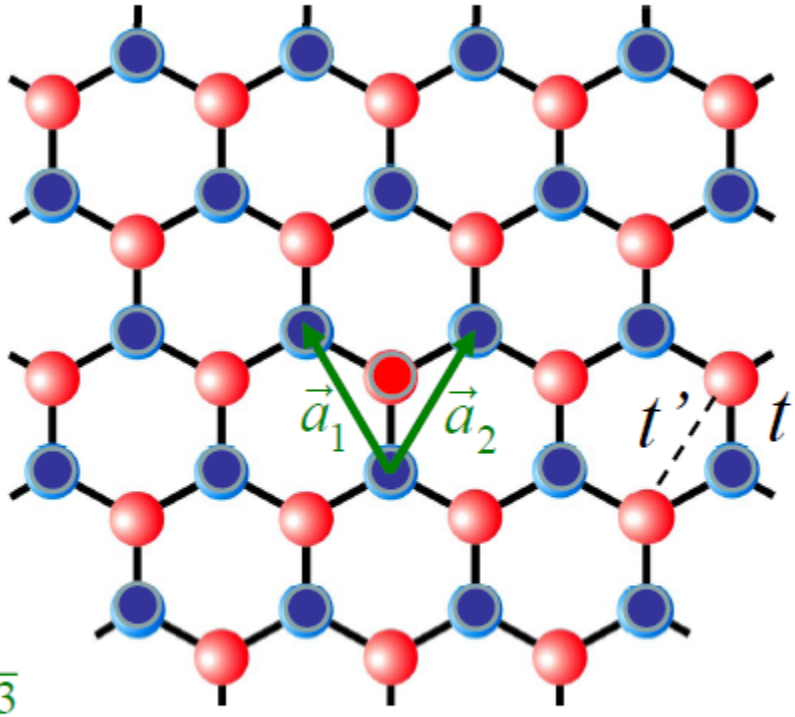
$$\vec{a}_2 = \frac{a}{2}\left(-\sqrt{3}\,\hat{x} + \hat{y}\right)$$

$$a = 2.456\ \text{Å}$$

$$\vec{b}_1 = \frac{2\pi}{a}\left(\frac{\sqrt{3}}{3}\,\hat{k}_x + \hat{k}_y\right)$$

$$\vec{b}_2 = \frac{2\pi}{a}\left(-\frac{\sqrt{3}}{3}\,\hat{k}_x + \hat{k}_y\right)$$

« Honeycomb lattice » is not a Bravais lattice



a=1.42 A

$t=2.8eV$

$t'=-0.2eV$

$a_0 = |\vec{a}_1| = a\sqrt{3}$

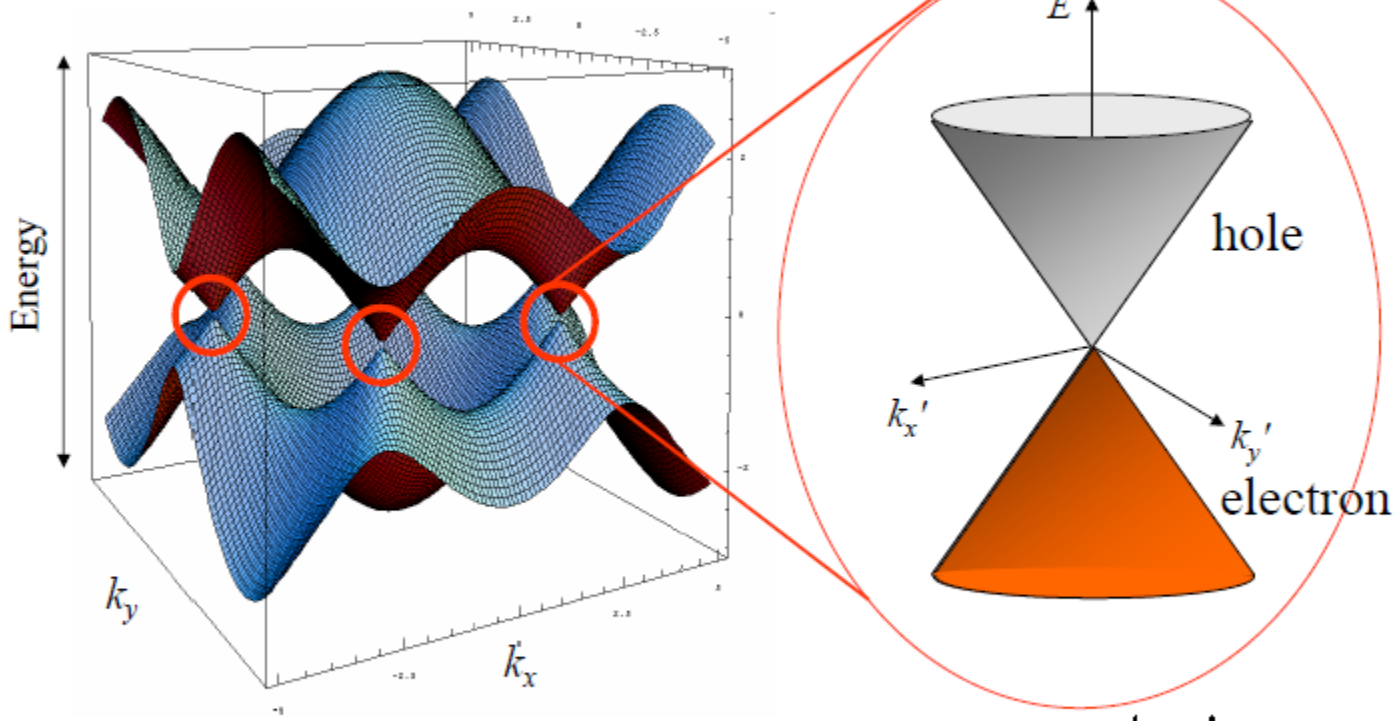
a = C-C distance
a_0 = lattice parameter

Triangular Bravais lattice + 2 atoms per unit cell

$$E_k = \pm t\sqrt{1 \pm 4\cos\frac{k_y a}{2}\cos\frac{\sqrt{3}k_x a}{2} + 4\cos^2\frac{k_y a}{2}}$$

Graphene : Dirac Particles in 2D Box

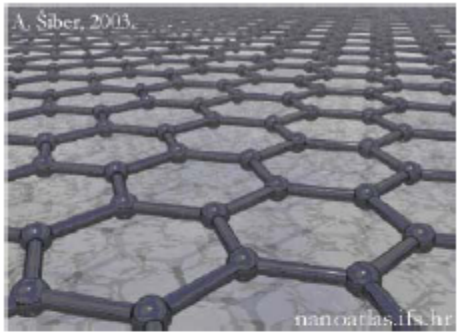
Band structure of graphene



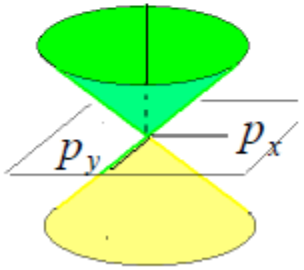
$$E \approx \hbar v_F \left| \vec{k}'_{\perp} \right|$$

Massless Dirac Particles with effective speed of light v_F.

Graphene (monolayer of graphite) is an atomically thin zero-gap two-dimensional semiconductor with linear dispersion of conduction and valence band electrons.



$$\varepsilon^{cond} = vp = v\sqrt{p_x^2 + p_y^2}$$



Electronic dispersion in the vicinity of the corner of the Brillouin zone: the same in both valleys.

$$\varepsilon^{val} = -vp = -v\sqrt{p_x^2 + p_y^2}$$

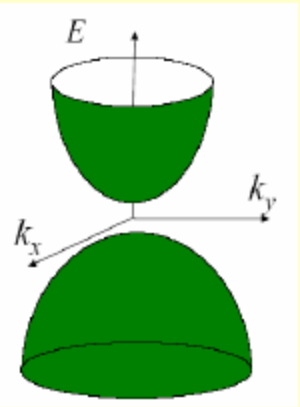
Graphene v.s. Conventional 2D Electron System

Conventional 2D Electron System

Band structures

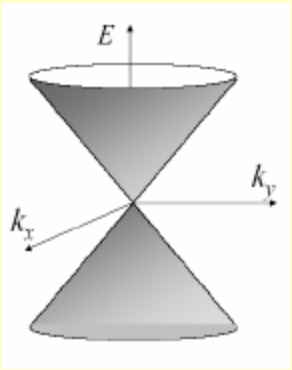
$$E = \frac{\hbar^2 k^2}{2m_e^*}$$

$$E = -\frac{\hbar^2 k^2}{2|m_h^*|}$$



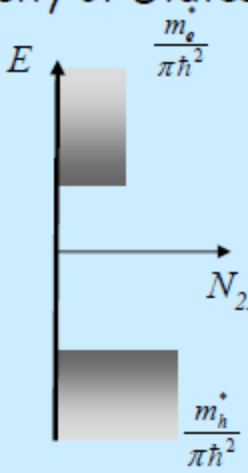
Graphene

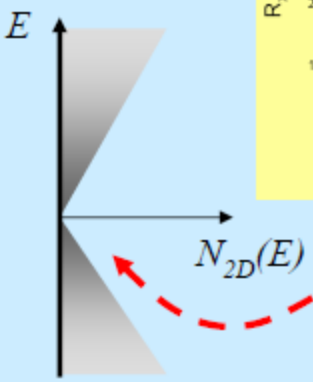
$$E = \hbar v_F \left|\vec{k}'_\perp\right|$$

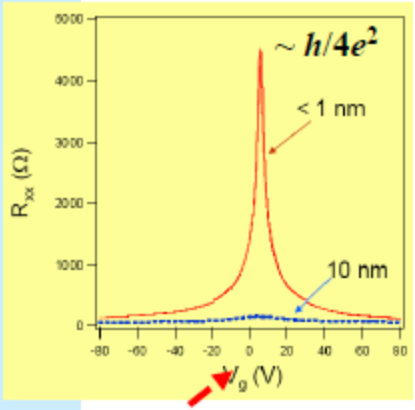


- **Zero band mass**
- **Strict electron hole symmetry**
- **Electron hole degeneracy**

Density of States







Science 306, 666 (2004)

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1]
Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

Vol 438|10 November 2005|doi:10.1038/nature04233 nature

LETTERS

Two-dimensional gas of massless Dirac fermions in graphene

K. S. Novoselov[1], A. K. Geim[1], S. V. Morozov[2], D. Jiang[1], M. I. Katsnelson[3], I. V. Grigorieva[1], S. V. Dubonos[2] & A. A. Firsov[2]

Vol 438|10 November 2005|doi:10.1038/nature04235 nature

LETTERS

Experimental observation of the quantum Hall effect and Berry's phase in graphene

Yuanbo Zhang[1], Yan-Wen Tan[1], Horst L. Stormer[1,2] & Philip Kim[1]

nature Vol 462|12 November 2009|doi:10.1038/nature08582

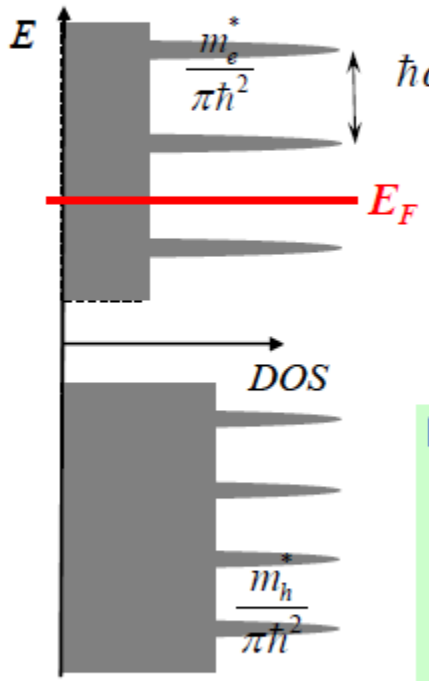
LETTERS

Observation of the fractional quantum Hall effect in graphene

Kirill I. Bolotin[1]*†, Fereshte Ghahari[1]*, Michael D. Shulman[2], Horst L. Stormer[1,2] & Philip Kim[1,2]

2D Gas in Quantum Limit : Conventional Case

Density of States



Landau Levels in Magnetic Field

$$\hbar\omega_c = \hbar eB / m^*$$

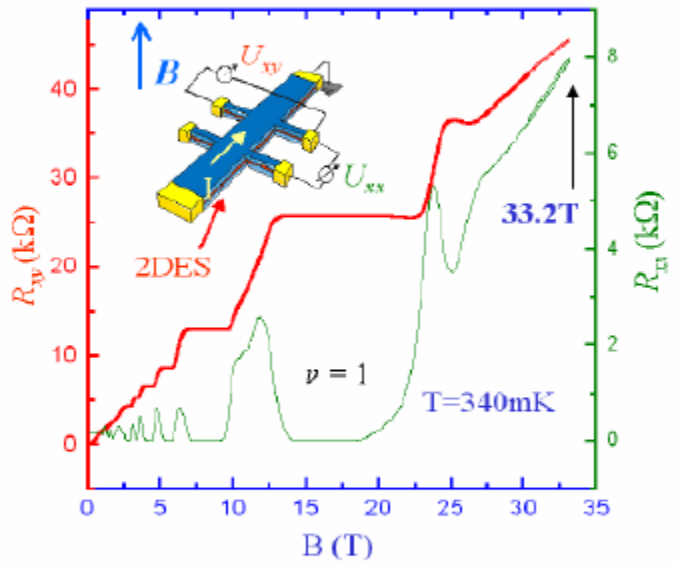
Integer Quantization:

$$R_{xy}^{-1} = \pm\nu \cdot g_s \cdot \frac{e^2}{h}$$

$\nu = 1, 2, 3 \ldots$

$g_s = 2$ (spin)

Quantum Hall Effect in GaAs 2DEG

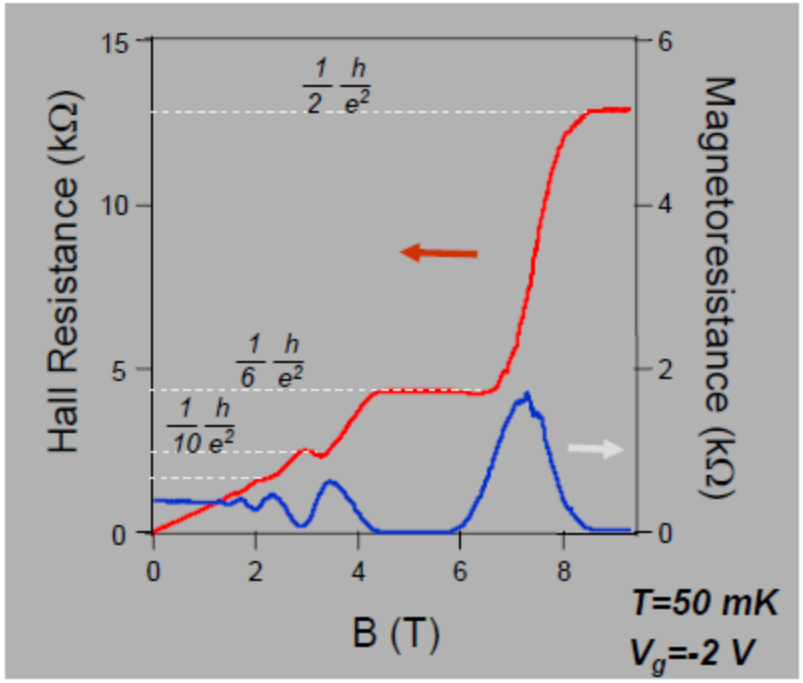


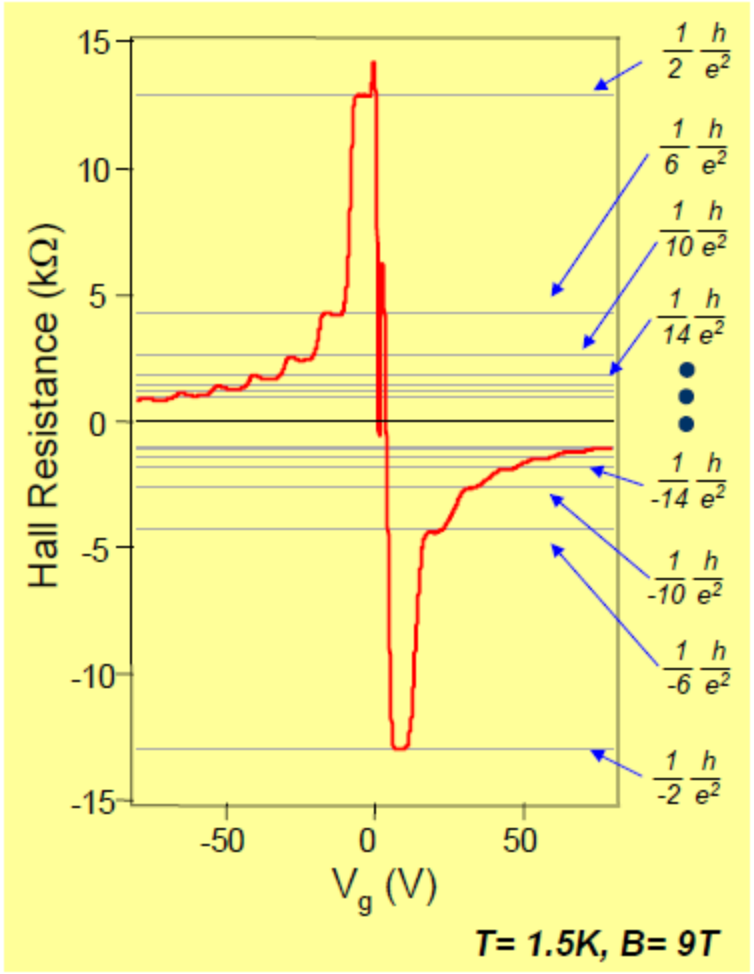
Graphene

- Vanishing carrier mass near Dirac point
- Strict electron hole symmetry
- Electron hole degeneracy

$$\omega_c = \frac{eB}{m^*}$$

Quantum Hall Effect in Graphene





Quantization:

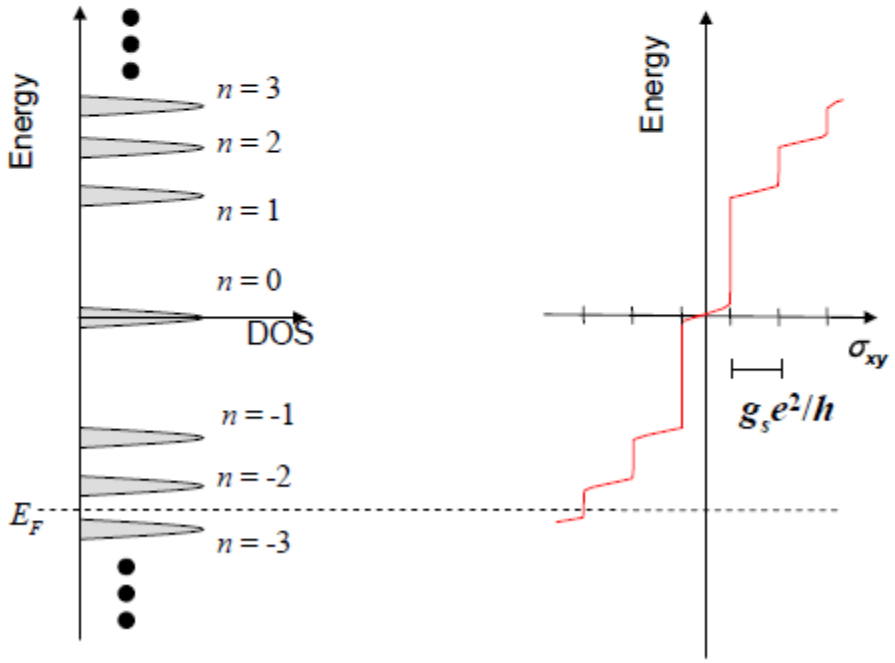
$$R_{xy}^{-1} = 4\left(n + \frac{1}{2}\right)\frac{e^2}{h}$$

Relativistic Landau Level and Half Integer QHE

Haldane, PRL (1988)

Landau Level $E_n = \pm\sqrt{2e\hbar v_F^2 |n|B}$

Landau Level Degeneracy
$g_s = 4$
2 for spin and 2 for sublattice



Quantized Condition

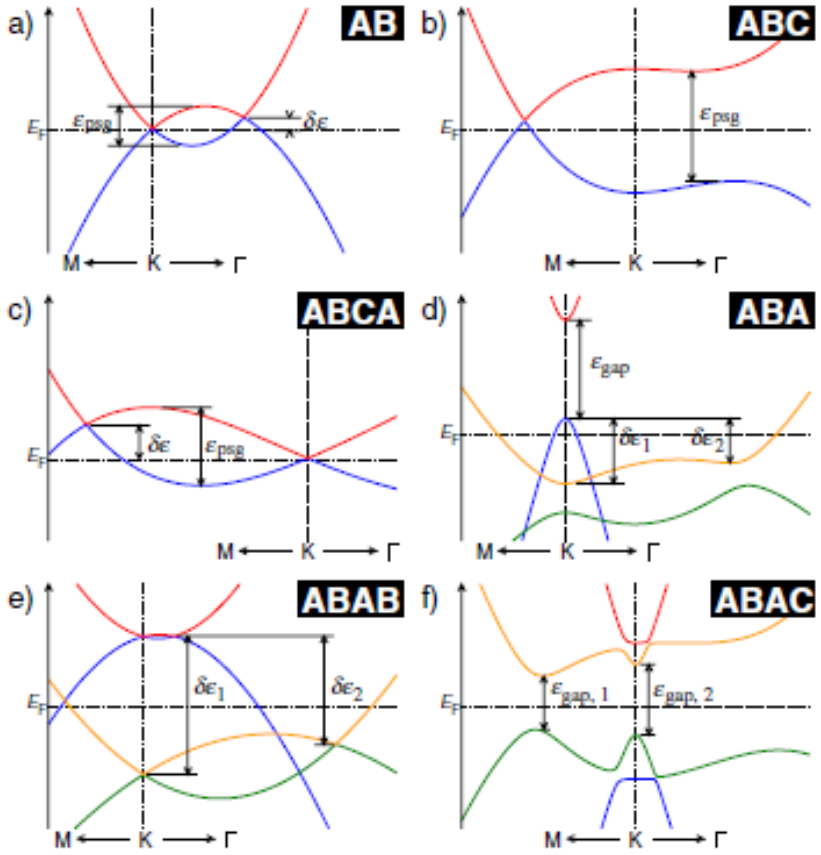
$$R_{xy}^{-1} = \pm g_s (n + \frac{1}{2}) \frac{e^2}{h}$$

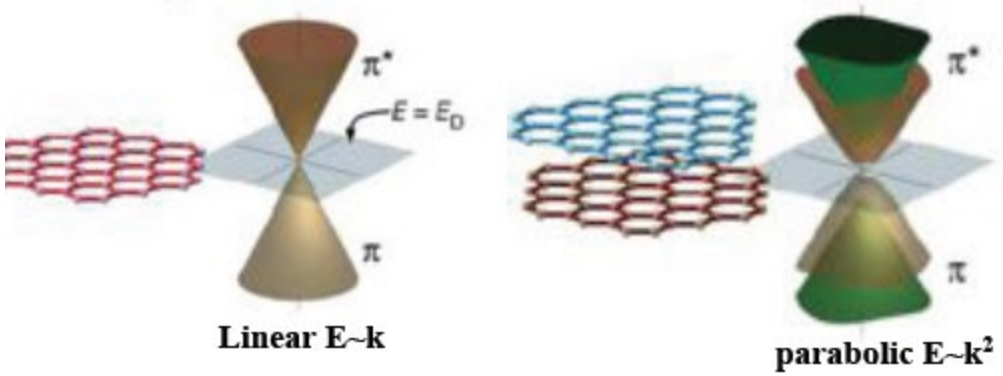
$$\nu = \pm g_s (n + 1/2)$$

T. Ando et al (2002)

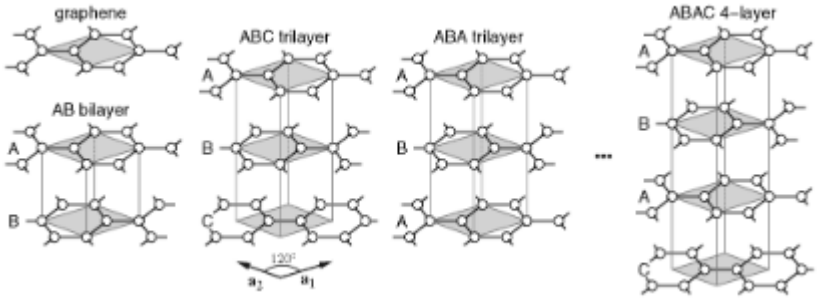
Charge Carriers in Few-Layer Graphene Films

Sylvain Latil and Luc Henrard



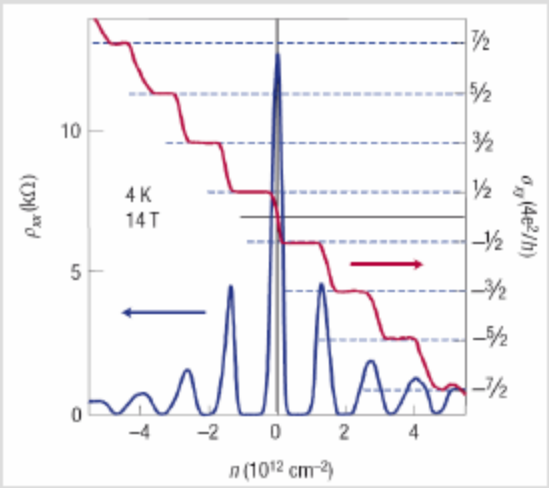


Taisuke Ohta, *et al.*, Science **313**, 951 (2006)



Geometry of stacking and the number of layers strongly affect band structure

half-integer QHE



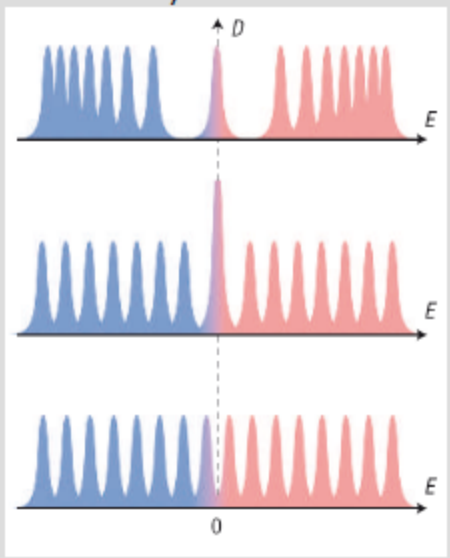
graphene:

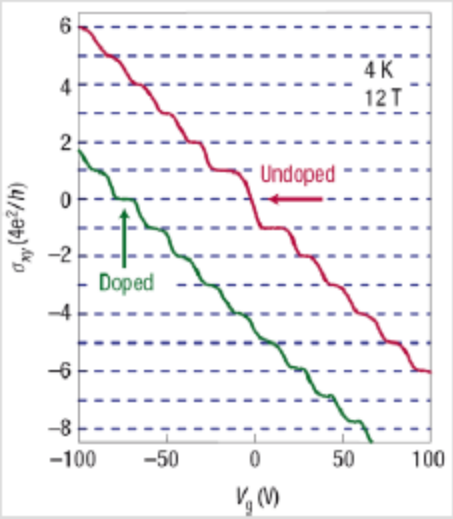
half-integer QHE

no plateau at zero energy

$$\sigma_{xy} = \pm 4e^2/h \ (N + \tfrac{1}{2})$$

Landau levels in the density of states





bilayer graphene:

integer QHE

but

N=0 plateau missing!

$$\sigma_{xy} = \pm N 4e^2/h$$

Novoselov et al., Nature Physics (2006)