Physics of Condensed Matter I

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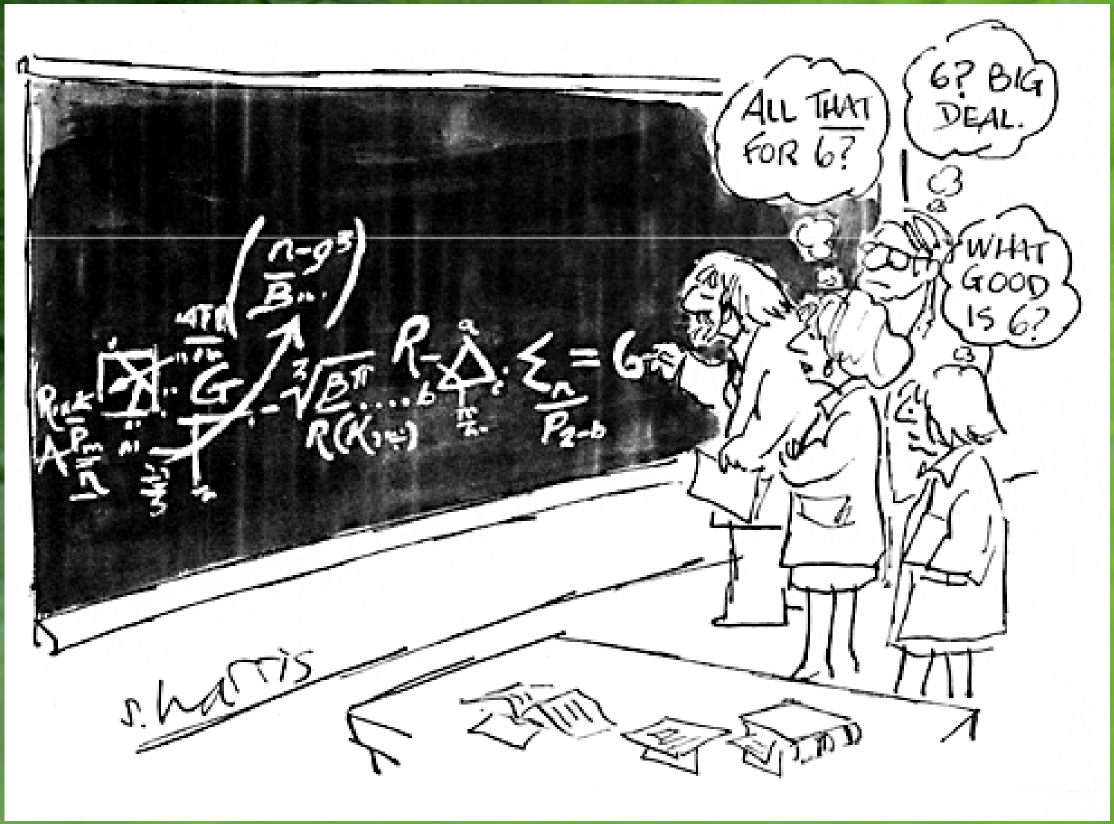

Molecules

Faculty of Physics UW

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inżynieria nanostruktur

Laboratorium magnetometrii SQUID

Adsorption of Doxorubicin onto Citrate-Stabilized Magnetic Nanoparticles
Krzysztof Nawara, Jerzy Romiszewski, Krystyna Kijewska, Jacek Szczytko, Andrzej Twardowski, Maciej Mazur, and Paweł Krysinski
J. Phys. Chem. C 2012, 116, 5598−5609.

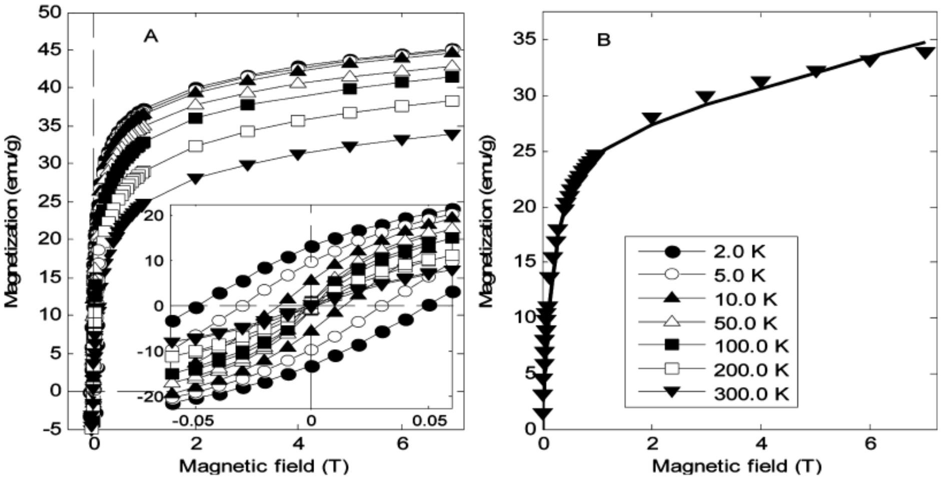


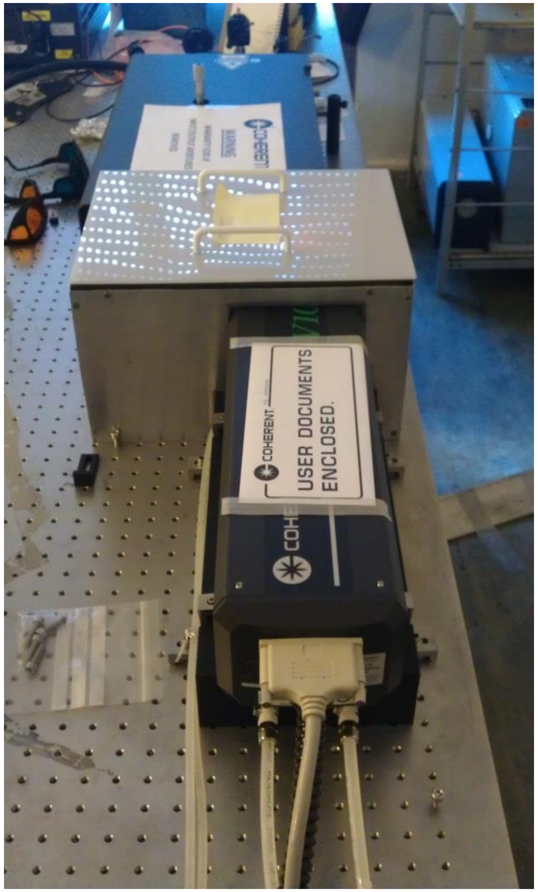
Figure 5. (A) Magnetization as a function of magnetic field at temperatures ranging from 2 to 300 K. The hysteresis loop is shown in the inset. (B) Magnetization at 300 K (points) and theoretical approach (solid line) proposed by Millan et al.[28] for parameters: diameter 12 nm, M_s = 35 emu/g, χ = 1.7e−4 emu/(g·Oe); see text for details.

Confocal microscopy

Confocal microscopy

Magnetic field up to 9T, temperatures down to 2.0K

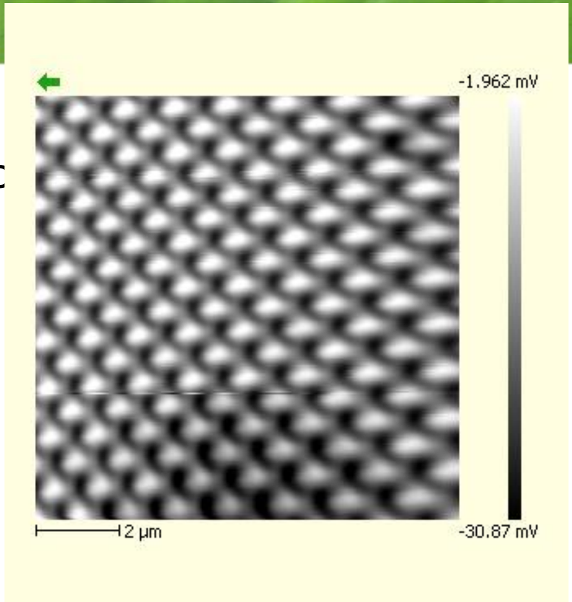
Ti-Sa tunable laser 700-1000 nm

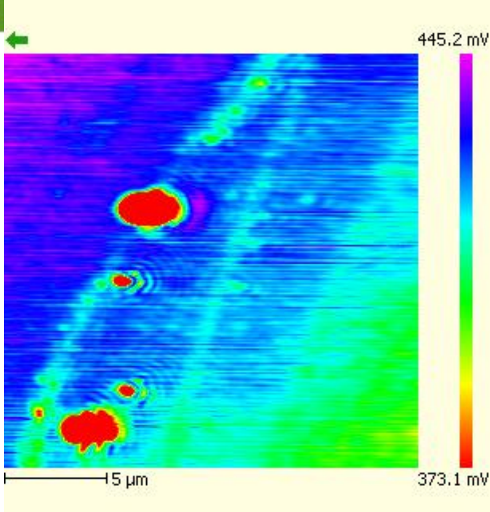


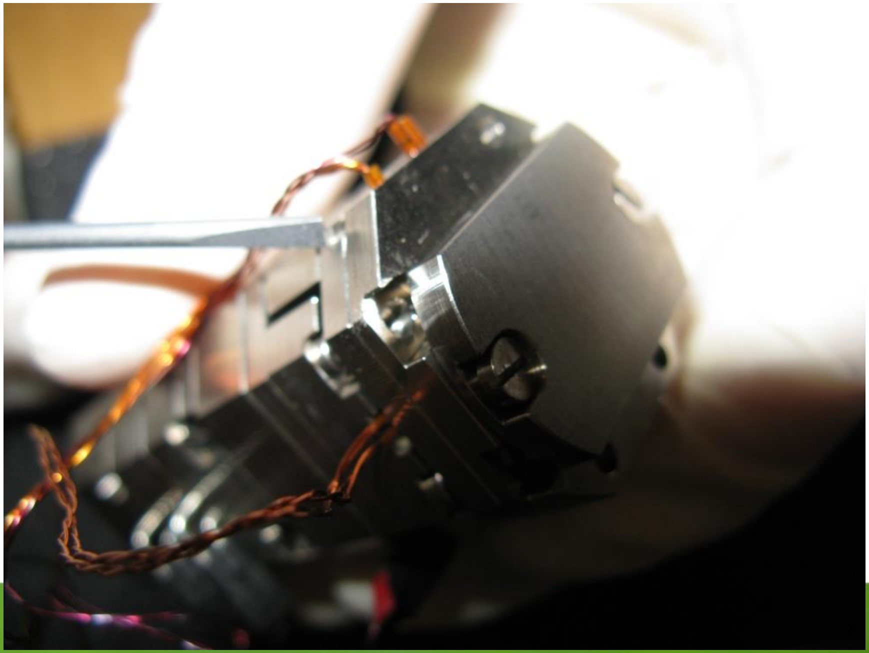
Confocal microscopy

Confocal microscopy

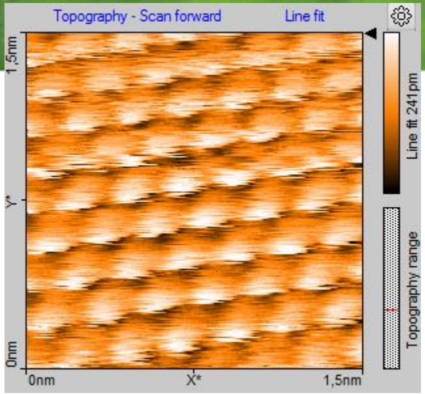
Magnetic field up to 9T, temperatures dc



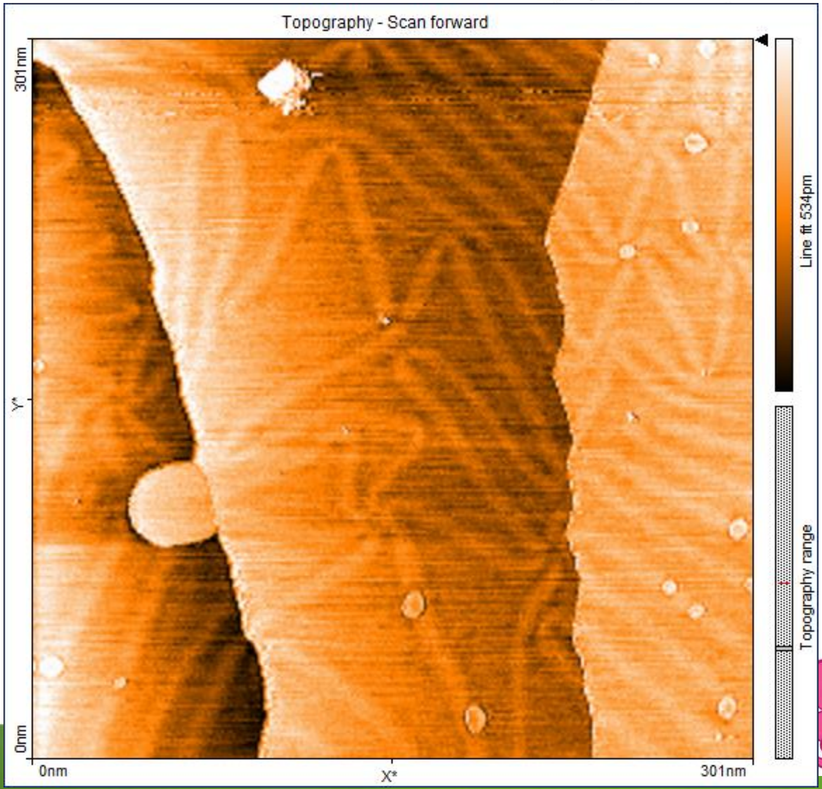


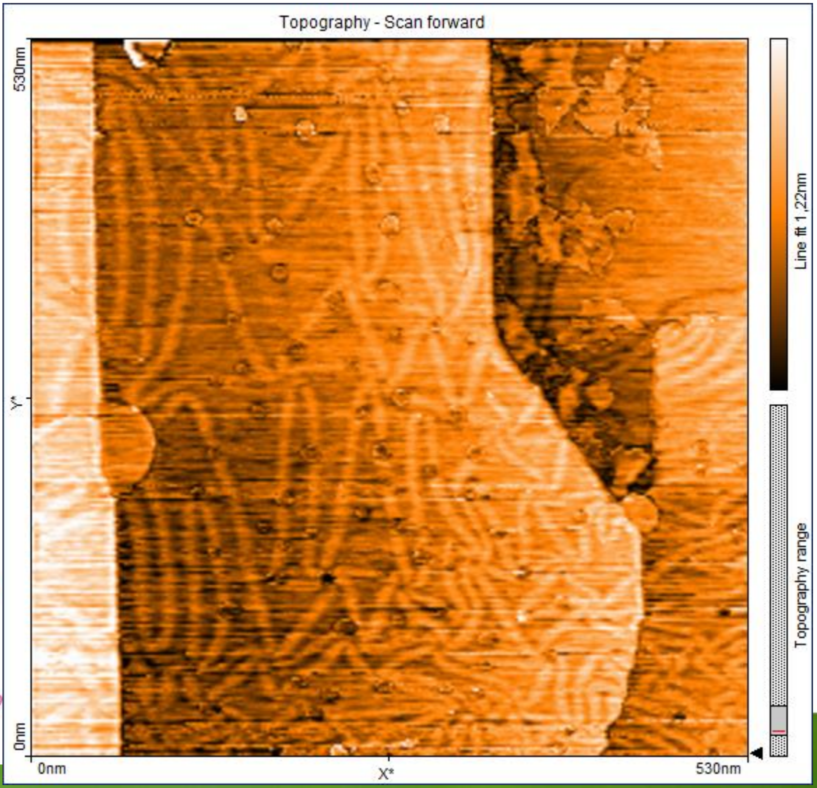


Tunneling microscope STM

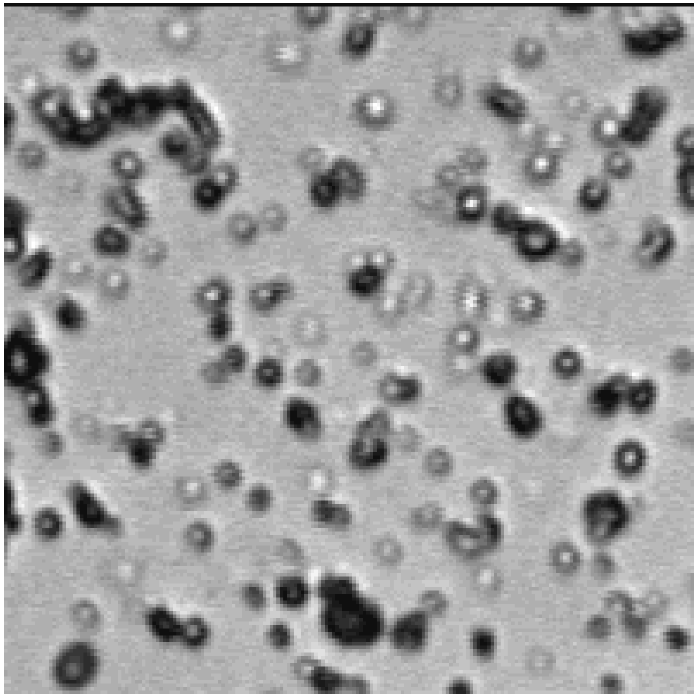


Nano *bark beetles*

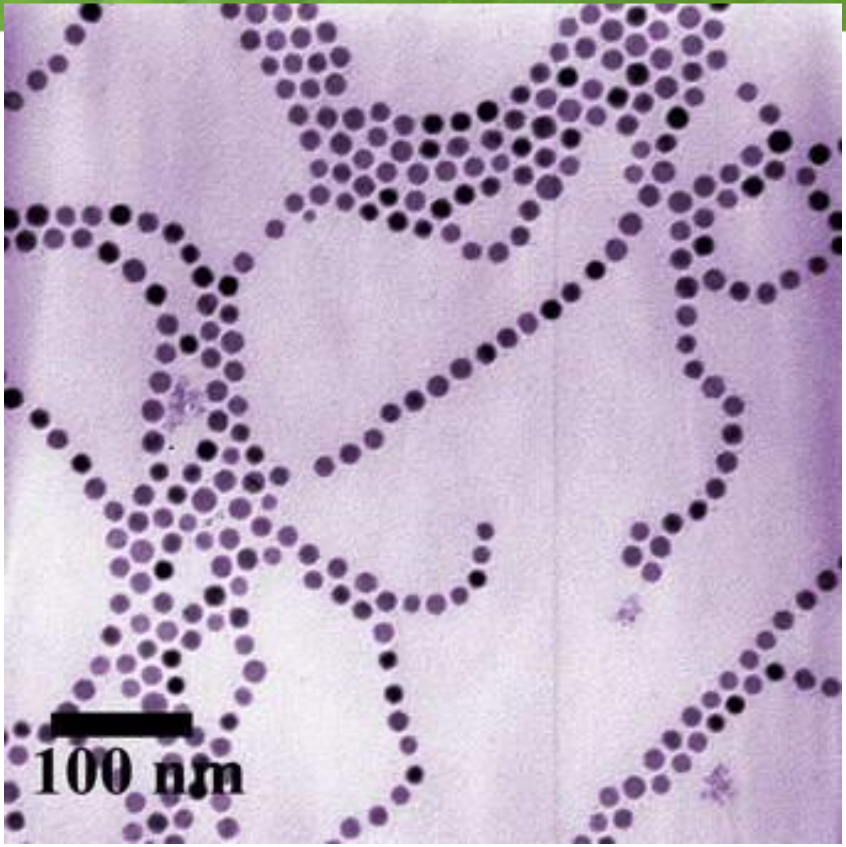




Zawiesina nanomagnesów w polu magnetycznym



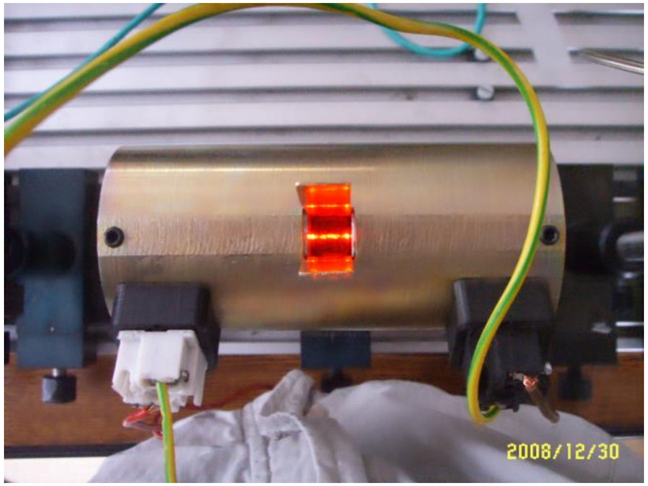
Piotr Habdas



Chains of 1 million magnetic nanoparticles have been assembled and disassembled in a solution of suspended particles in a controlled way, scientists at the National Institute of Standards and Technology (NIST) report.

http://www.physics.emory.edu/~weeks/lab/pics.html

Magnetic moment of a single metal nanoparticle determined from Faraday effect



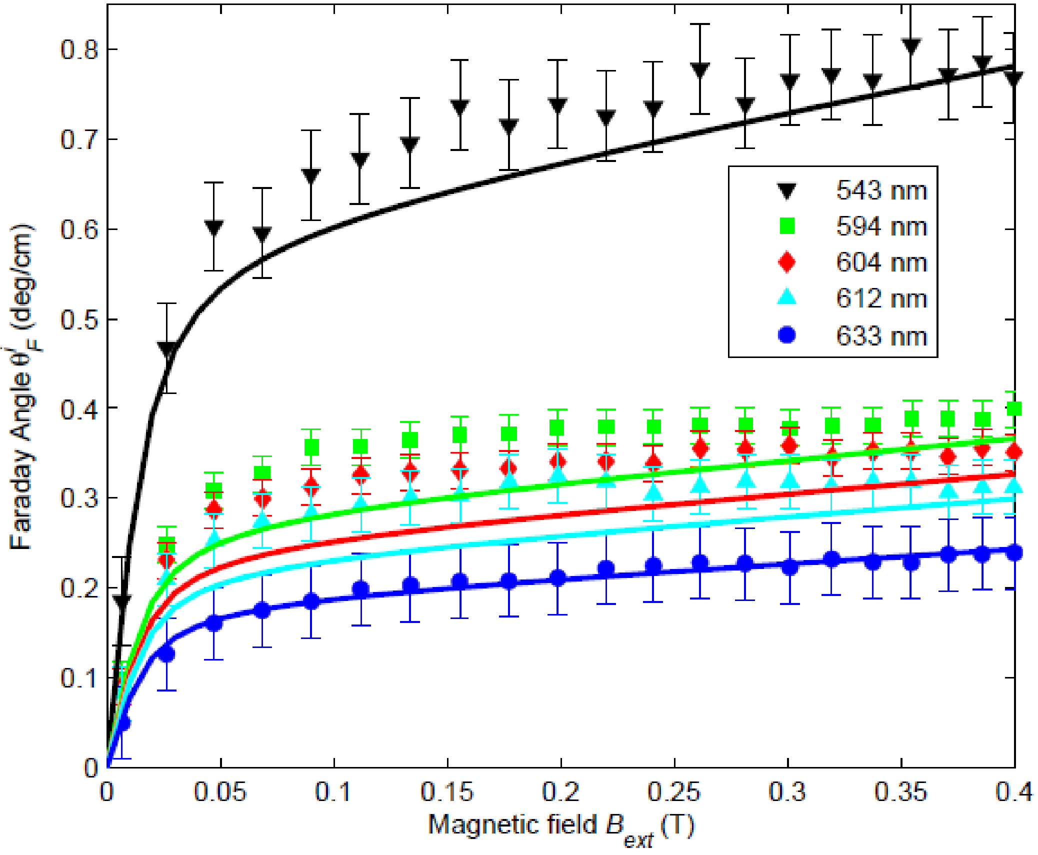
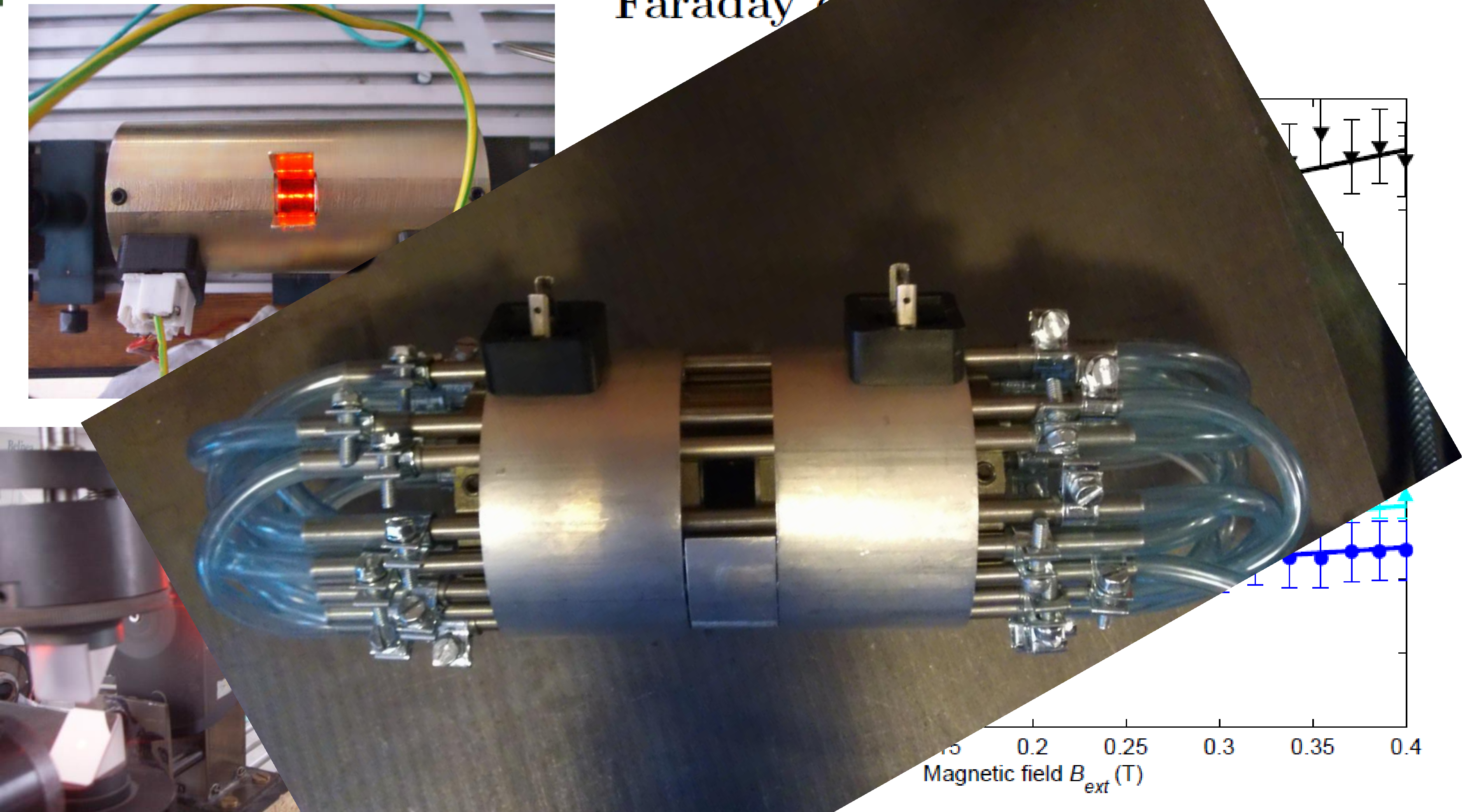


FIG. 1. Faraday rotation angle due to the inclusion of nanoparticles (θ_F^i) vs external magnetic field (B_{ext}) at different wavelengths of light. Experimental data are marked as points, theoretical curves are solid lines.

Magnetic moment of a single metal nano determined from

Faraday e



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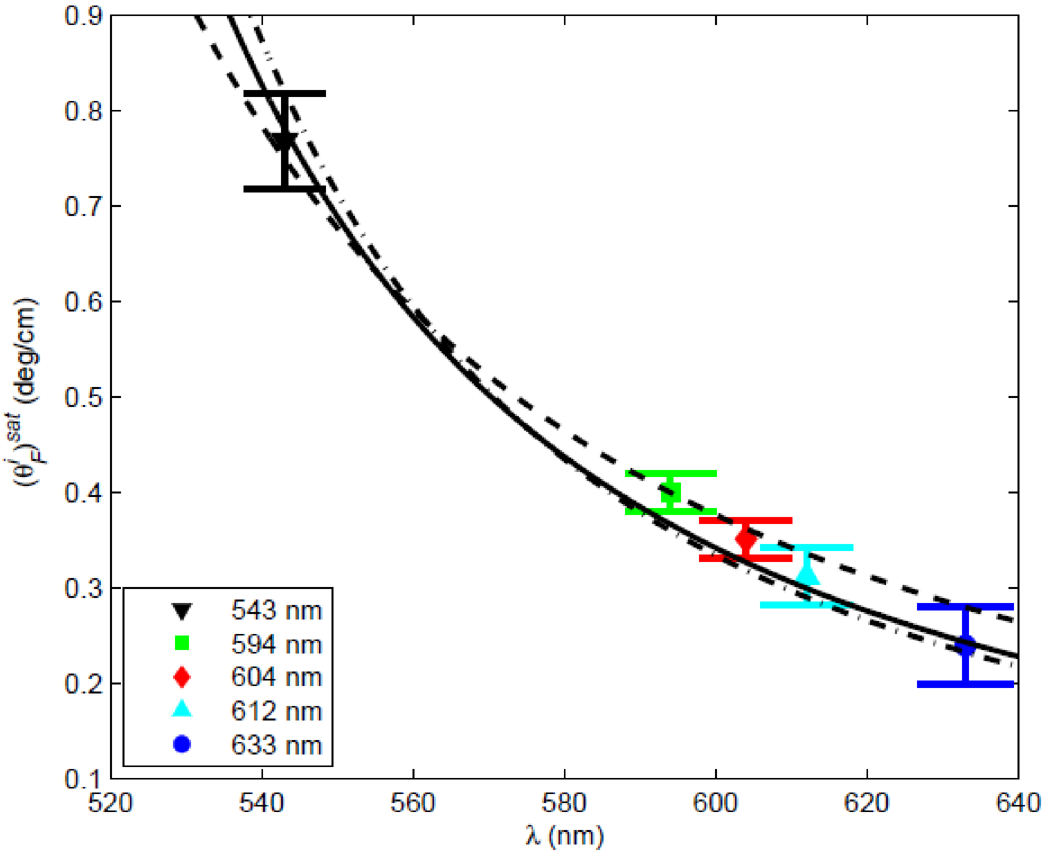


FIG. 2. Saturated value of Faraday rotation angle $(\theta_F^i)^{sat}$ vs. wavelength of light λ. Solid line represents fit with ω_p=198 nm, $f = 9.2 \times 10^{-5}$, dashed lines is for 188 nm ($f = 1.4 \times 10^{-4}$) and dot-dashed line is for 202 nm ($f = 7.8 \times 10^{-5}$). Experimental data are marked as points.

Magnetic moment of a single metal nanoparticle determined from Faraday effect

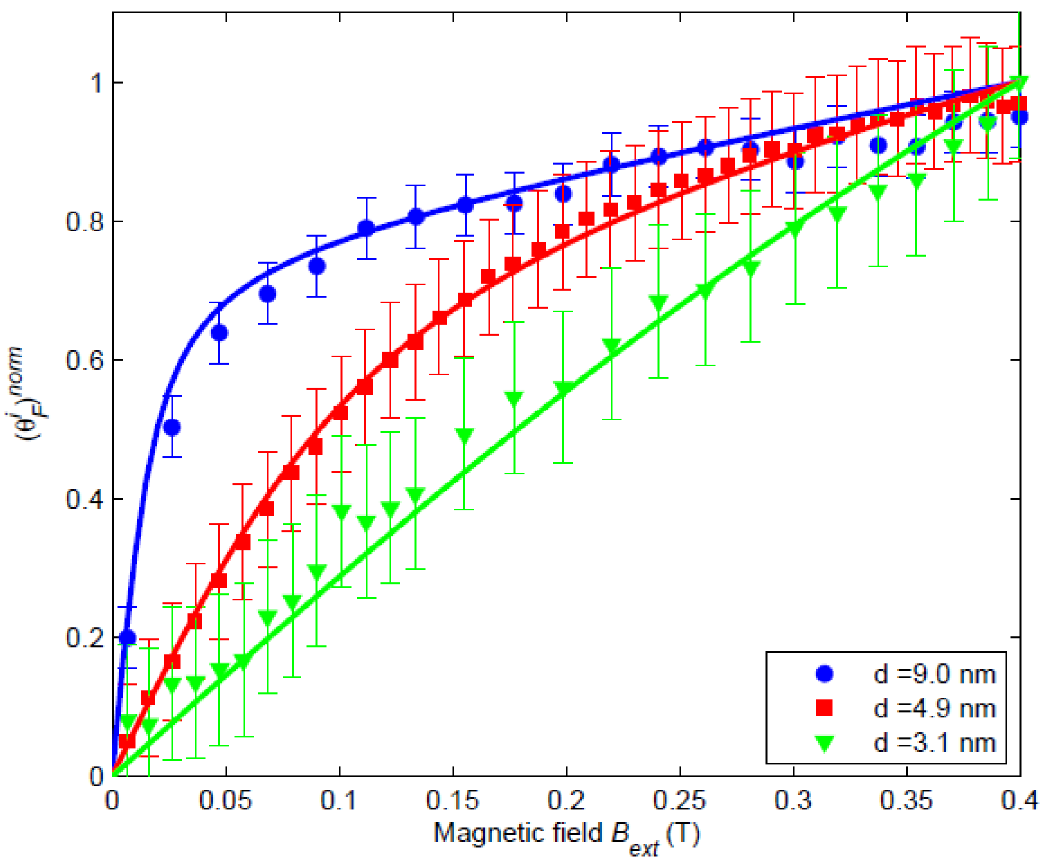


FIG. 3. The normalized Faraday rotation angle $(\theta_F^i)^{norm}$ vs. magnetic field (B_{ext}) for 3 solutions of particles with different diameters of the magnetic core. The diameter was calculated assuming the bulk value of the magnetic moment of an atom ($1.751\mu_B$). The experiment was performed with the He-Ne laser 633 nm line.

Chemical bonding and molecules

Born Oppenheimer approximation

Full non-relativistic Hamiltonian of the nuclei and electrons:

$$H(\vec{r},\vec{R})\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R})$$

$$H(\vec{r},\vec{R}) =$$

$$= -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_N \frac{\hbar^2}{2M_N}\nabla_N^2 - \frac{1}{4\pi\varepsilon_0}\sum_{N,i}\frac{Z_N e^2}{|\vec{r}_i - \vec{R}_N|} +$$

$$+\frac{1}{4\pi\varepsilon_0}\sum_{N<K}\frac{Z_N Z_K e^2}{|\vec{R}_N - \vec{R}_K|} + \frac{1}{4\pi\varepsilon_0}\sum_{i<j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} =$$

$$= \hat{T}_e + \hat{T}_N + V(\vec{r},\vec{R}) + V_e(\vec{r}) + G(\vec{R})$$

$m, \vec{r}_i, i$ – electrons
$M_N, \vec{R}_N, Z_N$ - nuclei

Coordinates of electrons subsystem and nuclei subsystem (ions) are mixed, separation of electronic and nuclear variables is impossible.

One should use the Born-Oppenheimer adiabatic approximation

Chemical bonding and molecules

Approximations

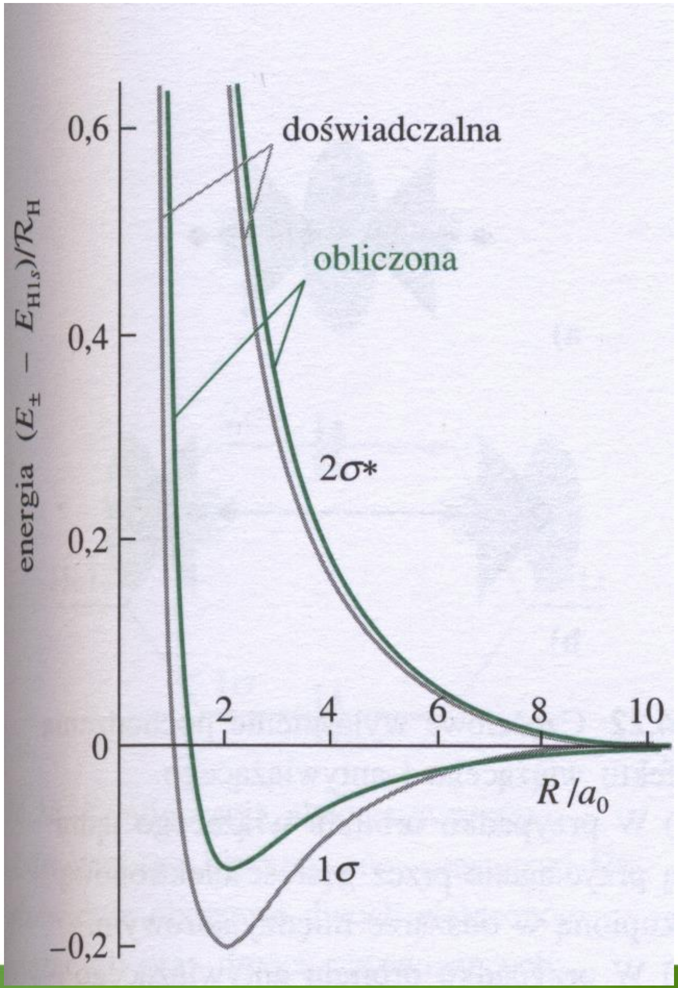
$$\left[\hat{T}_N + E_{el}(\vec{r},\vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

The kinetic energy separates on vibration (oscillation) and rotation energy – we assume "small" oscillations and slow speed of rotataion.

$$\left[\hat{T}_{osc} + \hat{T}_{rot} + E_{el}(\vec{r},\vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

Operators act on different coordinates: we can we separate the variables:

$$\chi^n(\vec{R}) = \chi^n_{osc}(R)\chi^n_{rot}(\theta,\varphi)$$
$$E^n = E^n_{osc} + E^n_{rot}$$



Altogether:

$$\Psi(\vec{r},\vec{R}) = \chi^n(\vec{R})\Psi^n_{el}(\vec{r},\vec{R}) = \chi^n_{osc}(R)\chi^n_{rot}(\theta,\varphi)\Psi^n_{el}(\vec{r},\vec{R})$$
$$E^n = E^n_{osc} + E^n_{rot} + E_{el}$$

Chemical bonding and molecules

Approximations

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Operators act on different coordinates: we ca separate the variables:

$$\chi^n(\vec{R}) = \chi^n_{osc}(R)\chi^n_{rot}(\theta,\varphi$$

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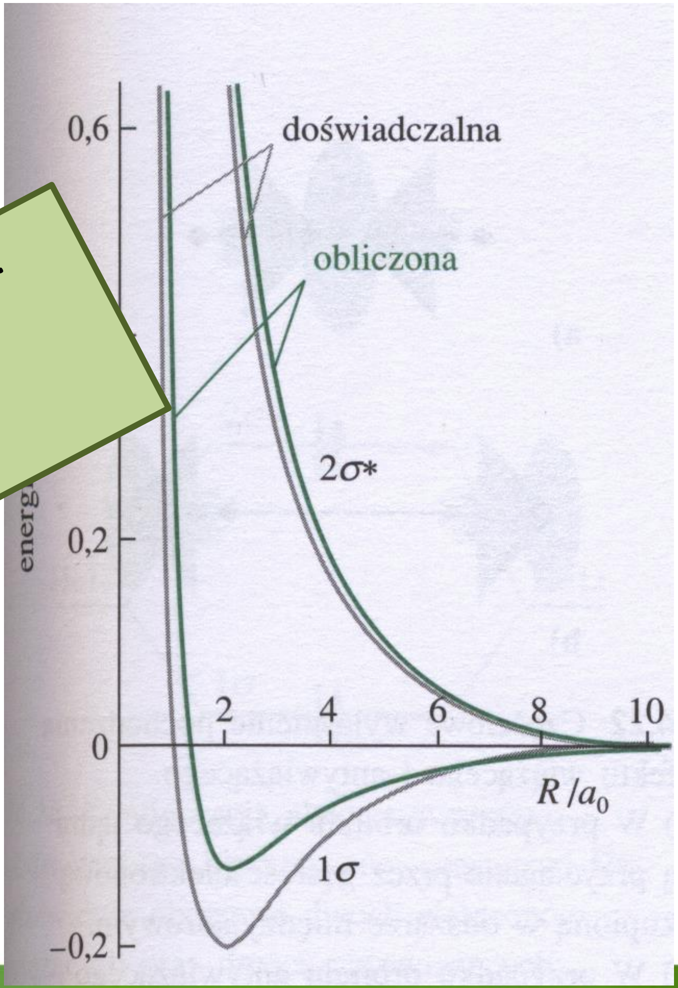
One by one we will discuss:

- electronic structure
- rotations
- oscillations

Altogether:

$$\Psi(\vec{r},\vec{R}) = \chi^n(\vec{R})\Psi^n_{el}(\vec{r},\vec{R}) = \chi^n_{osc}(R)\chi^n_{rot}(\theta,\varphi)\Psi^n_{el}(\vec{r},\vec{R})$$

$$E^n = E^n_{osc} + E^n_{rot} + E_{el}$$



Electronic structure of molecules

Electronic structure of molecules $E_{el}^{n}(\vec{R})$

Electronic Schrödinger equation takes into account the motion of all the electrons in the molecule, interacting with each other and with fixed potential of nuclei.
The most important is the electrostatic interaction and we take into account only this. Other effects can be considered as perturbation.

$$\hat{H}_{el} = \sum_{i} \hat{T}_i + \sum_{i} V_i + \sum_{i<j} V_{ij}$$

Kinetic energy

Electron-electron interaction

Interaction with nuclei

Hartree–Fock method

Approximation

Each electron moves in the electrostatic field created by fixed nuclei charges and the mean static charge distribution of all other electrons.

$$\hat{H}_{el}\Phi = E\Phi$$

$$\hat{H}_{el} = \sum_i \hat{H}_i^0$$

$$\downarrow$$

$$\hat{H}_i^0 = \hat{T}_i + V_i + U_i$$

$$\downarrow$$

$$\hat{H}_i^0\Psi_i = \varepsilon_i\Psi_i$$

The potential energy of the i-th electron in averaged electrostatic field generated by all other electrons.

The internal energy: The sum of the individual electron energies

$$E = \sum_i^n \varepsilon_i$$

Eigen function the product of one-electron wavefunctions

$$\Phi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots \vec{r}_n) = \Psi_1(\vec{r}_1)\,\Psi_2(\vec{r}_2)\,\Psi_3(\vec{r}_3)\ldots\Psi_n(\vec{r}_n)$$

Hartree–Fock method

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Molecular orbital: one-electron wavefunction

Eigen function the product of one-electron wavefunctions

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$$\downarrow$$

$$\hat{H}_i^0 \Psi_i = \varepsilon_i \Psi_i$$

First, we postulate U_i^0 and we find the molecular orbitals Ψ_i^0. With these molecular orbitals we calculate U_i^1 potential, then new molecular orbitals Ψ_i^0 used for U_i^2 etc.

Despite the simplification the problem is very difficult and possible to solve only numerically.

Eigen function the product of one-electron wavefunctions

$$\Phi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots \vec{r}_n) = \Psi_1(\vec{r}_1)\,\Psi_2(\vec{r}_2)\,\Psi_3(\vec{r}_3)\ldots\Psi_n(\vec{r}_n)$$

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$$\downarrow$$

$$\hat{H}_i^0 = \hat{T}_i + V_i + U_i$$

$$\downarrow$$

$$\hat{H}_i^0 \Psi_i = \varepsilon_i \Psi_i$$

$$\downarrow$$

$$\Psi_i(\vec{r}) = \sum_A c_A^i \varphi_A(\vec{r})$$

$$\downarrow$$

$$\left|c_A^i\right|^2$$

Molecular Orbital can be approximately represented as a linear combination of atomic functions which atomic orbitals φ_A, each of which describes a different state of the i-th electron, when it is close to the nucleus A.

The probability of finding electron close to th enucleus A

$$\Phi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots \vec{r}_n) = \Psi_1(\vec{r}_1)\, \Psi_2(\vec{r}_2)\, \Psi_3(\vec{r}_3) \dots \Psi_n(\vec{r}_n)$$

The Self-consistent Field Method

Molecular orbital theory

For each of the atomic orbitals φ_A the origin is at another point (orbitals are centered on different atomic nuclei). This method is called **LCAO-MO** (**L**inear **C**ombination of **A**tomic **O**rbitals – **M**olecular **O**rbitals).

Theoretically one can take any combination of atomic orbitals, but in reality we take some „adequate" orbitals (resulting from the symmetry - group theory).

The electron wavefunction as a product of molecular orbitals is not a strict eigenfunction of the Hamiltonian, because it does not take into account the correlation of electrons. This function can be improved by adding the expression corresponding to combinations of other atomic orbitals (different atomic configurations). This method is called Configuration Interaction - **CI** (**C**onfiguration **I**nteraction)

In most accurate calculation of the electron wave function for the ground state of the hydrogen molecule H_2 takes into account 100 atomic configuration (W. Kołos).

$$\Psi_i(\vec{r}) = \sum_A c_A^i \varphi_A(\vec{r})$$

The Self-consistent Field Method

LCAO

Numerical solution of electronic Hamiltonian

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = [\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Each of the single-electron spinorbital $\varphi_n^{sp}(\vec{r}_n, s_n)$ must be different - two spinorbitals may have for instance the same orbital part φ, but then must have different spin

$$\varphi_n^{sp}(\vec{r}_n, s_n) = \varphi_n^{sp}(\vec{r}_n)\begin{bmatrix}0\\1\end{bmatrix} \text{ or } \varphi_n^{sp}(\vec{r}_n)\begin{bmatrix}1\\0\end{bmatrix}$$

This $\Psi_{el}^{k}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots s_1, s_2, s_3, \dots)$ (below) is not a good wavefunction – why?

$$\Psi_{el}^{k}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots s_1, s_2, s_3, \dots) = \varphi_1^{sp}(\vec{r}_1, s_1)\varphi_2^{sp}(\vec{r}_2, s_2) \dots \varphi_n^{sp}(\vec{r}_n, s_n)$$

The Self-consistent Field Method

LCAO

Numerical solution of electronic Hamiltonian

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = [\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

LCAO-MO in Hartree-Fock approximation – self-consistent method, n-electrons wavefunction as a single **Slater determinant**, automatically providing antysymmetry of the wavefunction due to the interchanging the particles occupying any pair of states :

$$\Psi_{el}^{k}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\ldots s_1,s_2,s_3,\ldots) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \varphi_1^{sp}(\vec{r}_1,s_1) & \varphi_1^{sp}(\vec{r}_2,s_2) & \ldots & \varphi_1^{sp}(\vec{r}_n,s_n) \\ \varphi_2^{sp}(\vec{r}_1,s_1) & \varphi_2^{sp}(\vec{r}_2,s_2) & \ldots & \varphi_2^{sp}(\vec{r}_n,s_n) \\ \ldots & \ldots & & \ldots \\ \varphi_n^{sp}(\vec{r}_1,s_1) & \varphi_n^{sp}(\vec{r}_2,s_2) & \ldots & \varphi_n^{sp}(\vec{r}_n,s_n) \end{vmatrix}$$

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Molecules

Homonuclear diatomic molecules, eg. **H_2, Li_2, N_2, O_2**

Because molecule is diatomic we are looking for a combination of two orbitals φ_A and φ_B.

$$\Psi = c_A\varphi_A + c_B\varphi_B$$

If the nuclei are the same: $|c_A|^2 = |c_B|^2 \Rightarrow c_A = \pm c_B$

$$\Psi_+ = N_+(\varphi_A + \varphi_B)$$

$$\Psi_- = N_-(\varphi_A - \varphi_B)$$

$$S = \int \varphi_A\varphi_B \, d\vec{r}$$ overlap integral (*całka przekrycia*)

$$N_+ = \frac{1}{\sqrt{2(1+S)}} \qquad N_- = \frac{1}{\sqrt{2(1-S)}}$$

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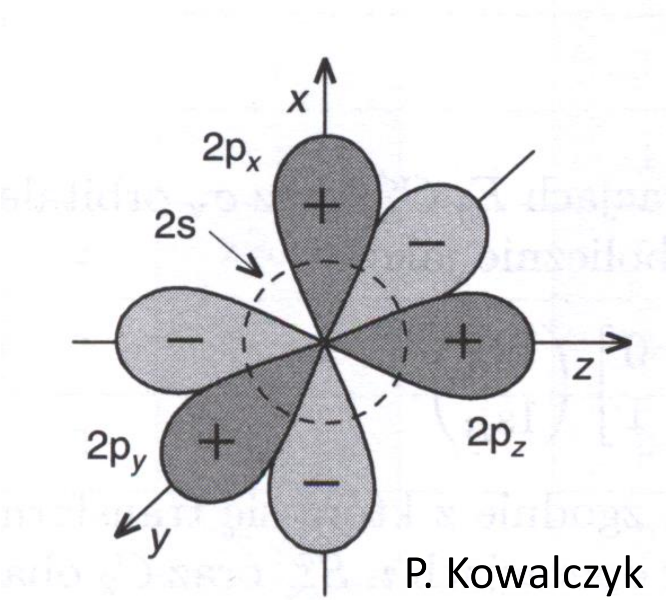
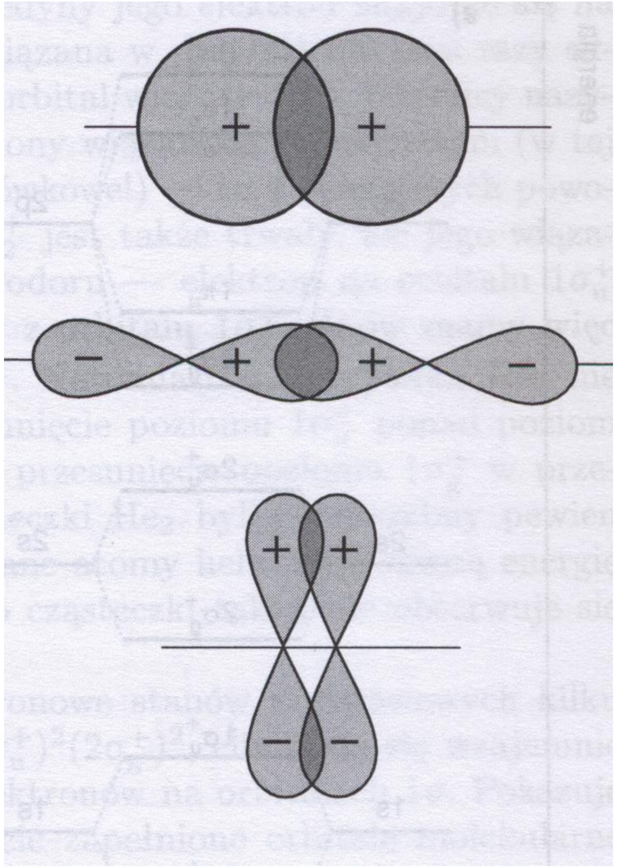


P. Kowalczyk



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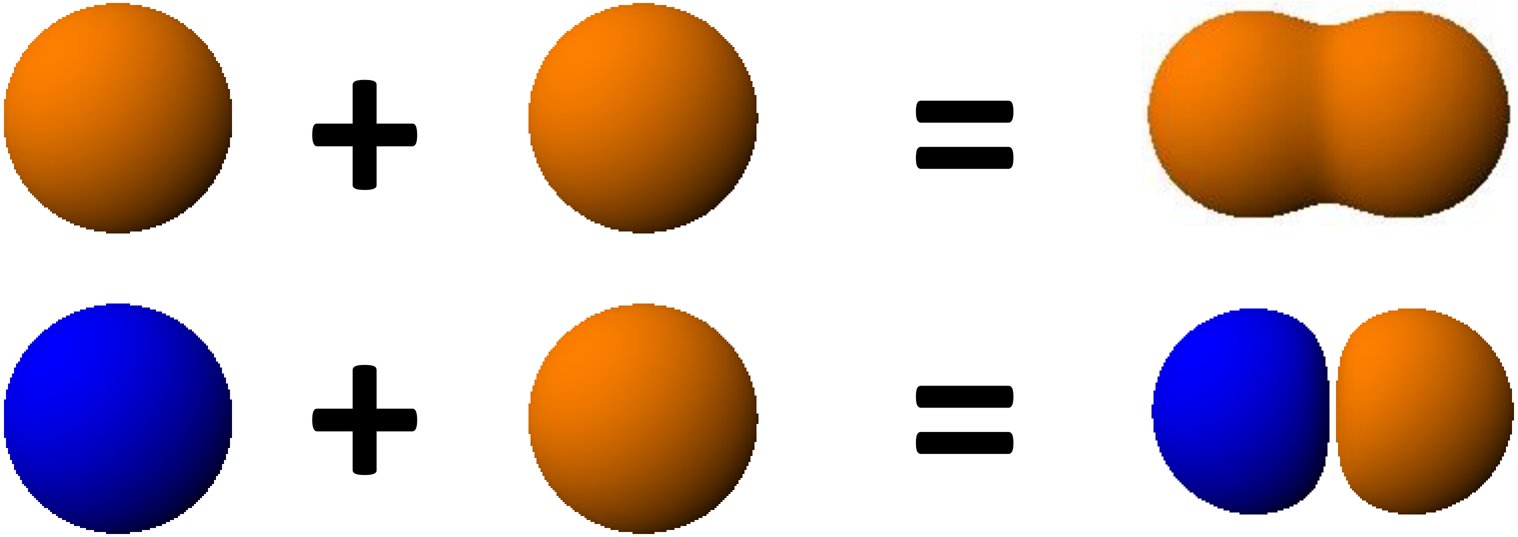
σ–orbital



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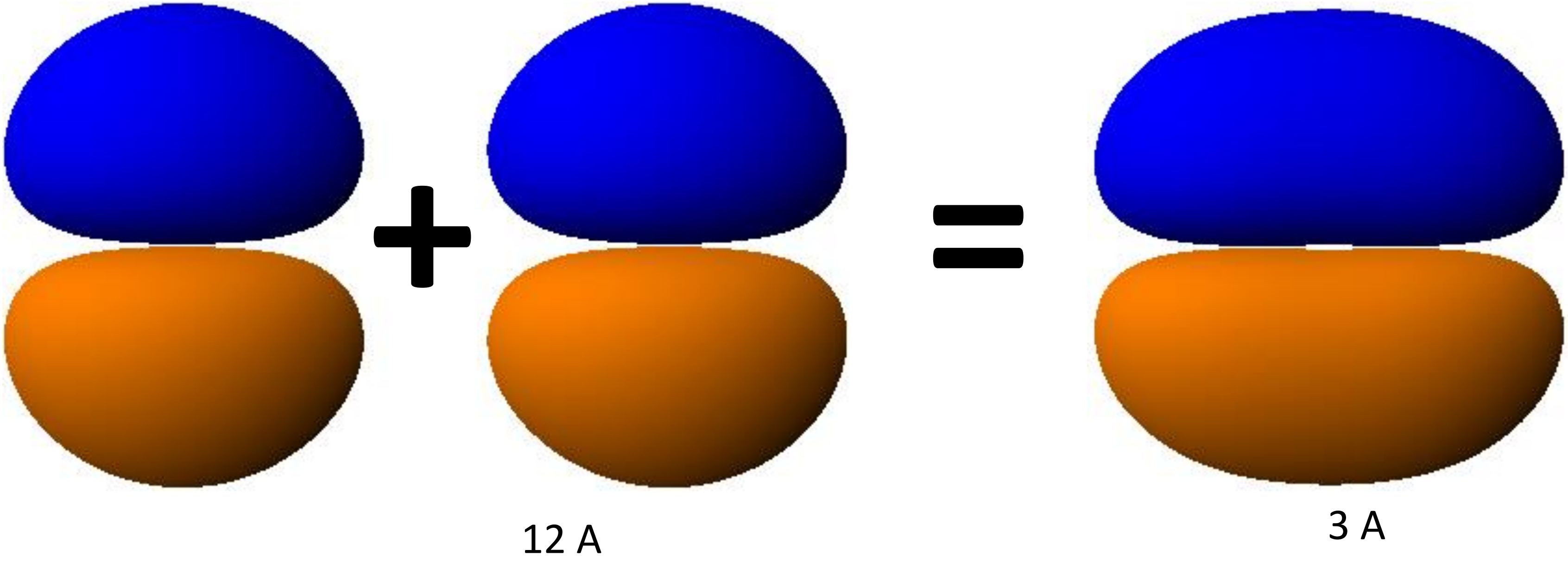
π–orbital



Molecules

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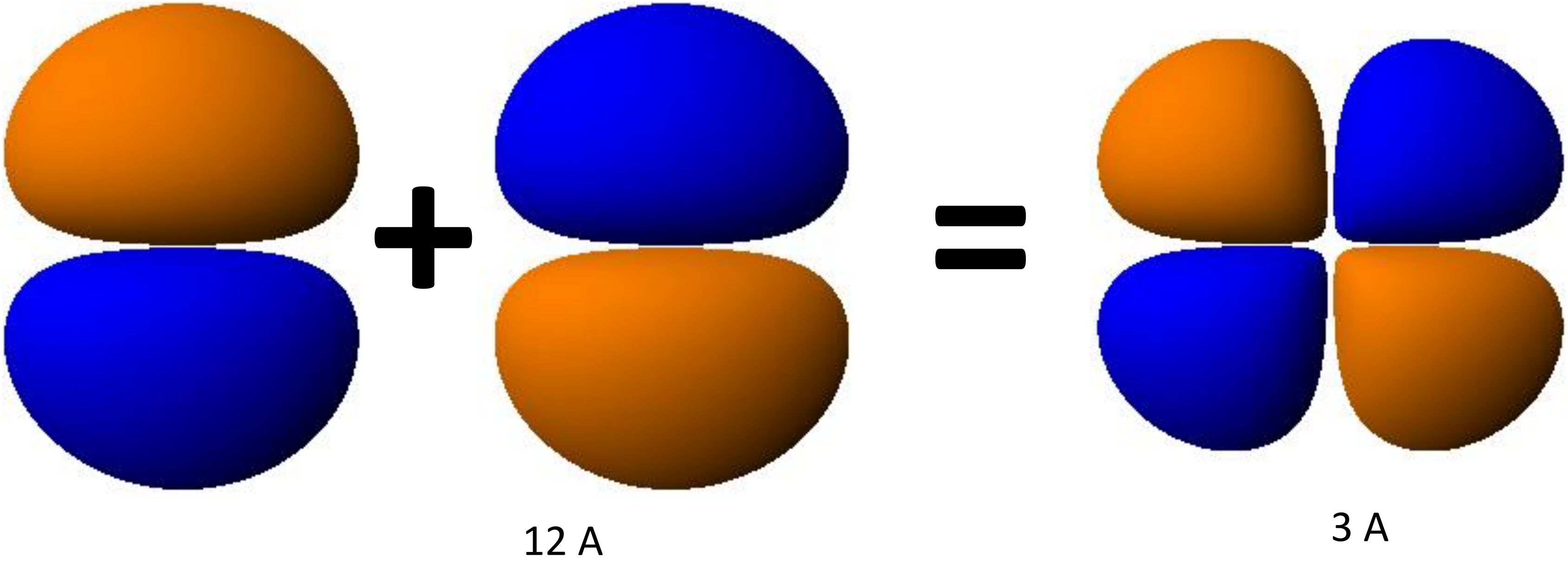
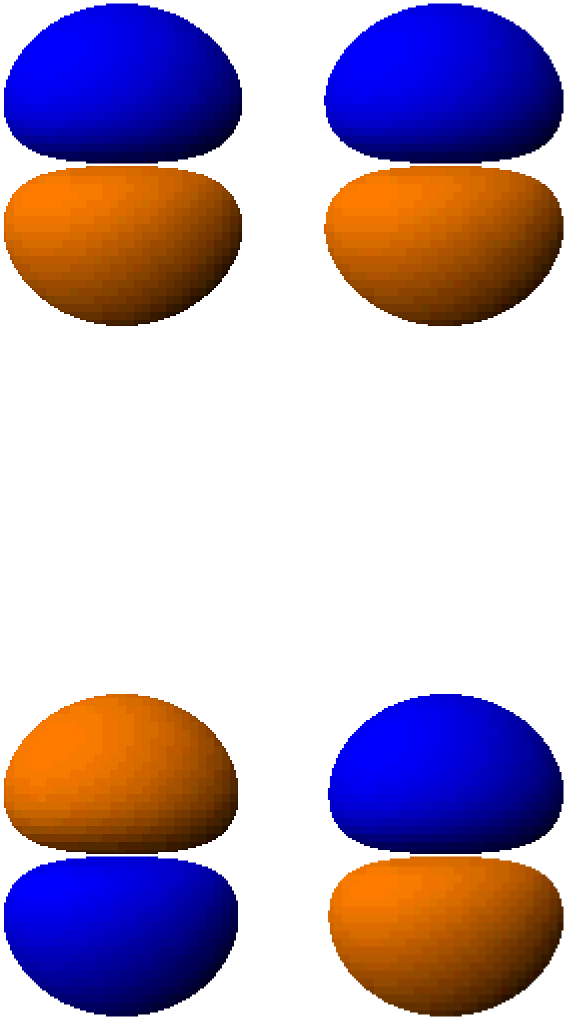
π–orbital





Molecules

Homonuclear diatomic molecules, eg. **H_2, Li_2, N_2, O_2**

Because molecule is diatomic we are looking for a combination of two orbitals φ_A and φ_B.

$$\Psi = c_A\varphi_A + c_B\varphi_B$$

$$S = \int \varphi_A\varphi_B \, d\vec{r}$$ overlap integral

$$\varepsilon_\pm = \int \Psi_\pm^* \hat{H}^0 \Psi_\pm d\vec{r}$$

$$\varepsilon_+ = \frac{H_{AA} + H_{AB} + H_{BA} + H_{BB}}{2(1+S)}$$

$$\varepsilon_- = \frac{H_{AA} - H_{AB} - H_{BA} + H_{BB}}{2(1-S)}$$

$$H_{AA} = \int \varphi_A^* \hat{H}^0 \varphi_A d\vec{r} = H_{BB} \approx E_{at}$$

$$H_{AB} = \int \varphi_A^* \hat{H}^0 \varphi_B d\vec{r} < 0$$

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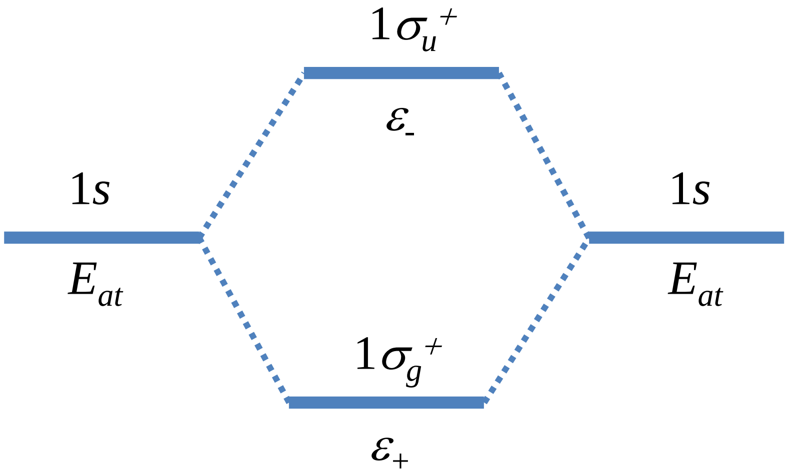
$$\Psi = c_A\varphi_A + c_B\varphi_B$$

$$S = \int \varphi_A\varphi_B \, d\vec{r} > 0$$ overlap integral

$$\varepsilon_\pm = \int \Psi_\pm^* \widehat{H}^0 \Psi_\pm d\vec{r}$$

$$\varepsilon_+ = \frac{E_{at} - |H_{AB}|}{1+S}$$ bonding orbital

$$\varepsilon_- = \frac{E_{at} + |H_{AB}|}{1-S}$$ antibonding orbital



$$H_{AA} = \int \varphi_A^* \widehat{H}^0 \varphi_A d\vec{r} = H_{BB} \approx E_{at}$$

$$H_{AB} = \int \varphi_A^* \widehat{H}^0 \varphi_B d\vec{r} < 0$$

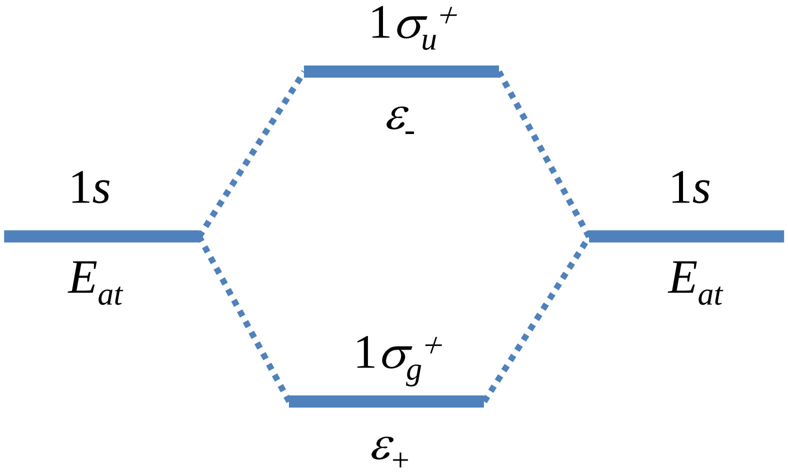
Molecules

Homonuclear diatomic molecules, eg. **H_2, Li_2, N_2, O_2**

Because molecule is diatomic we are looking for a combination of two orbitals φ_A and φ_B.

$$\Psi = c_A\varphi_A + c_B\varphi_B$$

$$S = \int \varphi_A\varphi_B \, d\vec{r} > 0$$ overlap integral



Orbital symbols

- λ=$|m_l|$orbital angular momentum around the internuclear axis
- λ = 0 – σ-orbitals. These orbitals are not affected by the rotation around the axis of the molecule
- λ = 1 – π-orbitals. These orbitals changes sign after the rotation around the axis of the molecule by π.
- g – gerade (even, *parzyste*) parity, inversion through the center of the molecule
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- ± - reflection symmetry with respect to any plane containing the axis of the molecule.
- The number at the beginning – the serial number of the particular orbital type.

Molecules

Homonuclear diatomic molecules, eg. H_2, Li_2, N_2, O_2

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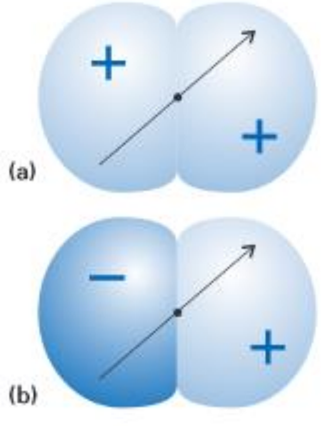
Atkins, Fridman *Molecular QM*



$1\sigma_g^{\ +}$

$1\sigma_u^{\ +}$

Fig. 8.13 The parity classification of orbitals in a homonuclear diatomic molecule: (a) g, (b) u.

Orbital symbols

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Molecules

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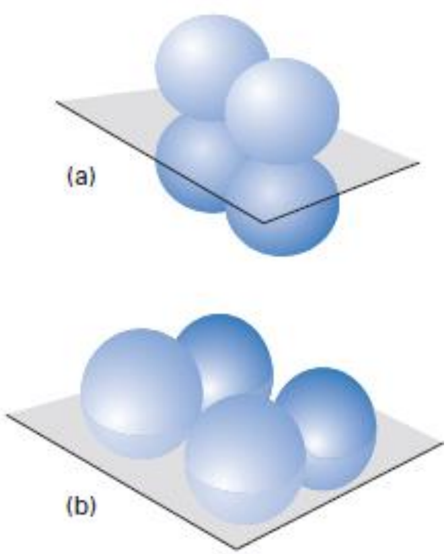

Fig. 8.20 The origin of the +/– symmetry classification: (a) a π_--orbital, (b) a π_+-orbital.

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Orbital symbols

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- The number at the beginning – the serial number of the particular orbital type.

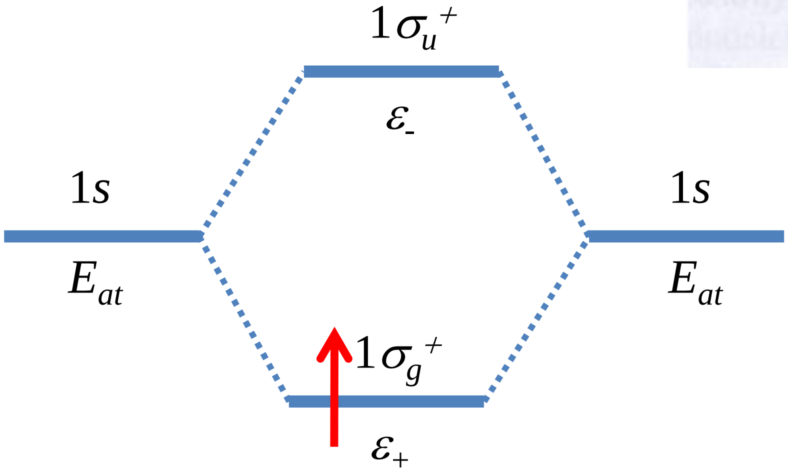
Molecules

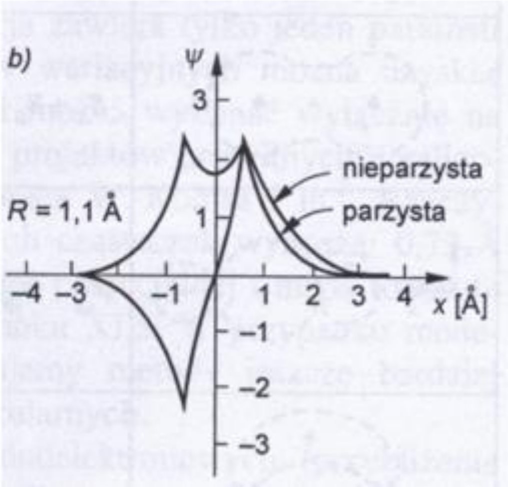
H_2^+ ion

Trial functions of the hydrogen atom (variational method)

$$\Psi_+ = N_+(1s_A + 1s_B)$$

$$\Psi_- = N_-(1s_A - 1s_B)$$





P. Atkins

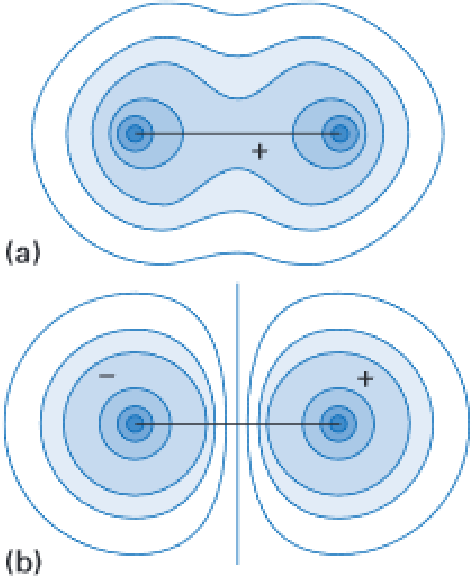


Fig. 8.6 Contour diagrams of the (a) bonding and (b) antibonding orbitals (1σ and 2σ, respectively) of the hydrogen molecule–ion in the LCAO approximation.

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Molecules

H_2^+ ion

Trial functions of the hydrogen atom (variational method)

$$\Psi_+ = N_+(1s_A + 1s_B)$$

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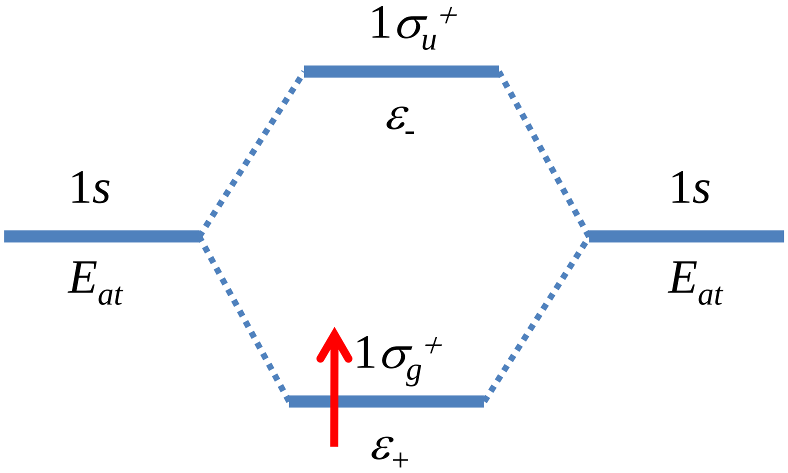


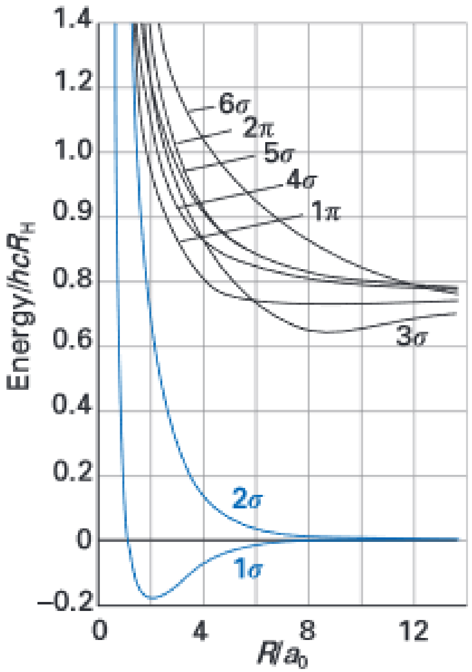
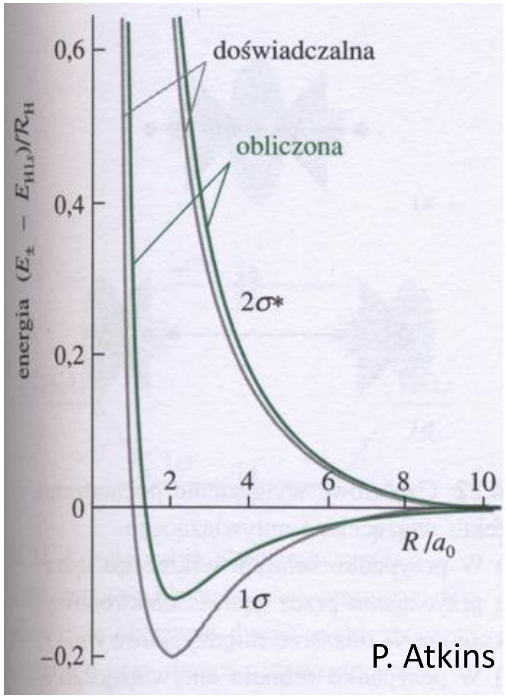


Fig. 8.5 The molecular potential energy curves for the hydrogen molecule–ion.



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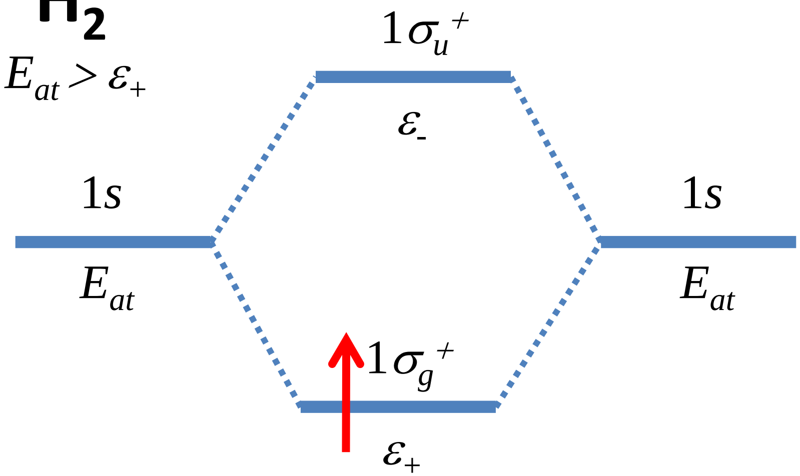
Molecules

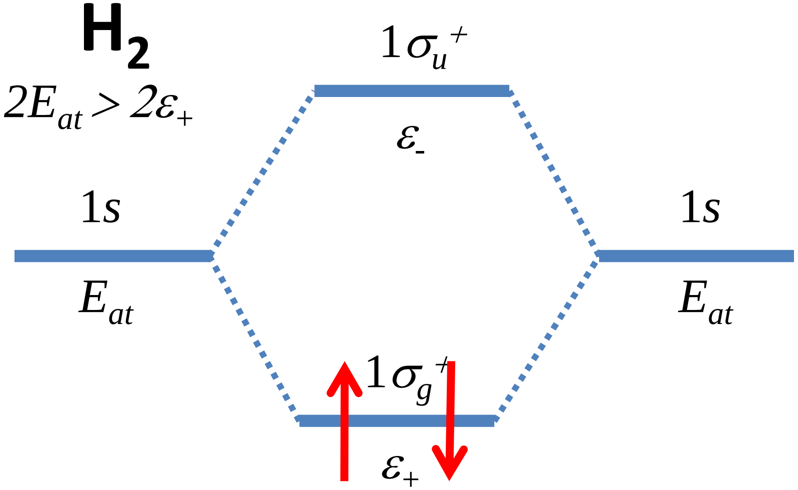
H_2^+

$E_{at} > \varepsilon_+$



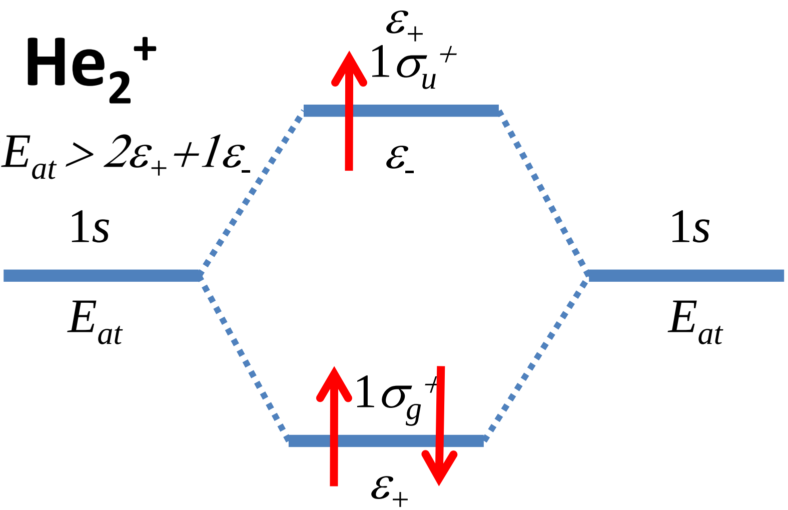
H_2

$2E_{at} > 2\varepsilon_+$



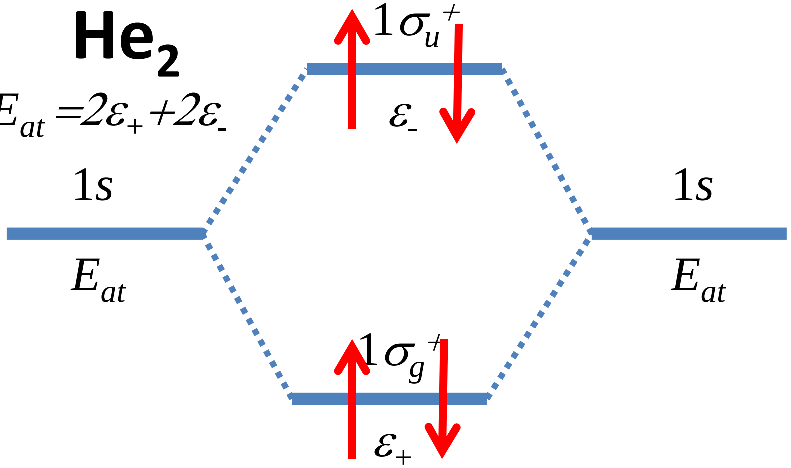
He_2^+

$3E_{at} > 2\varepsilon_+ + 1\varepsilon_-$

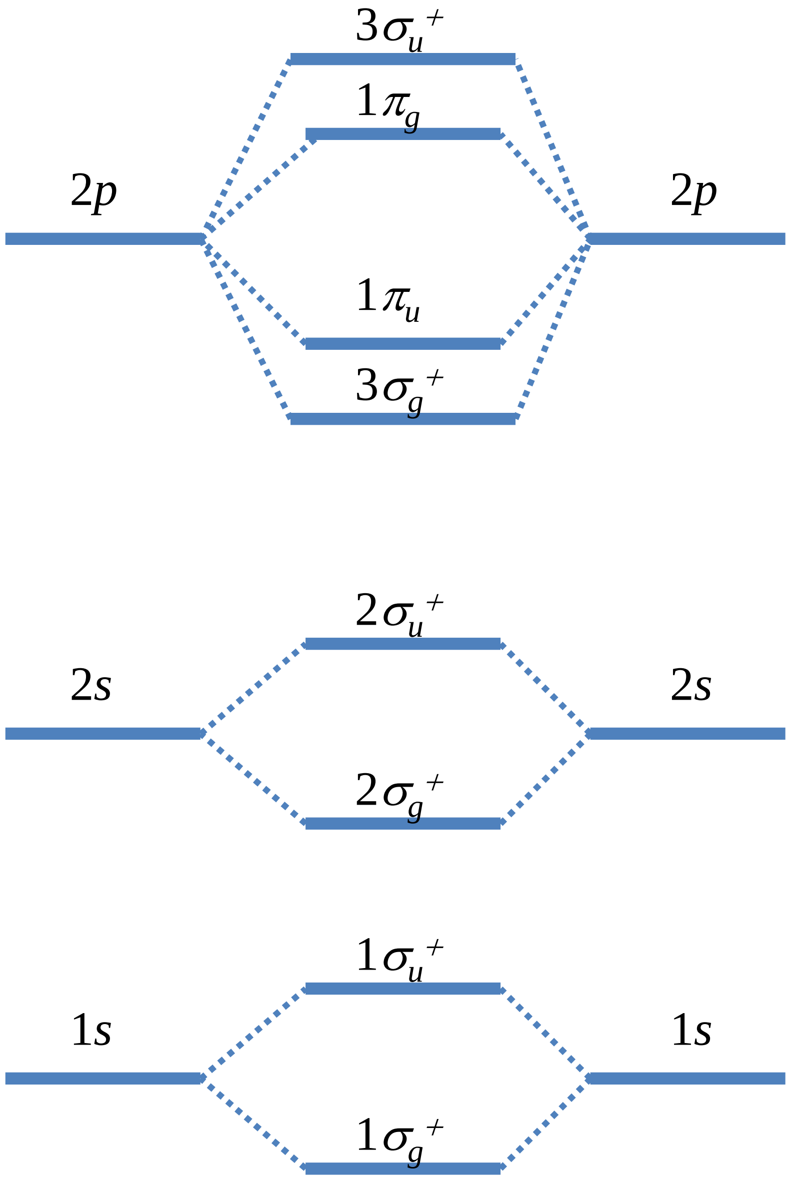


He_2

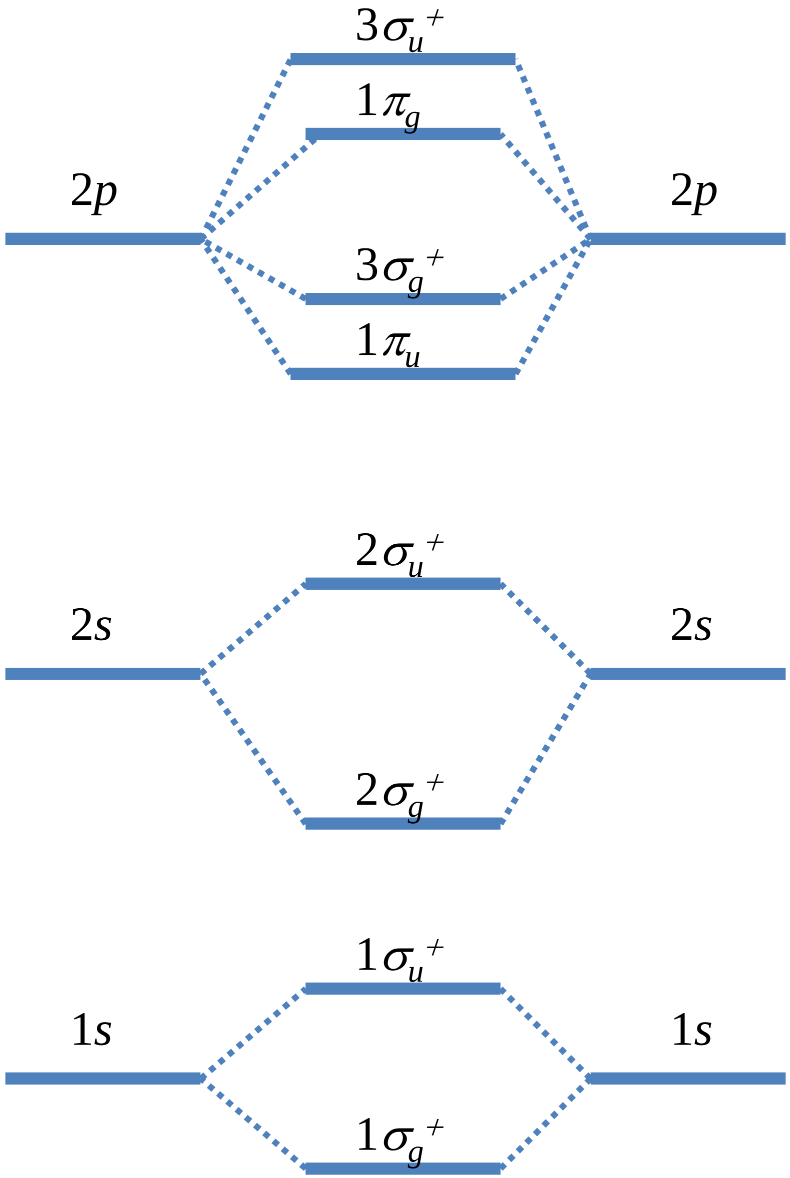
$4E_{at} = 2\varepsilon_+ + 2\varepsilon_-$



Homonuclear diatomic molecules molecular orbital energy scheme



Most of the molecules



Light molecules (incl. N_2)

Electronic states

LCAO

Numerical solution of electronic Hamiltonian

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = \left[\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})\right]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

LCAO-MO in Hartree-Fock approximation – self-consistent method, n-electrons wavefunction as a single **Slater determinant**, automatically providing antysymmetry of the wavefunction due to the interchanging the particles occupying any pair of states :

$$\Psi_{el}^{k}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\dots s_1,s_2,s_3,\dots) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \varphi_1^{sp}(\vec{r}_1,s_1) & \varphi_1^{sp}(\vec{r}_2,s_2) & \dots & \varphi_1^{sp}(\vec{r}_n,s_n) \\ \varphi_2^{sp}(\vec{r}_1,s_1) & \varphi_2^{sp}(\vec{r}_2,s_2) & \dots & \varphi_2^{sp}(\vec{r}_n,s_2) \\ \dots & \dots & & \dots \\ \varphi_n^{sp}(\vec{r}_1,s_1) & \varphi_n^{sp}(\vec{r}_2,s_2) & \dots & \varphi_n^{sp}(\vec{r}_n,s_n) \end{vmatrix}$$

Each of the single-electron spinorbital $\varphi_n^{sp}(\vec{r}_n,s_n)$ must be different - two spinorbitals may have forinstance the same orbital part φ, but then must have different spin

$$\varphi_n^{sp}(\vec{r}_n,s_n) = \varphi_n^{sp}(\vec{r}_n)\begin{bmatrix}0\\1\end{bmatrix} \text{ or } \varphi_n^{sp}(\vec{r}_n)\begin{bmatrix}1\\0\end{bmatrix}$$

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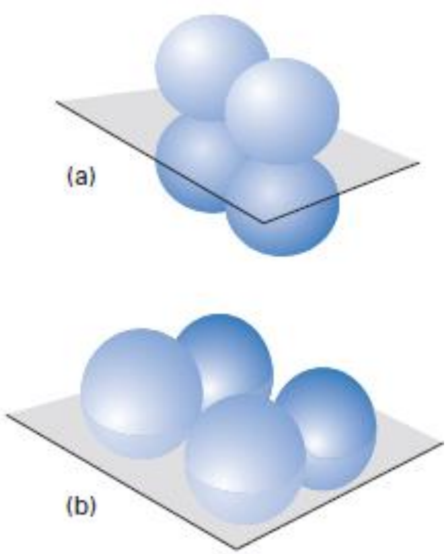

Fig. 8.20 The origin of the $+/-$ symmetry classification: (a) a π_--orbital, (b) a π_+-orbital.

Atkins, Fridman *Molecular QM*

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Molecules

Homonuclear diatomic molecules, eg. **H_2, Li_2, N_2, O_2**

Term symbols

Term symbols $^{2s+1}\Lambda$

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See: Atkins, Fridman *Molecular Quantum Mechanics*

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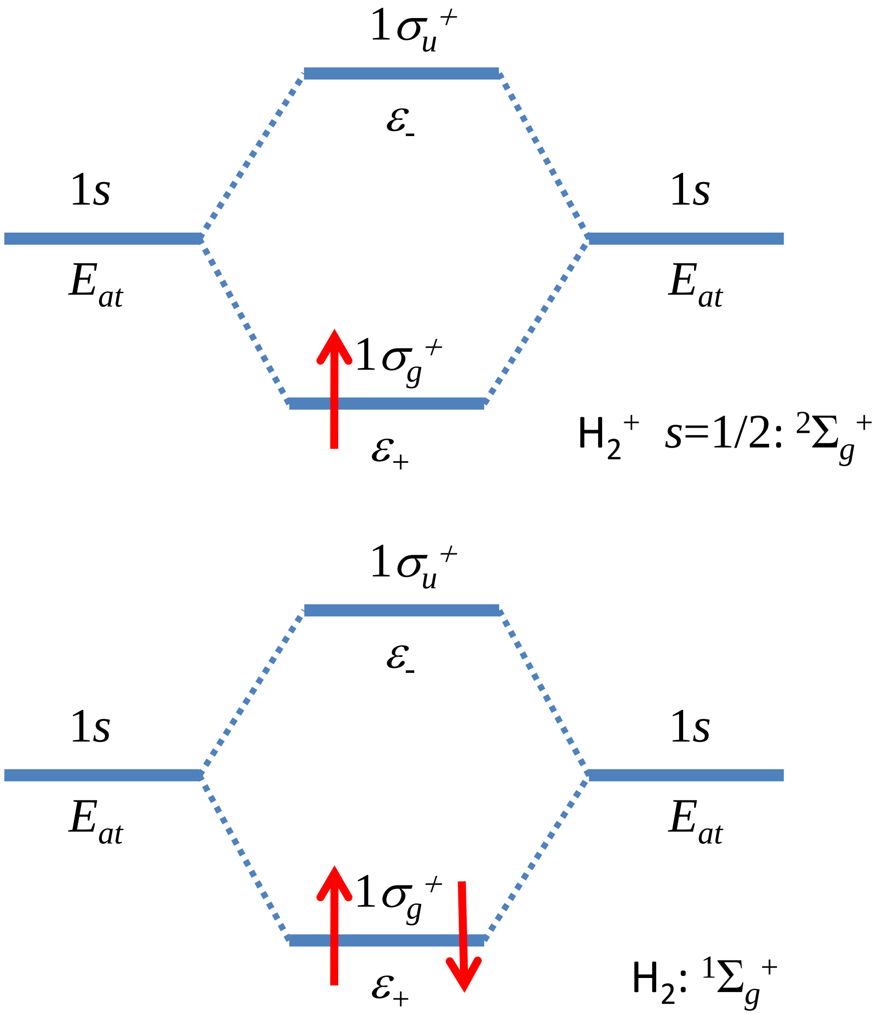
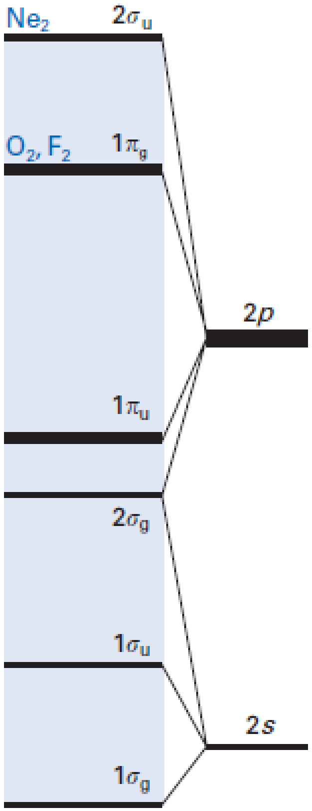
See: Atkins, Fridman *Molecular Quantum Mechanics*



Molecules

Homonuclear diatomic molecules, eg. $\mathbf{H_2}$, $\mathbf{Li_2}$, $\mathbf{N_2}$, $\mathbf{O_2}$

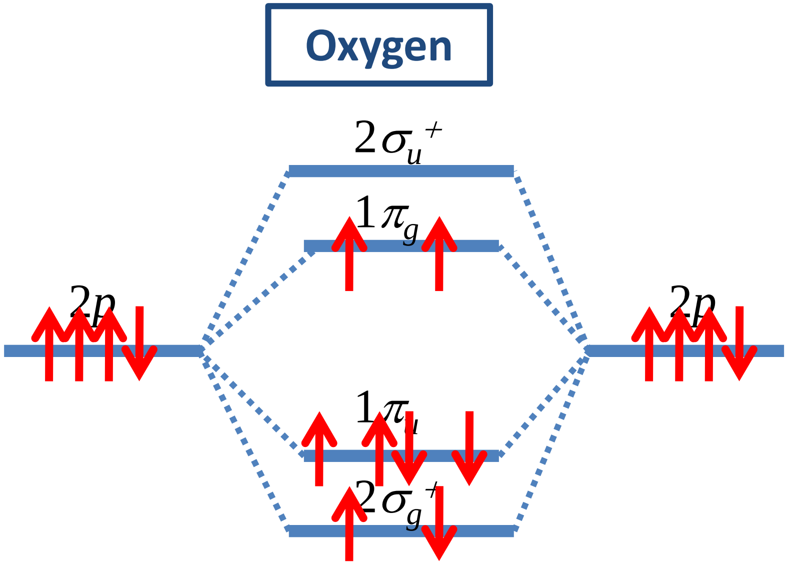
Term symbols



Atkins, Fridman *Molecular QM*

O_2: $2\times[(1s)^2(2s)^2(2p)^4]$

$(1\sigma_g^{\,+})^2(1\sigma_u^{\,+})^2(2\sigma_g^{\,+})^2(2\sigma_u^{\,+})^2(3\sigma_g^{\,+})^2(1\pi_u)^4(1\pi_g)^2$



ground state $^3\Sigma_g^-$

Molecules

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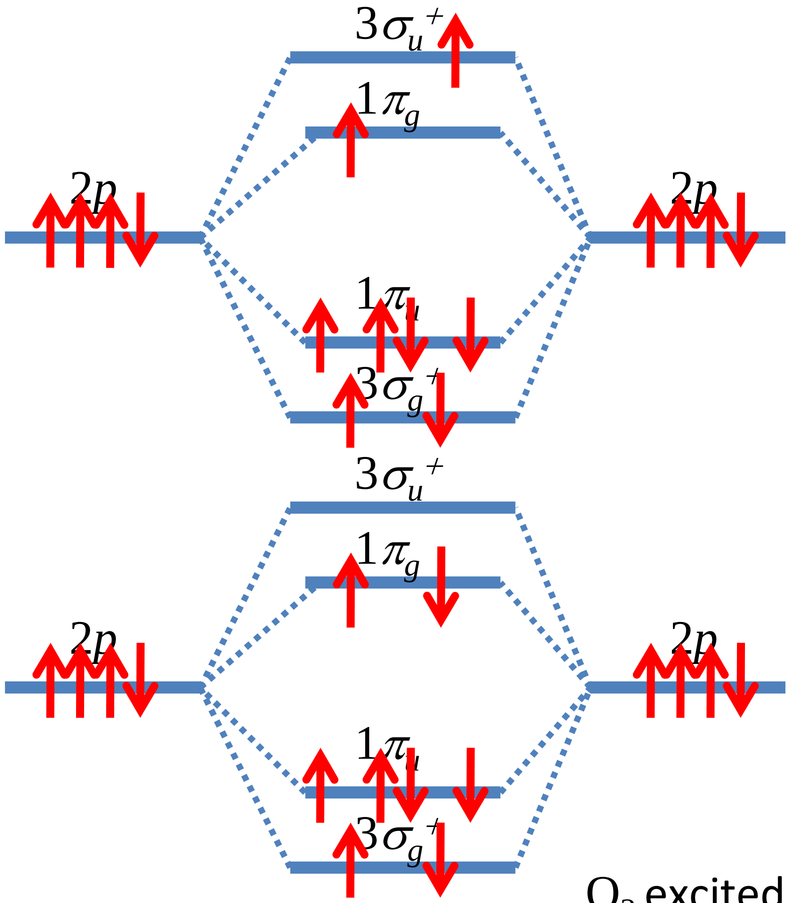
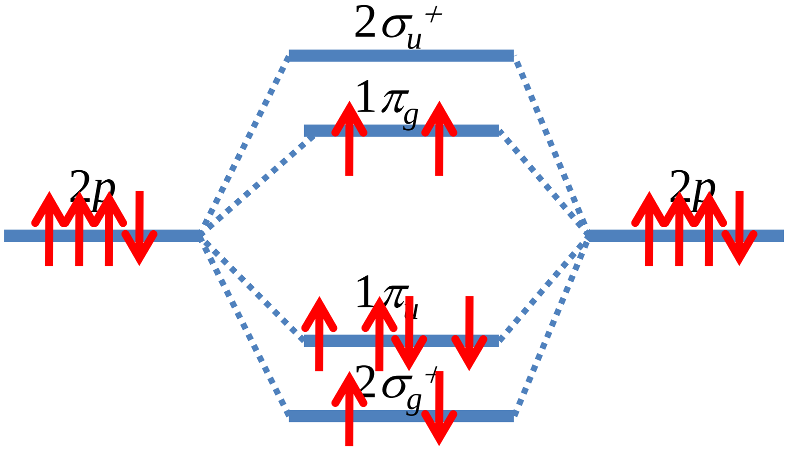
$(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(2\sigma_u^+)^2(3\sigma_g^+)^2(1\pi_u)^4(1\pi_g)^2$



O_2 excited states

Oxygen



ground state $^3\Sigma_g^-$

Molecules

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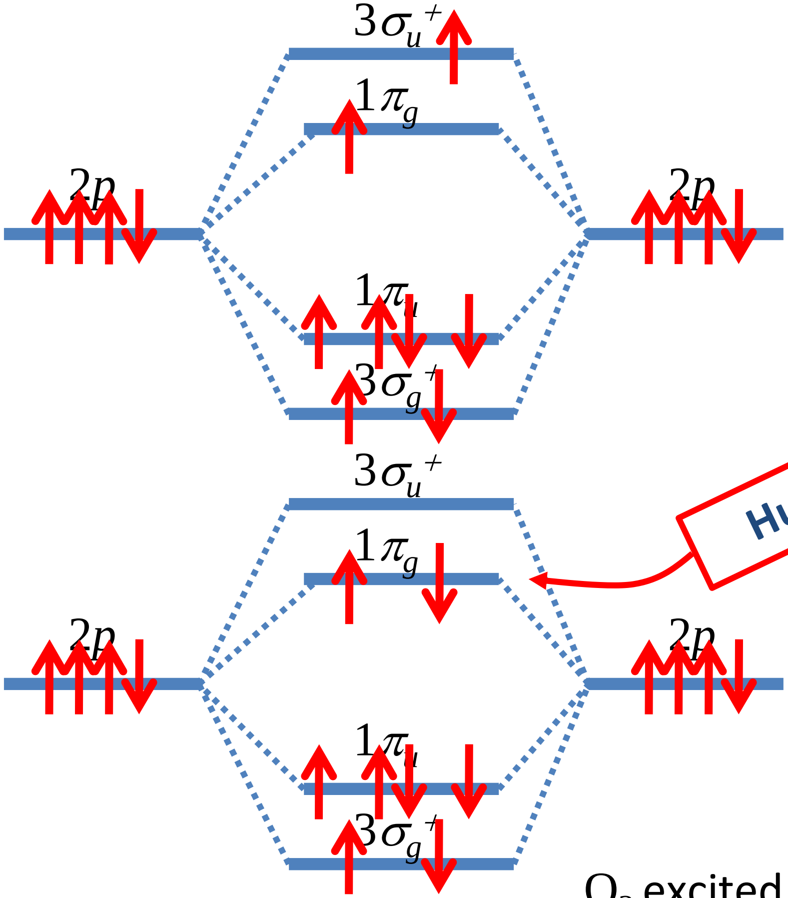
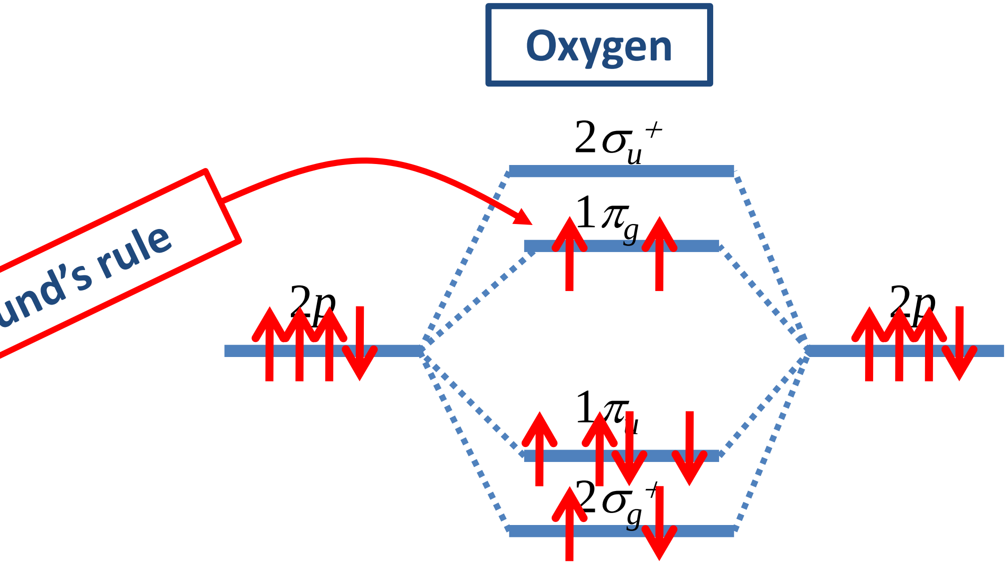


O_2 excited states



ground state $^3\Sigma_g^-$

Electronic states

Electrons energy strongly depends on the distance between nuclei.

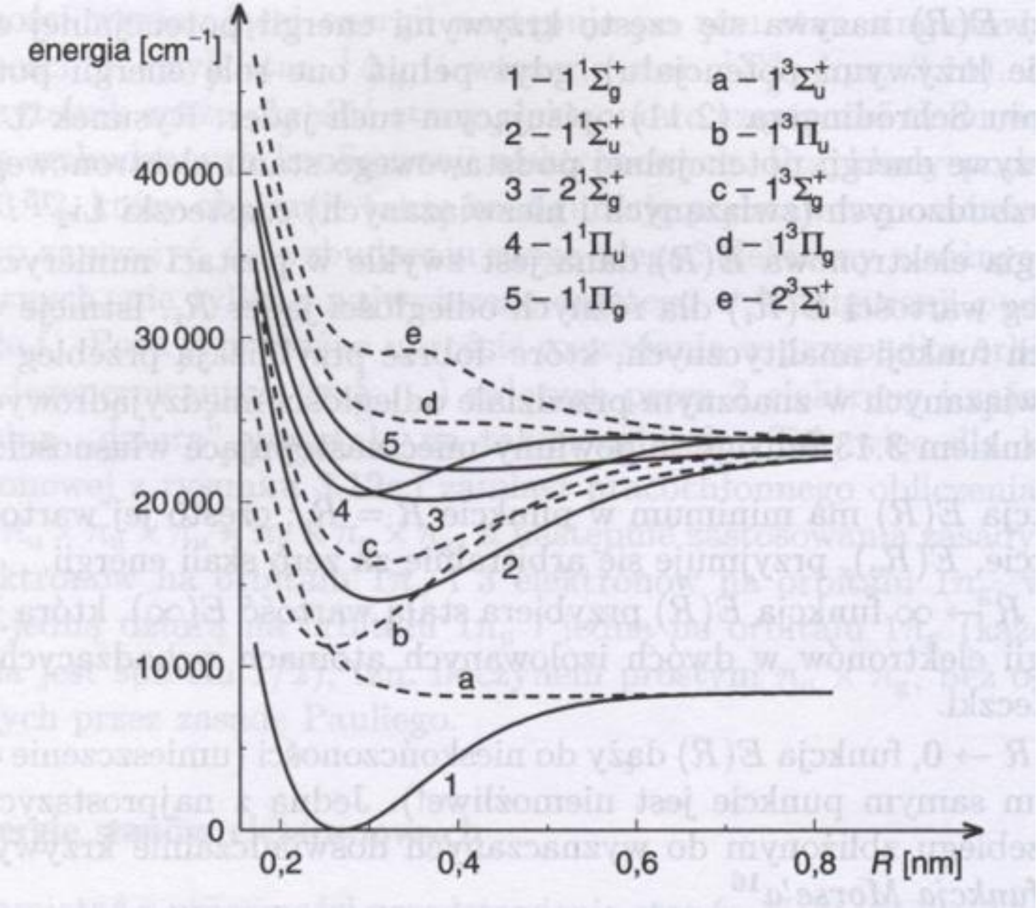
$E(R)$ - usually in numerical form.

Approximations: Morse potential
eg. Lithium

$$V(r) = D_e\left[1 - e^{-\alpha(r-r_0)}\right] + V(r_0)$$

Approximations: Lenard-Jones potential

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + V(r_0)$$



P. Kowalczyk

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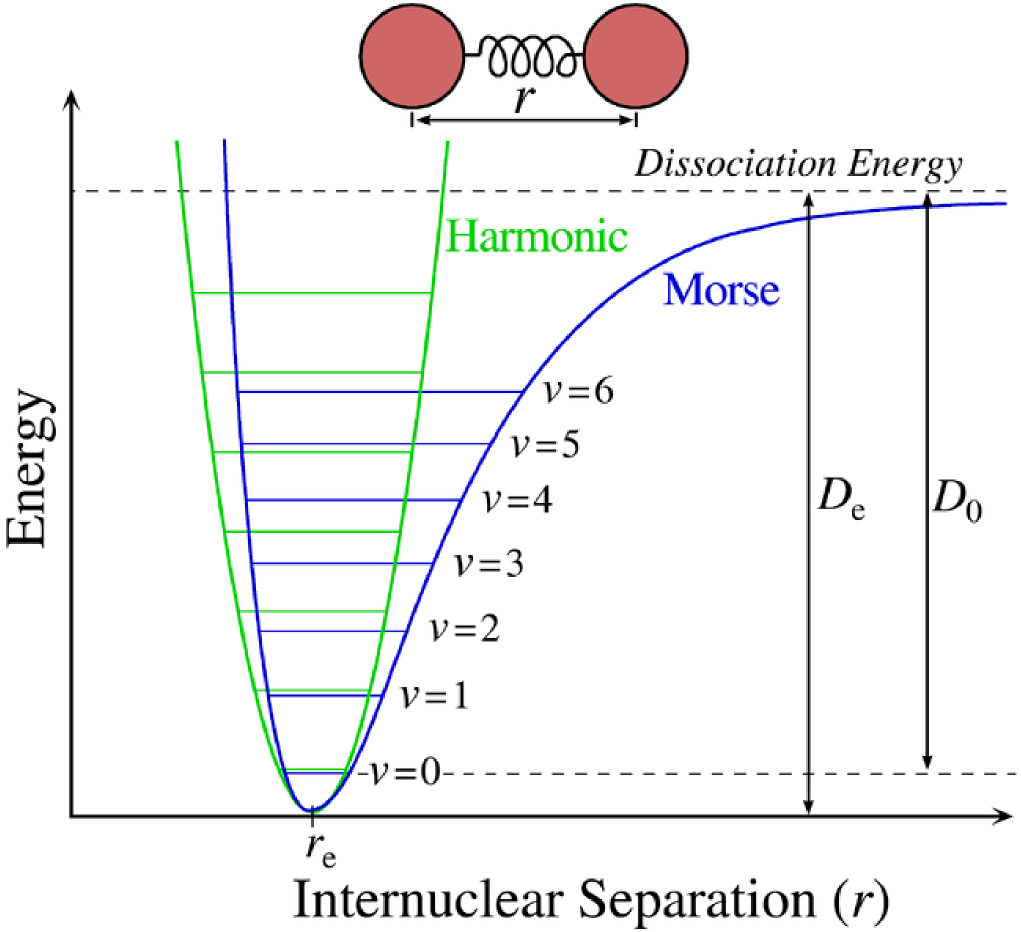

Wikipedia

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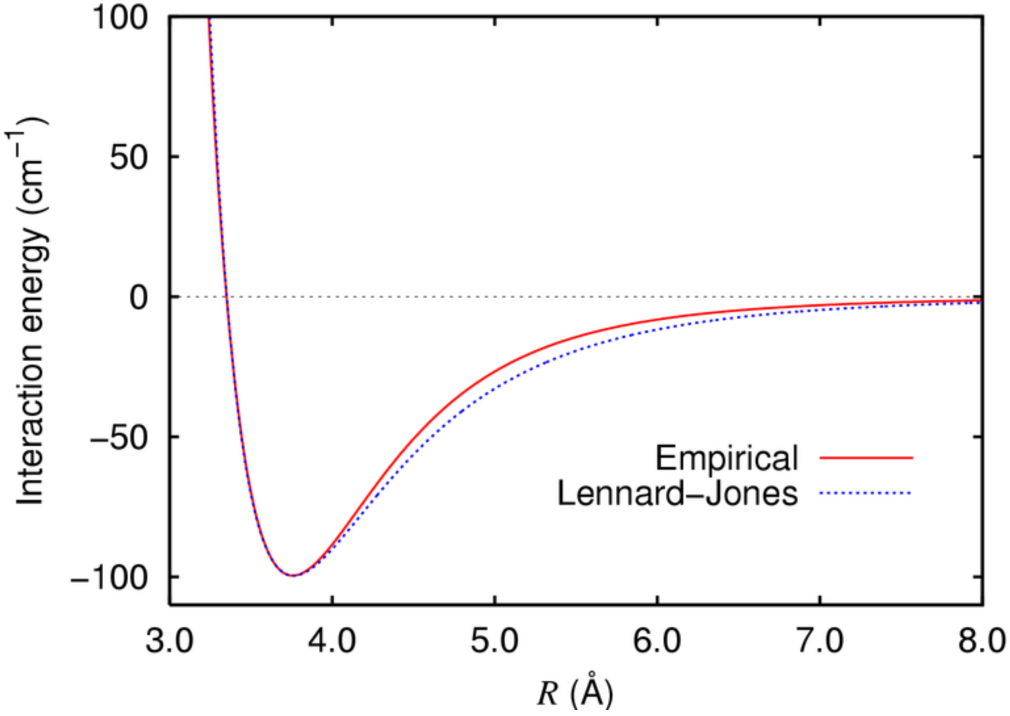


Wikipedia

Molecules

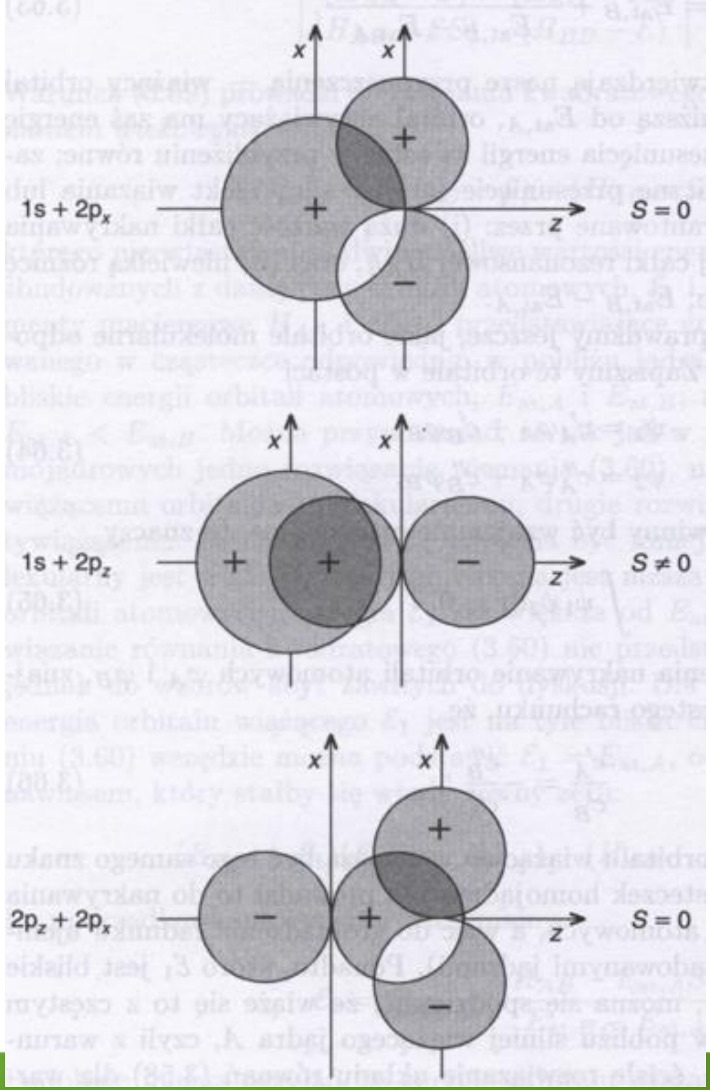
Homonuclear diatomic molecules, eg. **H_2, Li_2, N_2, O_2**

$$\Psi = c_A\varphi_A + c_B\varphi_B \qquad |c_A|^2 = |c_B|^2 \Rightarrow c_A = \pm c_B$$

$$S = \int \varphi_A\varphi_B \, d\vec{r} > 0$$ overlap integral

$E_{at,B}$

$E_{at,A}$



Molecules

These were

Homonuclear diatomic molecules, eg. **H_2, Li_2, N_2, O_2**

The molecule is diatomic so we are looking for a combination of two orbitals φ_A and φ_B.

$$\Psi = c_A\varphi_A + c_B\varphi_B \qquad |c_A|^2 = |c_B|^2 \Rightarrow c_A = \pm c_B$$

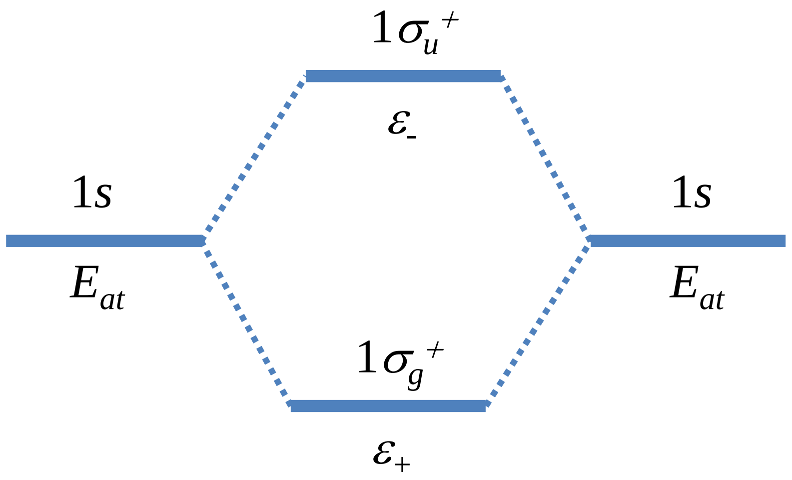
$$S = \int \varphi_A\varphi_B \, d\vec{r} > 0$$ overlap integral

$$\varepsilon_\pm = \int \Psi_\pm^* \hat{H}^0 \Psi_\pm d\vec{r}$$

$$N_+ = \frac{1}{\sqrt{2(1+S)}} \qquad N_- = \frac{1}{\sqrt{2(1-S)}}$$

$$\varepsilon_+ = \frac{E_{at} - |H_{AB}|}{1+S}$$ bonding orbital

$$\varepsilon_- = \frac{E_{at} + |H_{AB}|}{1-S}$$ antibonding orbital



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Molecules

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$$\Psi = c_A\varphi_A + c_B\varphi_B \qquad |c_A|^2 \neq |c_B|^2$$

$$S = \int \varphi_A\varphi_B \, d\vec{r} > 0$$

variational method $\varepsilon < \dfrac{\int \Psi_\pm^* \widehat{H}^0 \Psi_\pm d\vec{r}}{\int \Psi_\pm^* \Psi_\pm d\vec{r}}$

$$\varepsilon(c_A^2 + c_B^2 + 2c_Ac_BS) = c_A^2H_{AA} + c_B^2H_{BB} + 2c_Ac_BS\,H_{AB}$$

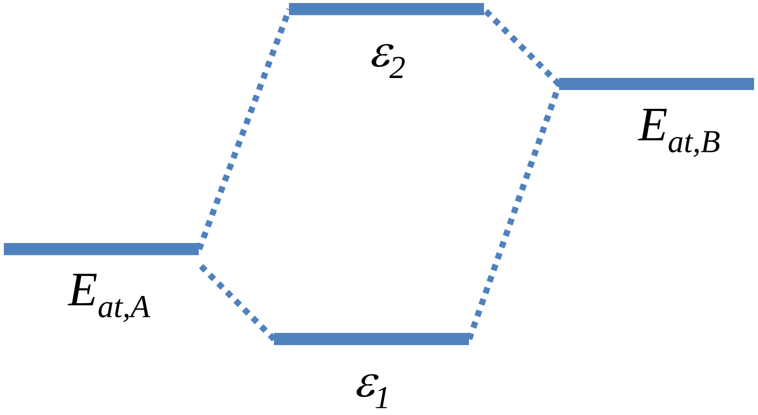
$$\frac{\partial\varepsilon}{\partial c_A} = \frac{\partial\varepsilon}{\partial c_B} = 0$$

$$\begin{bmatrix} H_{AA} - \varepsilon & H_{AB} - \varepsilon S \\ H_{AB} - \varepsilon S & H_{BB} - \varepsilon \end{bmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0$$

$$H_{AA} \approx E_{at,A}$$

$$H_{BB} \approx E_{at,B}$$

Let's assume that $E_{at,A} < E_{at,B}$



Molecules

Homonuclear diatomic molecules, eg. **H_2, Li_2, N_2, O_2**

The molecule is diatomic so we are looking for a combination of two orbitals φ_A and φ_B.

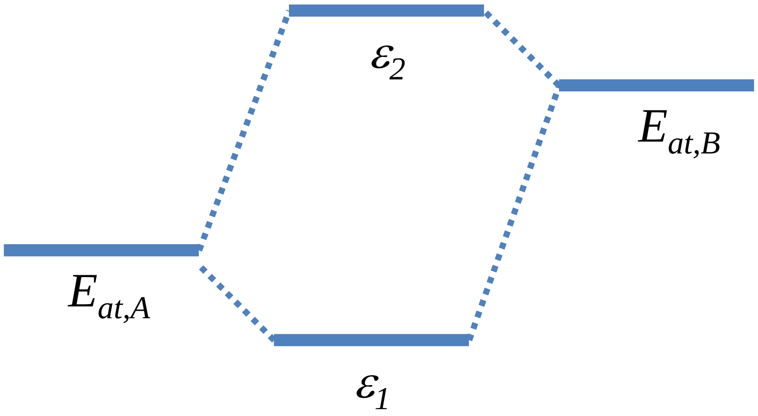
$$\Psi = c_A\varphi_A + c_B\varphi_B \qquad |c_A|^2 \neq |c_B|^2$$

$$S = \int \varphi_A\varphi_B \, d\vec{r} > 0$$

variational method $\varepsilon < \dfrac{\int \Psi_\pm^* \widehat{H}^0 \Psi_\pm d\vec{r}}{\int \Psi_\pm^* \Psi_\pm d\vec{r}}$

$$\varepsilon(c_A^2 + c_B^2 + 2c_Ac_BS) = c_A^2 H_{AA} + c_B^2 H_{BB} + 2c_Ac_BS\, H_{AB}$$

$$\frac{\partial\varepsilon}{\partial c_A} = \frac{\partial\varepsilon}{\partial c_B} = 0$$



$$\begin{bmatrix} H_{AA} - \varepsilon & H_{AB} - \varepsilon S \\ H_{AB} - \varepsilon S & H_{BB} - \varepsilon \end{bmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0$$

$$\varepsilon_1 \approx E_{at,A} - \frac{\left(H_{AB} - E_{at,A}S\right)^2}{E_{at,B} - E_{at,A}}$$

$$\varepsilon_2 \approx E_{at,B} - \frac{\left(H_{AB} - E_{at,B}S\right)^2}{E_{at,B} - E_{at,A}}$$

Molecules

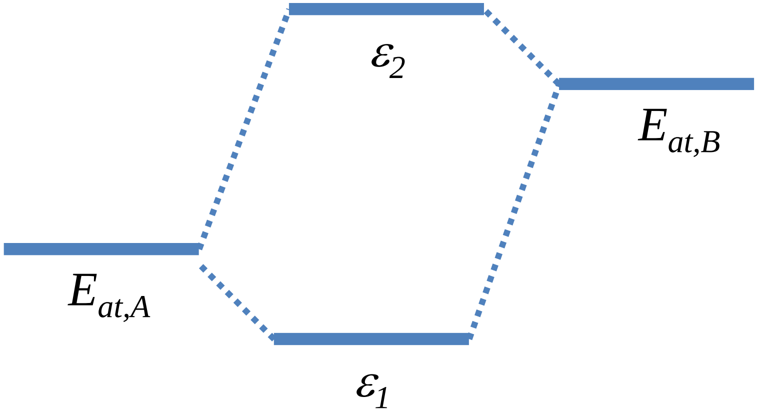
The bonding is strong when:

The large value of the overlap integral S and proportional to it integral H_{AB}.
The small difference of the energy of atomic orbitals $E_{at,A}$, $E_{at,B}$.
Molecular orbitals **do not have to** be constructed with atomic orbitals of the same type ($s-s$ or $p-p$).

$$\varepsilon(c_A^2 + c_B^2 + 2c_A c_B S) = c_A^2 H_{AA} + c_B^2 H_{BB} + 2c_A c_B S\, H_{AB}$$

$$\frac{\partial\varepsilon}{\partial c_A} = \frac{\partial\varepsilon}{\partial c_B} = 0$$

$$\begin{bmatrix} H_{AA}-\varepsilon & H_{AB}-\varepsilon S \\ H_{AB}-\varepsilon S & H_{BB}-\varepsilon \end{bmatrix}\begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0$$



$$\varepsilon_1 \approx E_{at,A} - \frac{\left(H_{AB} - E_{at,A}S\right)^2}{E_{at,B} - E_{at,A}}$$

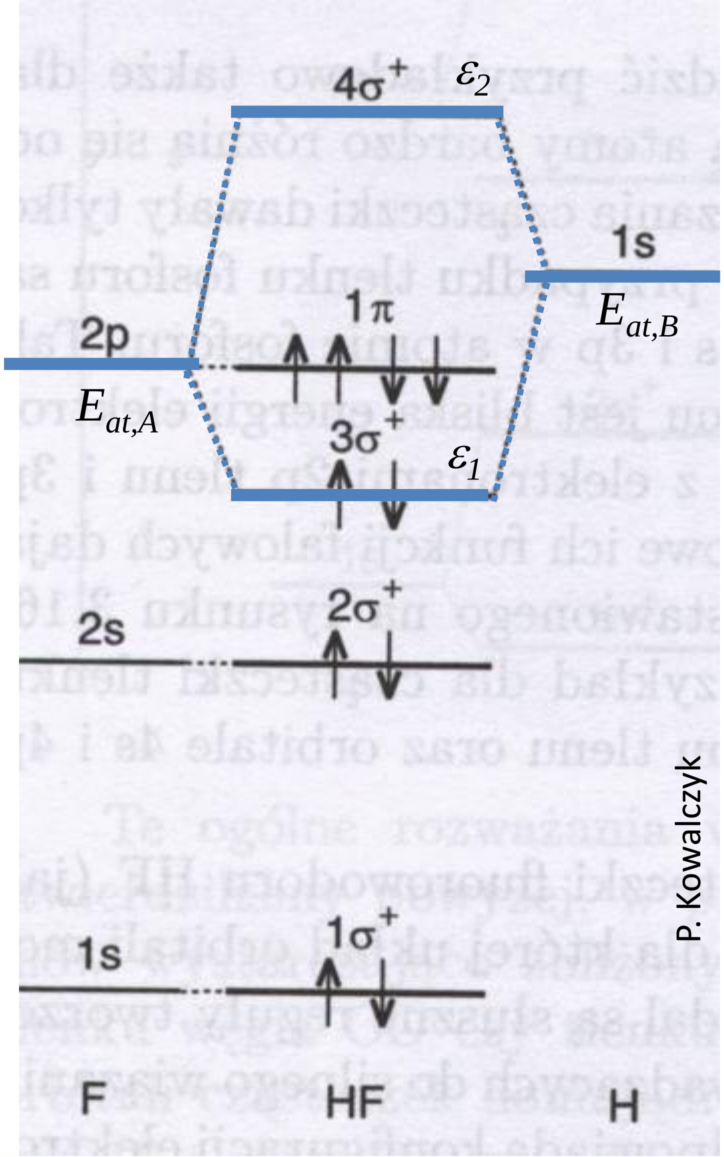
$$\varepsilon_2 \approx E_{at,B} - \frac{\left(H_{AB} - E_{at,B}S\right)^2}{E_{at,B} - E_{at,A}}$$

Molecules

Example: HF molecule

F: $(1s)^2(2s)^2(2p)^5$ H: $(1s)^1$

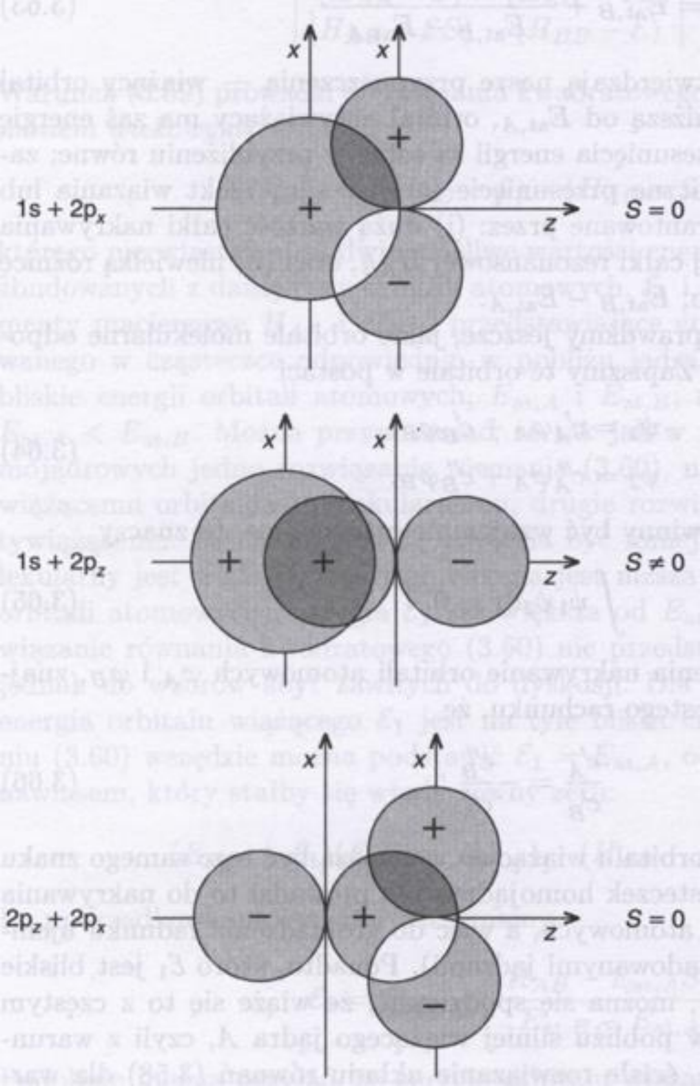
1. Similar energy values have $2p$ of F and $1s$ of H.
2. Only $2p_z$ orbital gives non-zero overlap integral with $1s$ (bonding orbital σ).
3. 2 Fluorine electrons $2p_x$ i 2 electrons $2p_y$ are not involved in the HF molecular bonding and are called **lone pair** (***wolna para elektronowa***)
4. Similarly fluorine 1s and 2s atomic orbitals do not form a bond with the 1s hydrogen electron because of the large energy difference
5. Ground state: $^1\Sigma^+$



P. Kowalczyk

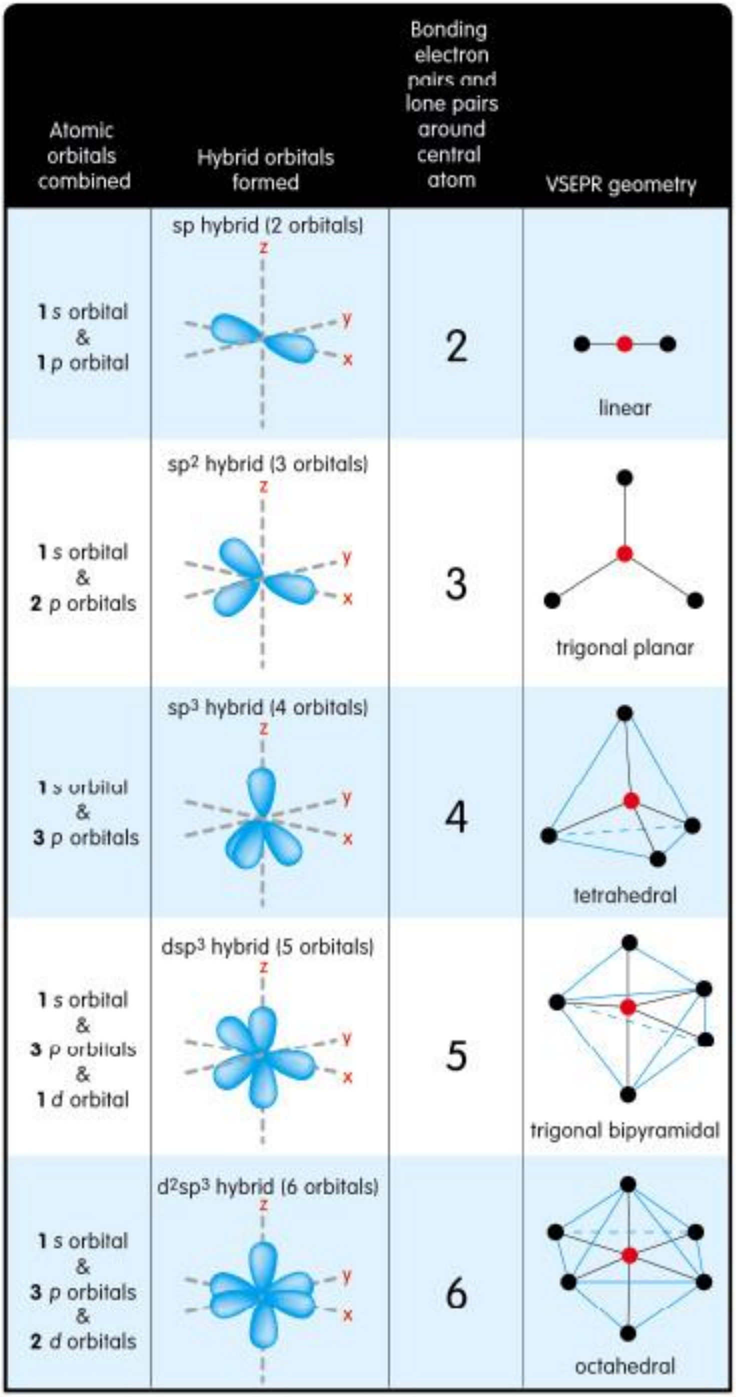
Molecules

Hybridization and overlap integrals



P. Kowalczyk

http://sparkcharts.sparknotes.com/chemistry/organicchemistry1/section2.php

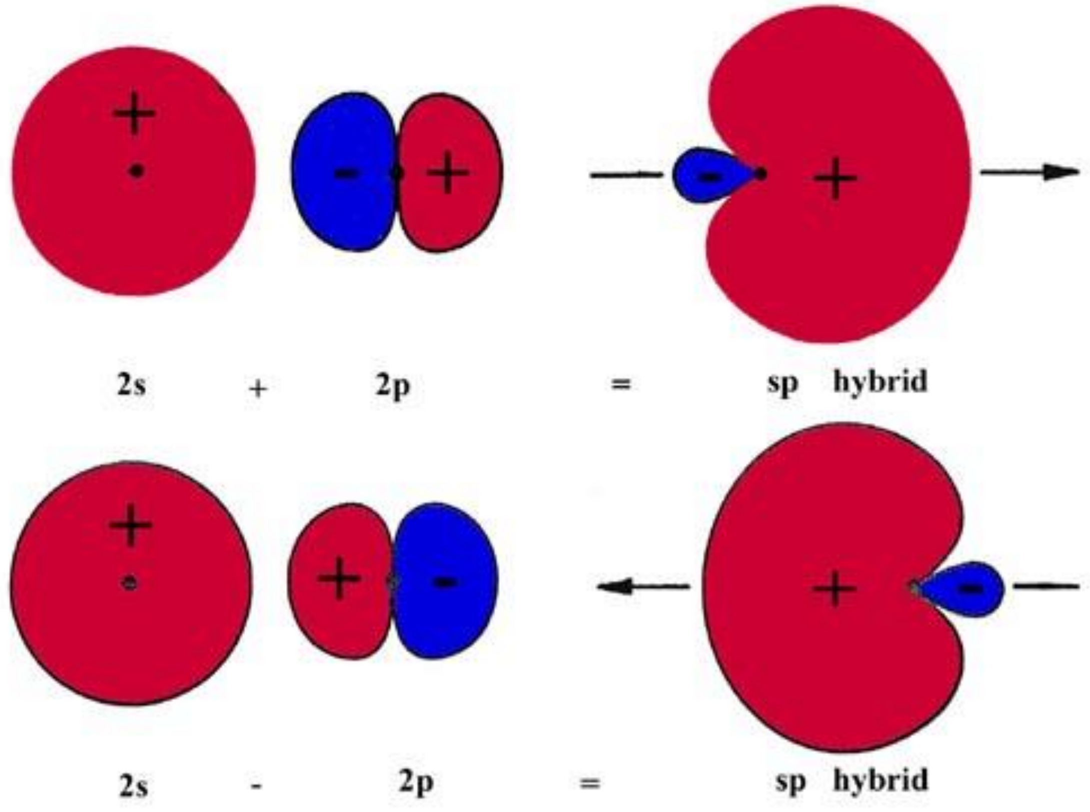


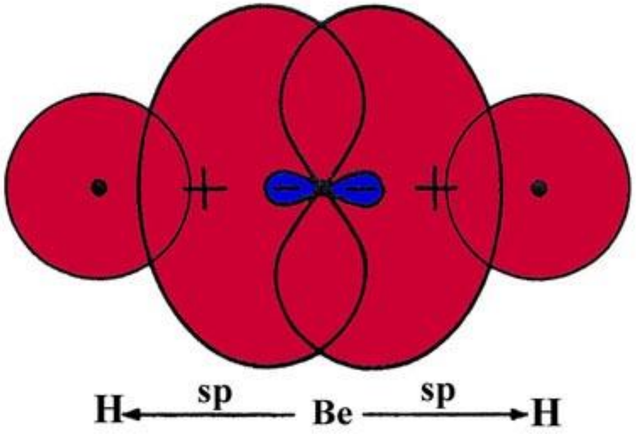
Atomic orbitals combined	Hybrid orbitals formed	Bonding electron pairs and lone pairs around central atom	VSEPR geometry
1 *s* orbital & 1 *p* orbital	sp hybrid (2 orbitals)	2	linear
1 *s* orbital & 2 *p* orbitals	sp² hybrid (3 orbitals)	3	trigonal planar
1 *s* orbital & 3 *p* orbitals	sp³ hybrid (4 orbitals)	4	tetrahedral
1 *s* orbital & 3 *p* orbitals & 1 *d* orbital	dsp³ hybrid (5 orbitals)	5	trigonal bipyramidal
1 *s* orbital & 3 *p* orbitals & 2 *d* orbitals	d²sp³ hybrid (6 orbitals)	6	octahedral

Molecules

Hybridization sp, eg. BeH$_2$

The angle between the bonds is 180˚.





$$h_1 = \frac{1}{\sqrt{2}} s - \frac{1}{\sqrt{2}} p_x$$

$$h_2 = \frac{1}{\sqrt{2}} s + \frac{1}{\sqrt{2}} p_x$$

Molecules

Hybridization sp^2, eg. C_2H_4

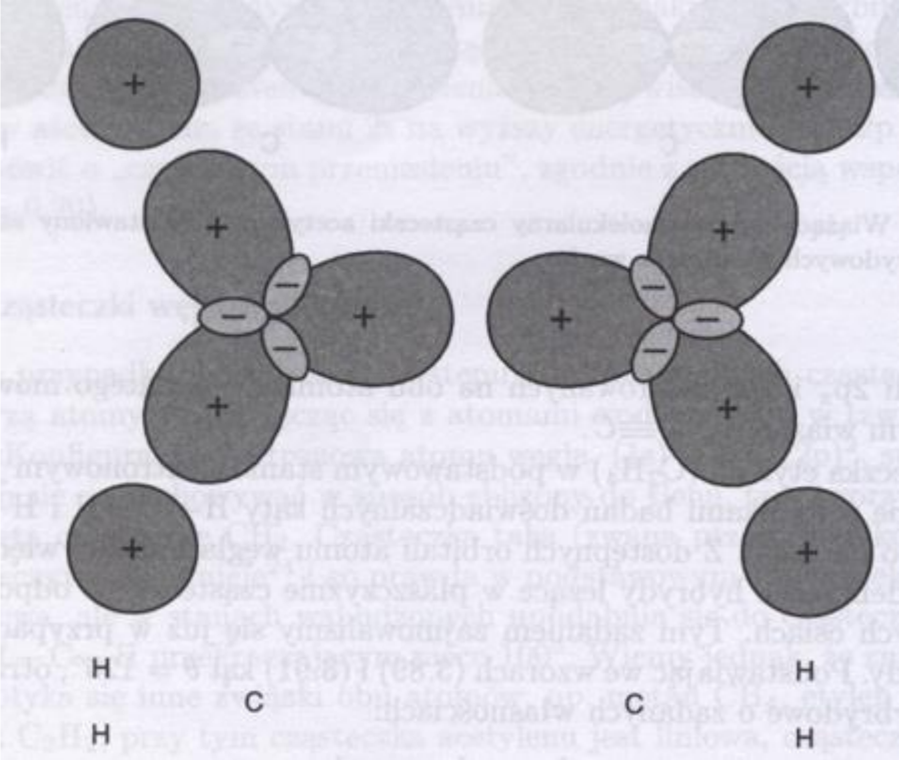
The angle between the bonds is 120˚.

Ethylene C_2H_4

$$h_1 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{2}}p_x - \frac{1}{\sqrt{6}}p_z$$

$$h_2 = \frac{1}{\sqrt{3}}s + \frac{1}{\sqrt{2}}p_x - \frac{1}{\sqrt{6}}p_z$$

$$h_3 = \frac{1}{\sqrt{3}}s + \frac{1}{\sqrt{2}}p_z$$



P. Kowalczyk

Molecules

Hybridization sp^3, eg. CH_4

The angle between the bonds is 109,5˚.

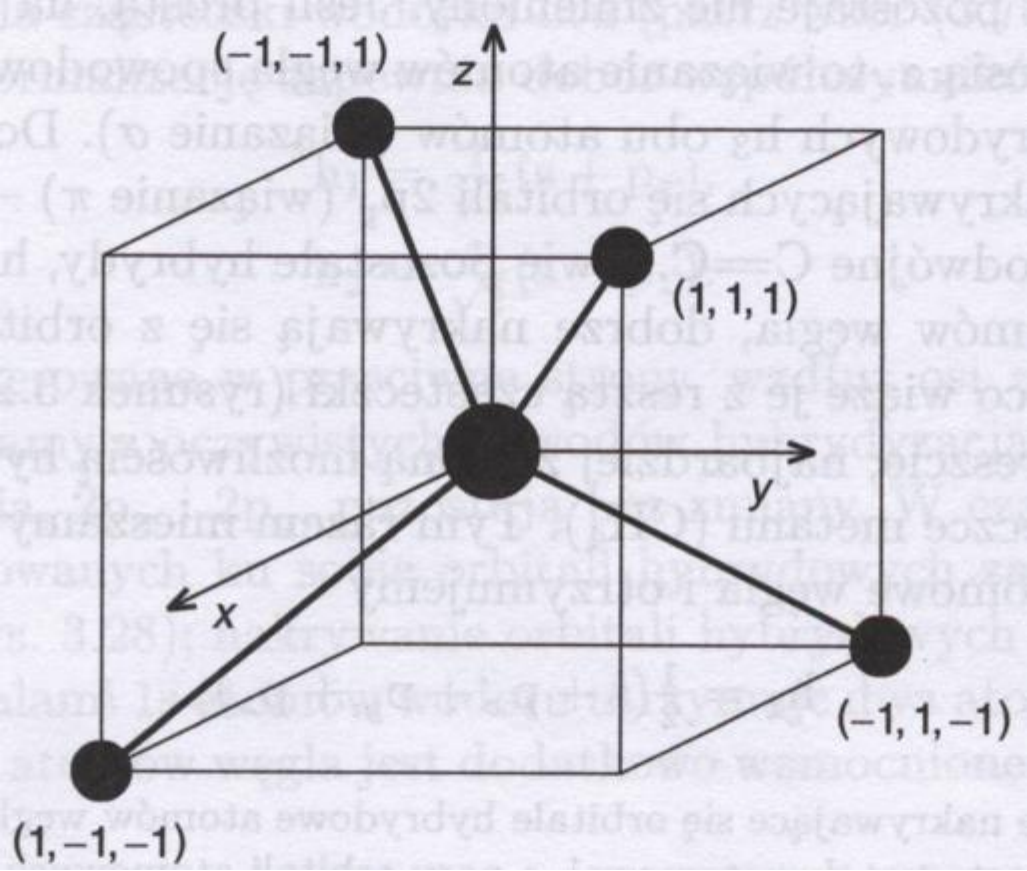
Methane CH_4

$$h_1 = \frac{1}{2}(s + p_x + p_y + p_z)$$

$$h_2 = \frac{1}{2}(s + p_x - p_y - p_z)$$

$$h_3 = \frac{1}{2}(s - p_x + p_y - p_z)$$

$$h_4 = \frac{1}{2}(s - p_x - p_y + p_z)$$



P. Kowalczyk

Molecules

Hybridization sp^3, eg. CH_4

The angle between the bonds is 109,5˚.

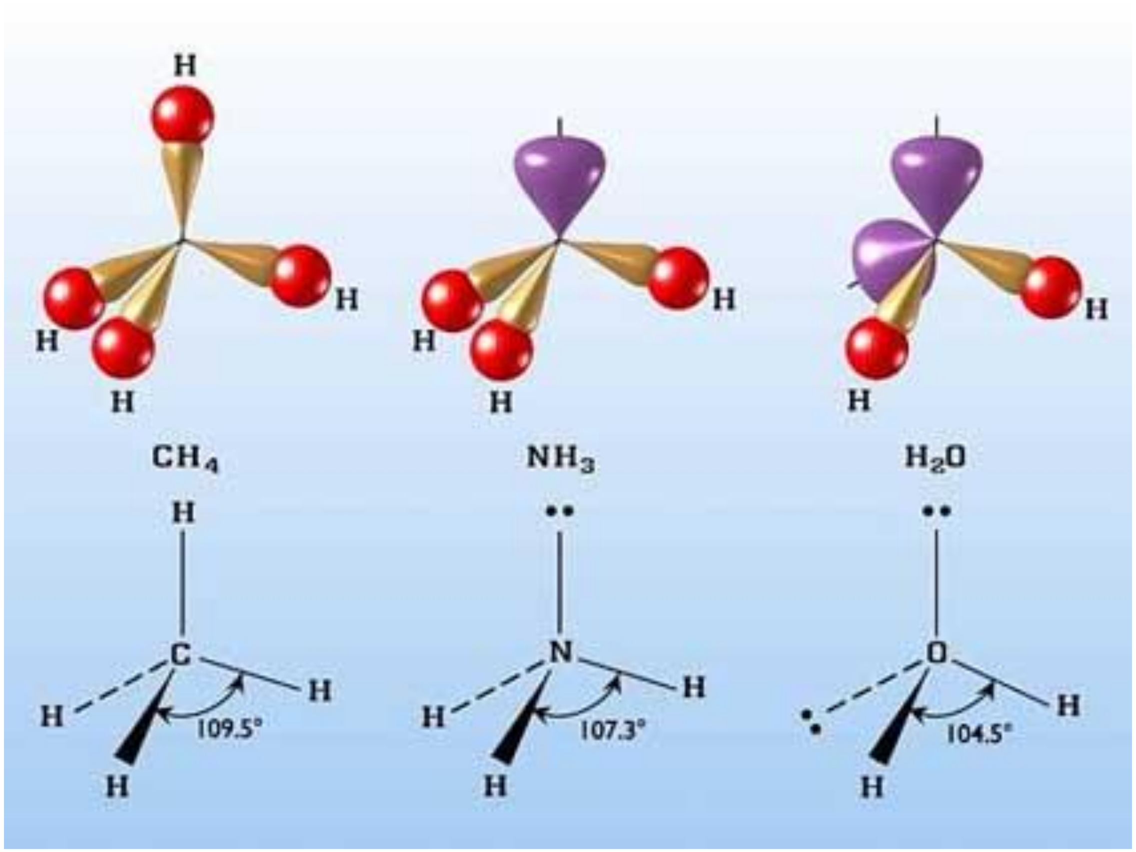
$$h_1 = \frac{1}{2}(s + p_x + p_y + p_z)$$

$$h_2 = \frac{1}{2}(s + p_x - p_y - p_z)$$

$$h_3 = \frac{1}{2}(s - p_x + p_y - p_z)$$

$$h_4 = \frac{1}{2}(s - p_x - p_y + p_z)$$

Methane CH_4 **Ammonia NH_3** **Water H_2O**



http://oen.dydaktyka.agh.edu.pl/dydaktyka/chemia/a_e_chemia/1_3_budowa_materii/01_04_03_2b.htm

Molecules

Hybridization sp^3, eg. CH$_4$

The angle between the bonds is 109,5˚.

$$h_1 = \frac{1}{2}(s + p_x + p_y + p_z)$$

$$h_2 = \frac{1}{2}(s + p_x - p_y - p_z)$$

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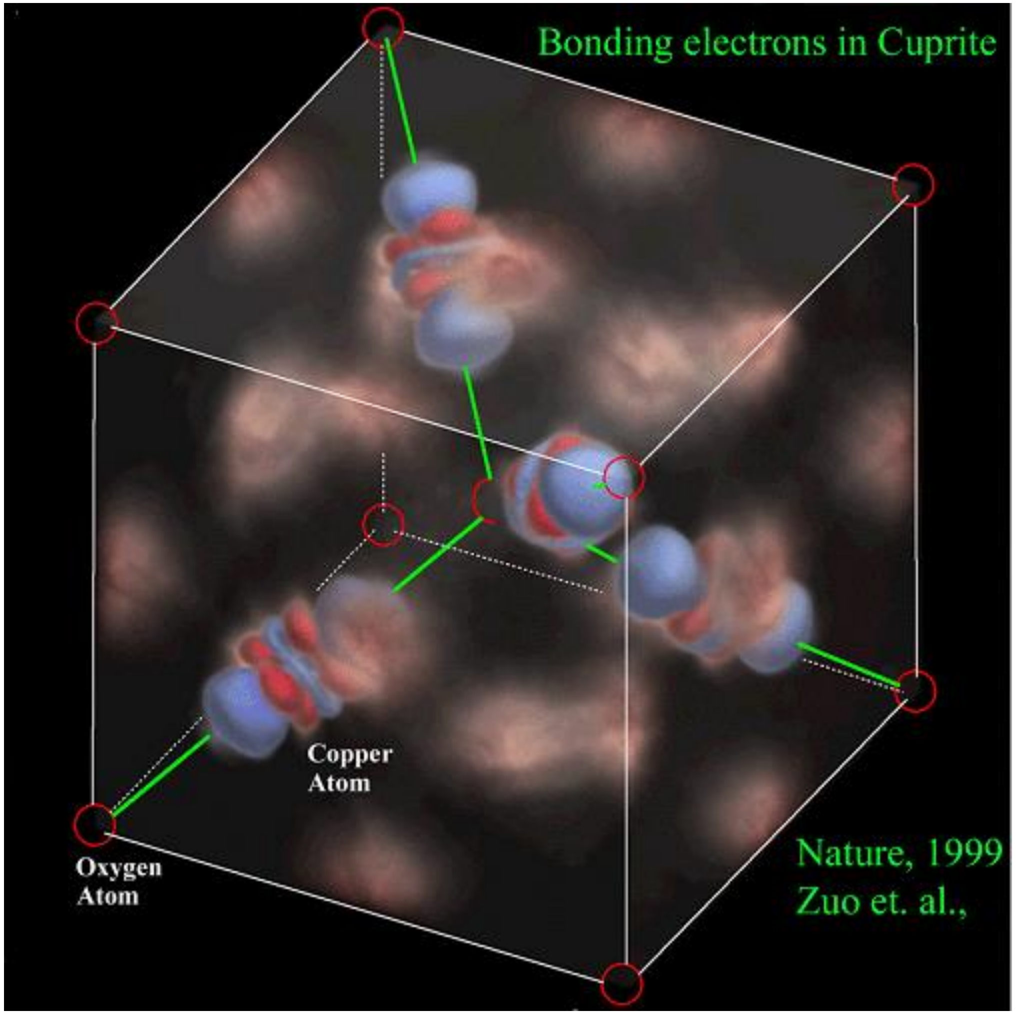


Molecules

Hybridization

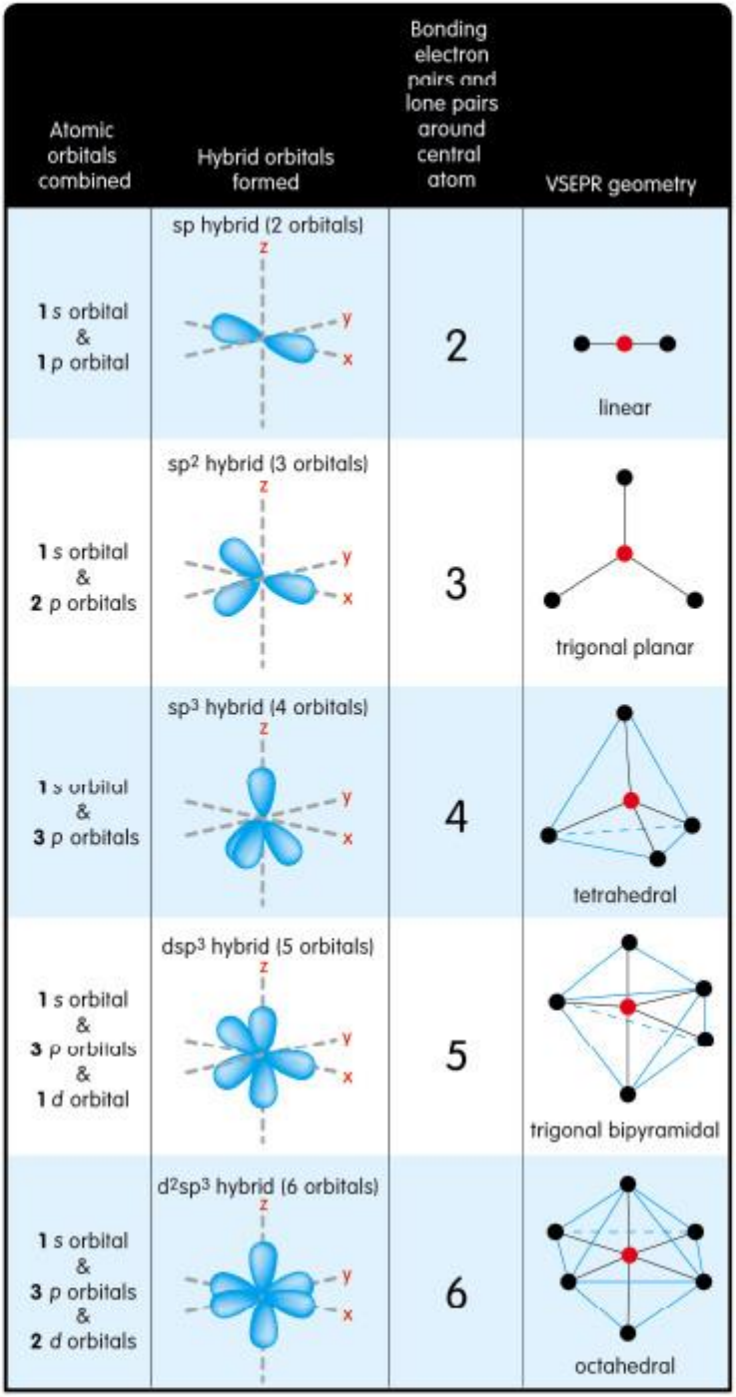
http://www.science.uwaterloo.ca/~cchieh/cact/c120/hybrid.html

A summary of hybrid orbitals, valence bond theory, VSEPR, resonance structures, and octet rule.

Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
sp	*sp*^{2}	*sp*^{3}	*dsp*^{3}	*d*^{2}*sp*^{3}
BeH_2	BH_3	CH_4	PF_5	SF_6
BeF_2	BF_3	CF_4	PCl_5	IOF_5
CO_2	CH_2O	CCl_4	$PFCl_4$	PF_6^-
HCN	(>C=O)	CH_3Cl	$:SF_4$	SiF_6^{2-}
HC°CH	>C=C<	NH_4^+	$:TeF_4$	$:BrF_5$
	CO_3^{2-}	$:NH_3$	$::ClF_3$	$:IF_5$
	benzene	$:PF_3$	$::BrF_3$	$::XeF_4$
	graphite	$:SOF_2$	$:::XeF_2$	
	fullerenes	$::OH_2$	$:::I_3^-$	
	$\bullet NO_2$	$::SF_2$	$(:::I\ I_2^-)$	
	N_3^-		$:::ICl_2^-$	
	$:OO_2$ (O_3)	SiO_4^{4-}		
	$:SO_2$	PO_4^{3-}		
	SO_3	SO_4^{2-}		
		ClO_4^-		

• a lone odd electron : a lone electron pair

http://sparkcharts.sparknotes.com/chemistry/organicchemistry1/section2.php



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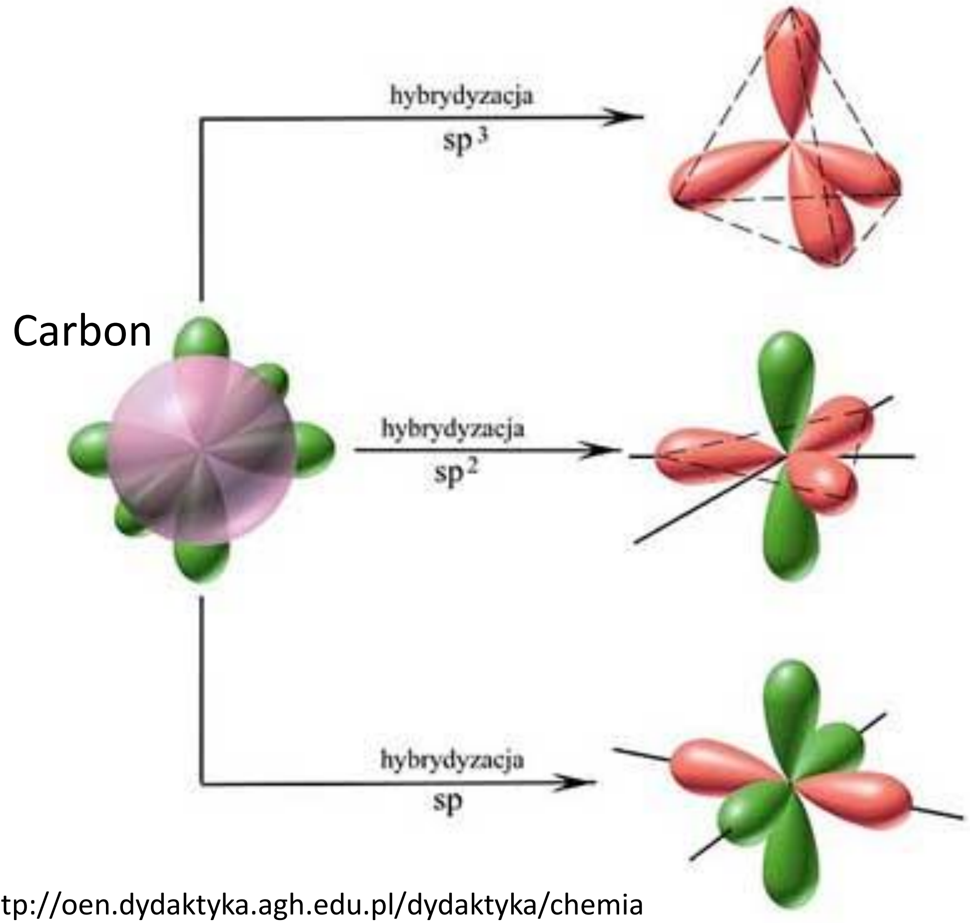
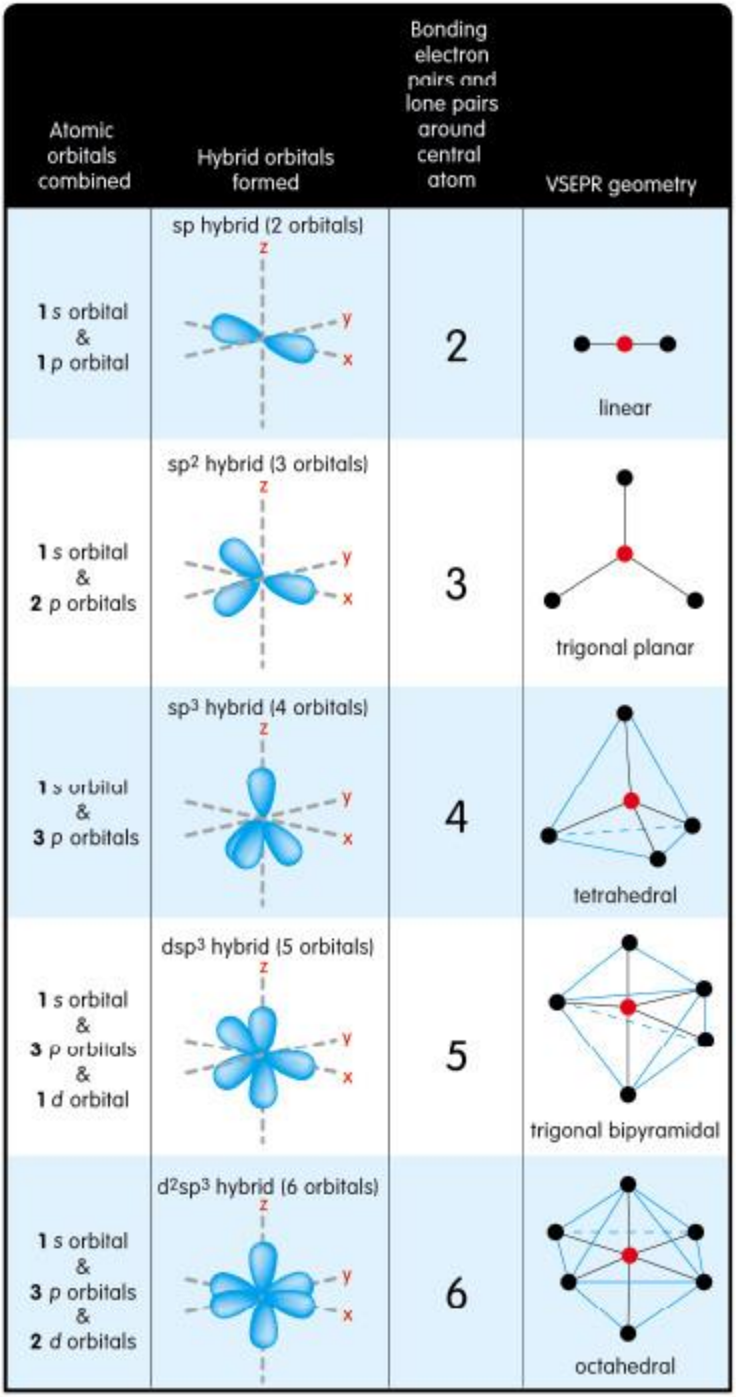
1 *s* orbital & 3 *p* orbitals & 2 *d* orbitals	d²sp³ hybrid (6 orbitals)	6	octahedral

Molecules

Hybridization



http://oen.dydaktyka.agh.edu.pl/dydaktyka/chemia



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1 *s* orbital & 3 *p* orbitals	sp^3 hybrid (4 orbitals)	4	tetrahedral
1 *s* orbital & 3 *p* orbitals & 1 *d* orbital	dsp^3 hybrid (5 orbitals)	5	trigonal bipyramidal
1 *s* orbital & 3 *p* orbitals & 2 *d* orbitals	d^2sp^3 hybrid (6 orbitals)	6	octahedral

http://sparkcharts.sparknotes.com/chemistry/organicchemistry1/section2.php

Molecules

Benzene molecule

σ-bonds (sp^2) are "localized" and form a rigid skeleton, while π-electrons forming a bond are delocalized.

$$\Psi_k = \frac{1}{\sqrt{6}} \sum_{n=1}^{6} e^{\frac{2\pi i}{6} kn} p_{z,n}$$

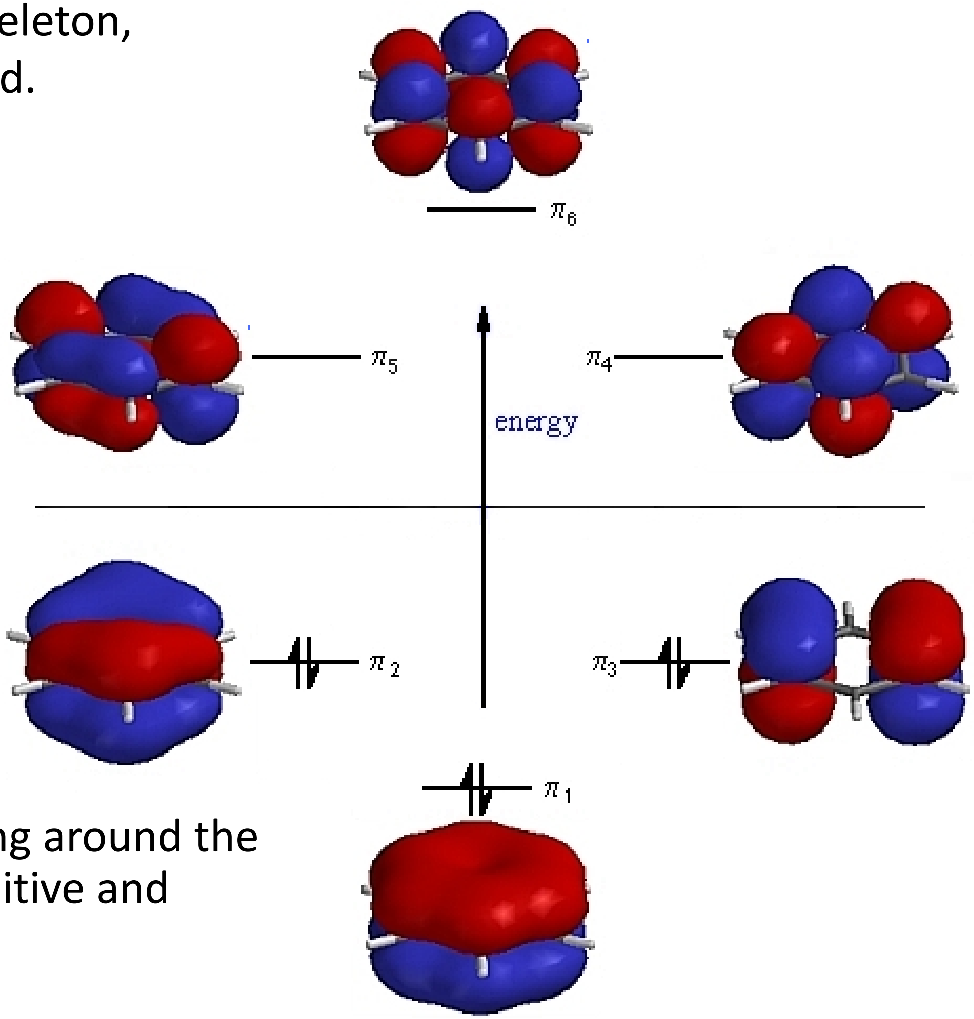
$$E_k = \alpha + 2\beta \cos\left(\frac{2\pi i}{6} k\right)$$

$$k = 0, \pm 1, \pm 2, 3$$

Six of atomic orbitals $2p_z$ gives an equal contribution to all of the molecular orbitals.

These functions correspond to the waves running around the carbon atoms ring in opposite directions for positive and negative values of k

Benzene



Molecules

Benzene molecule

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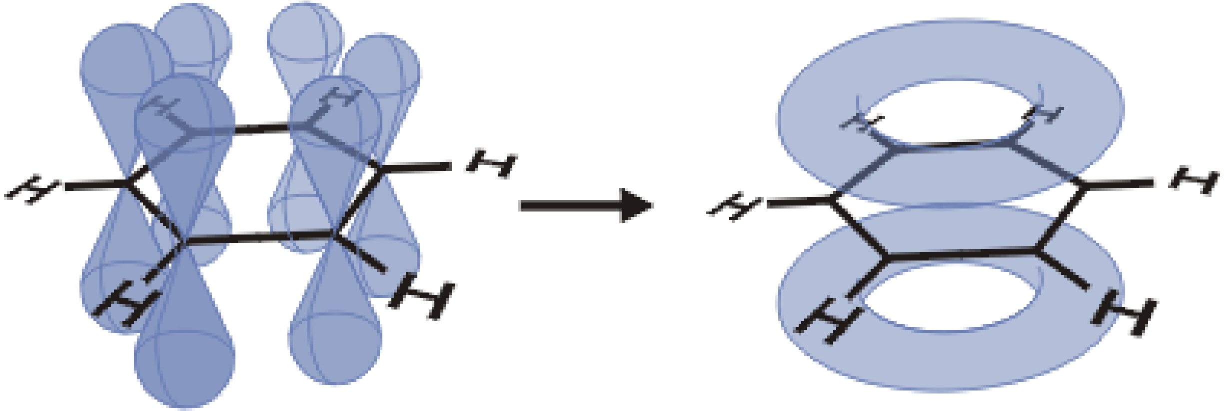
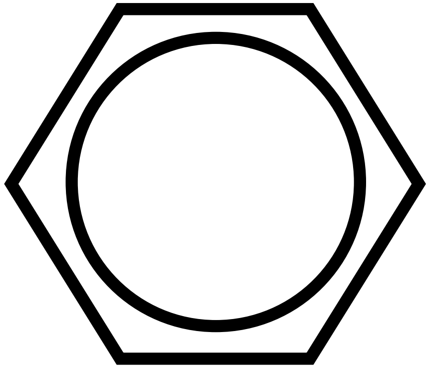
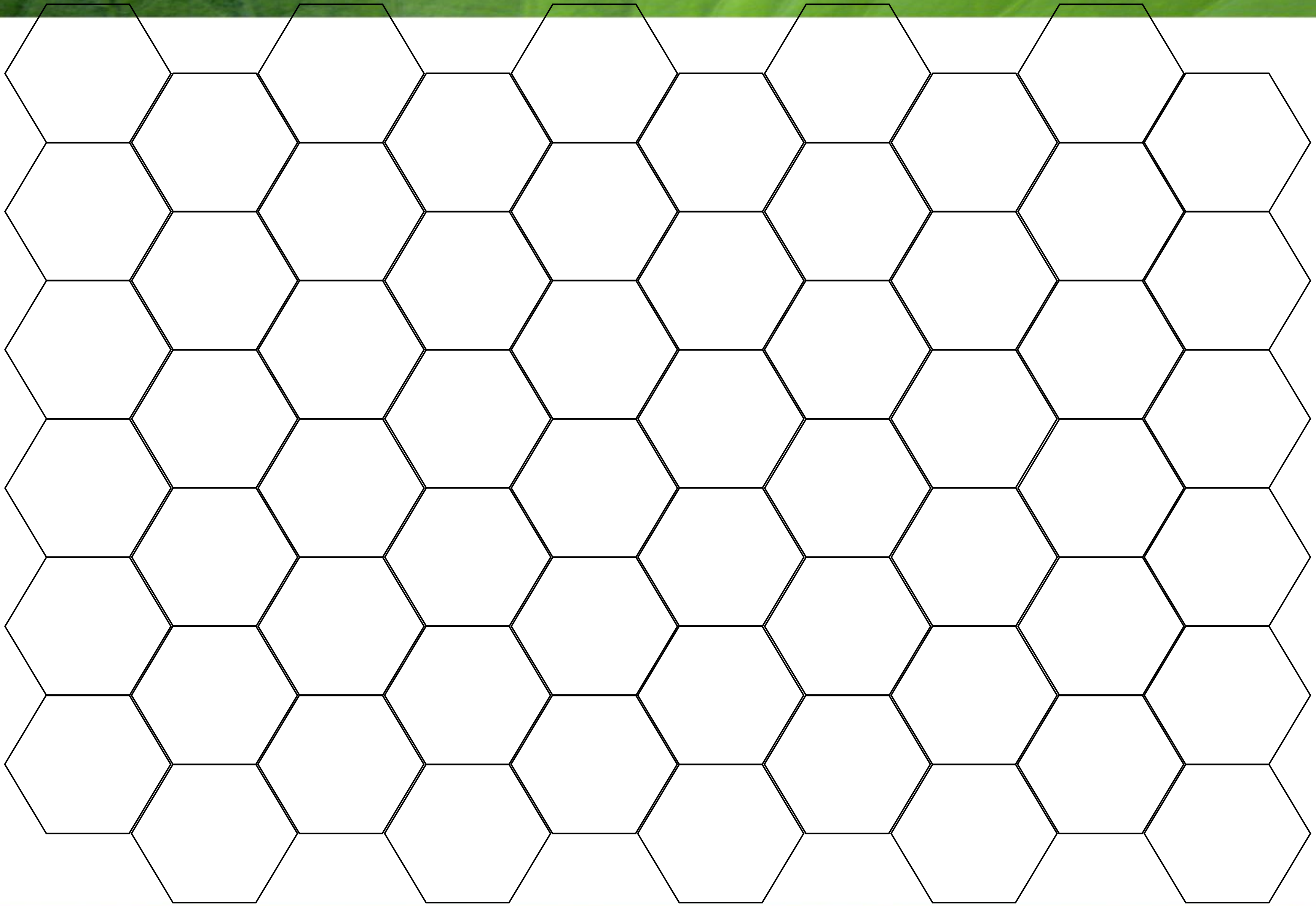
$$k = 0, \pm 1, \pm 2, 3$$

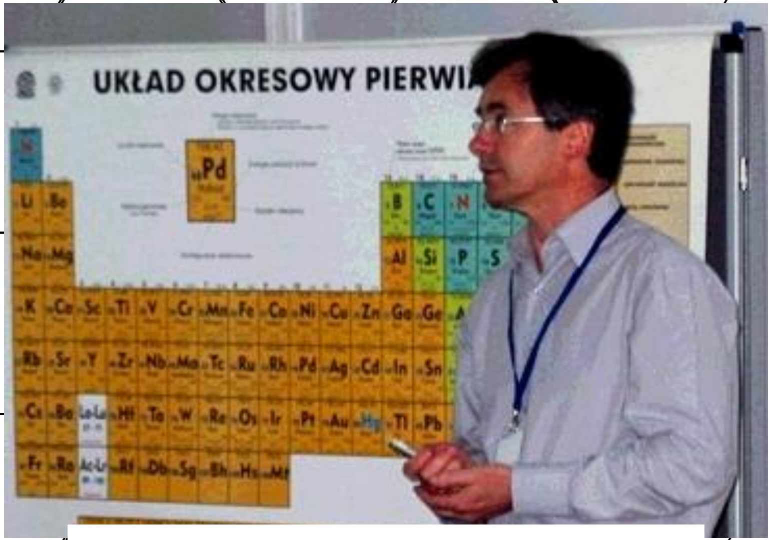
Friedrich August Kekule 1829 - 1896







The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov



dr inż. Włodzimierz Strupiński,

ITME

dr hab. **Andrzej Wysmołek**

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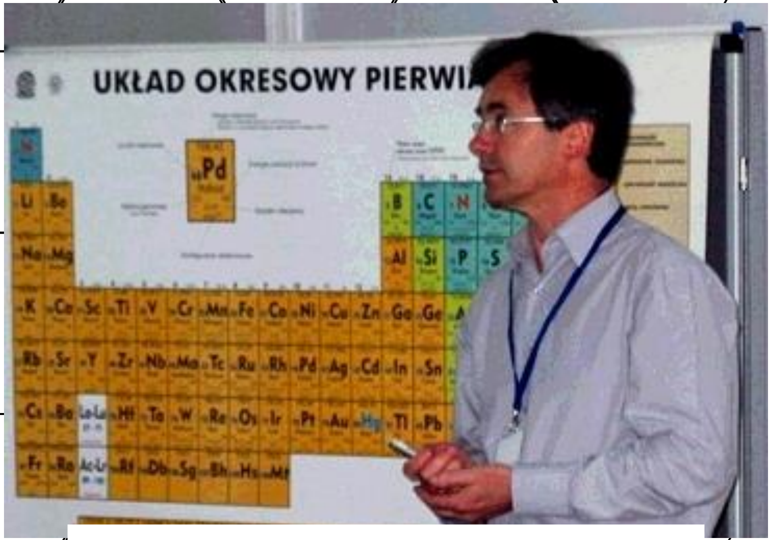

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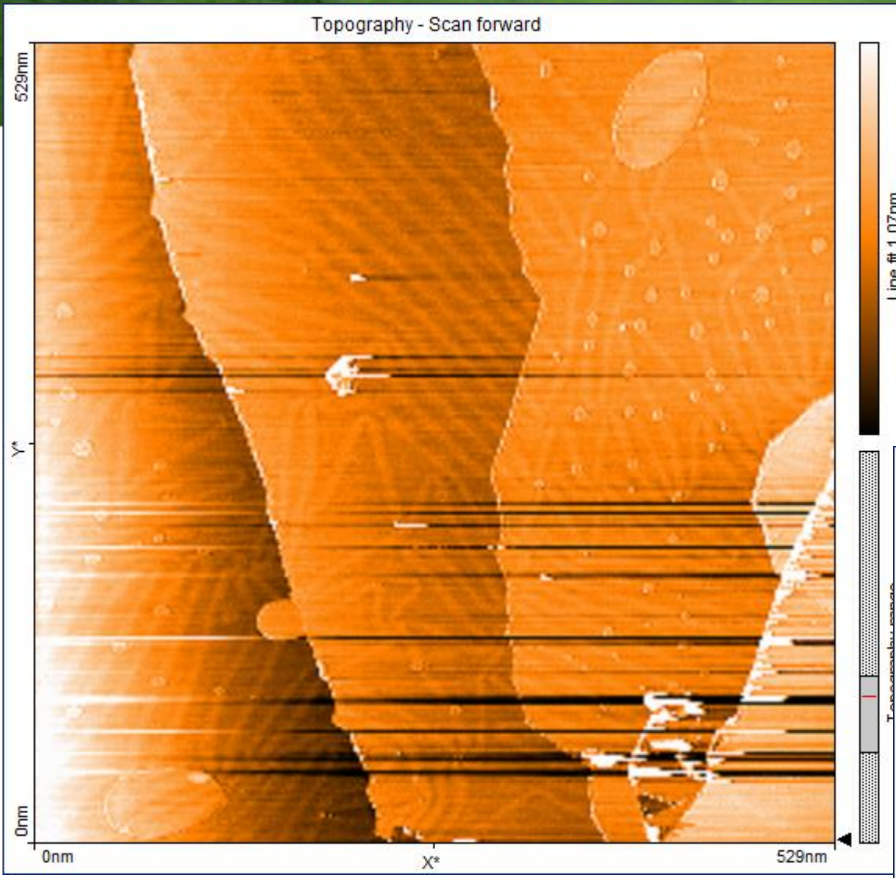
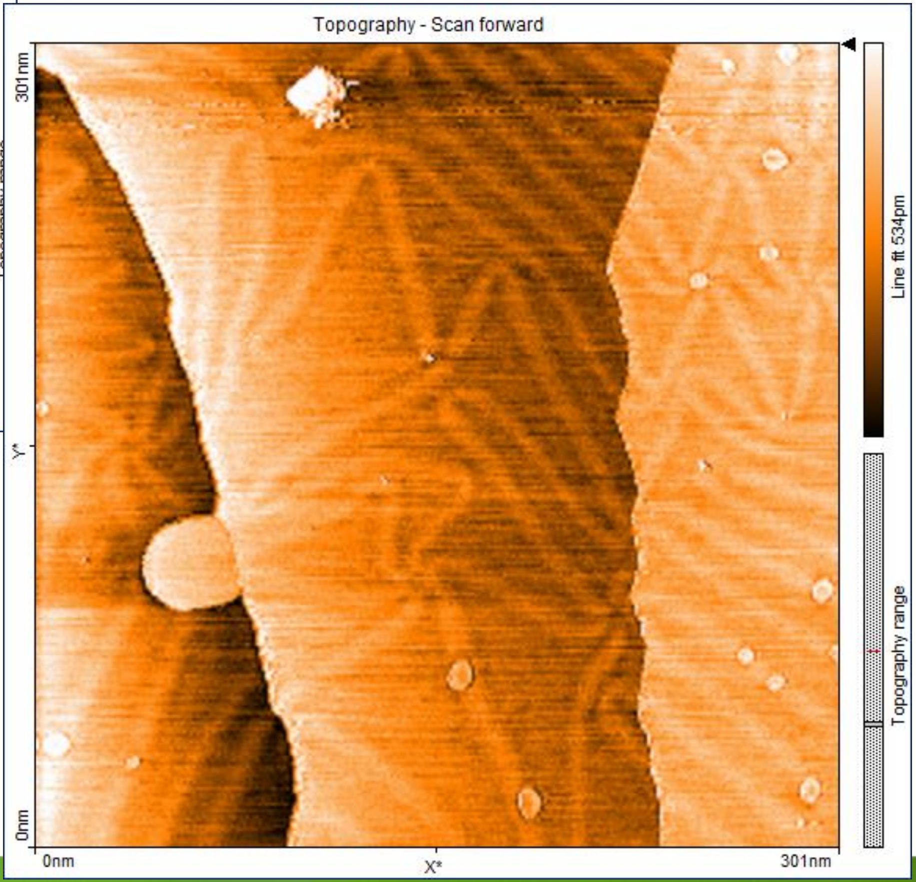

Topography - Scan forward


Topography - Scan forward

dr Jacek Szczytko
Michał Kluz
Izabela Rytarowska

inżynieria nanostruktur

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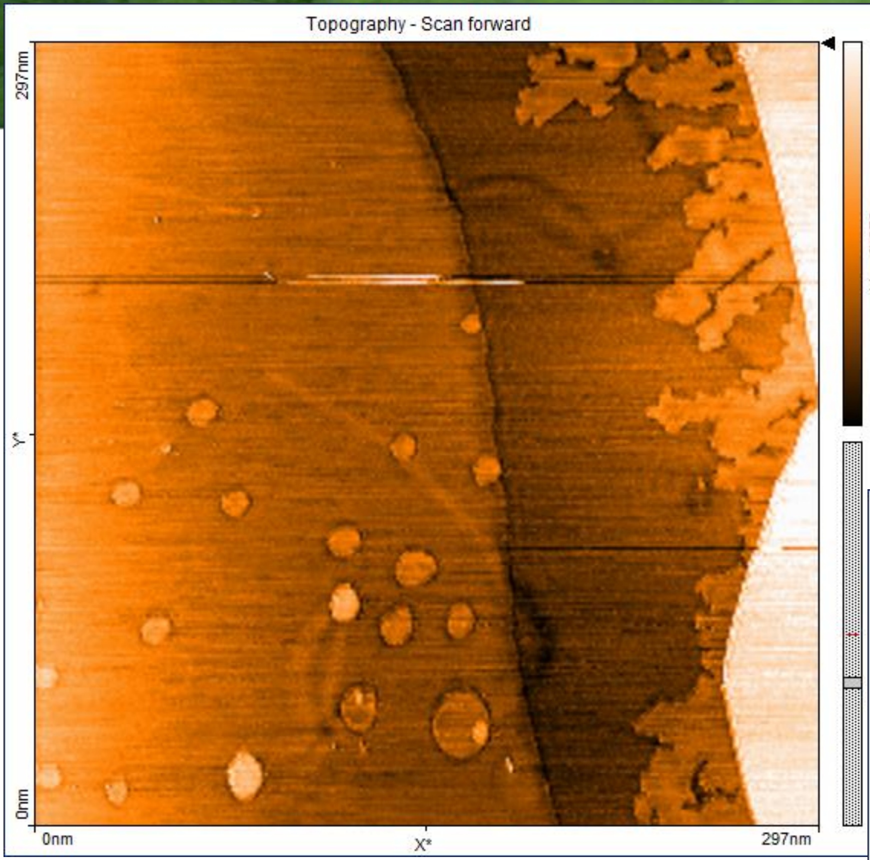

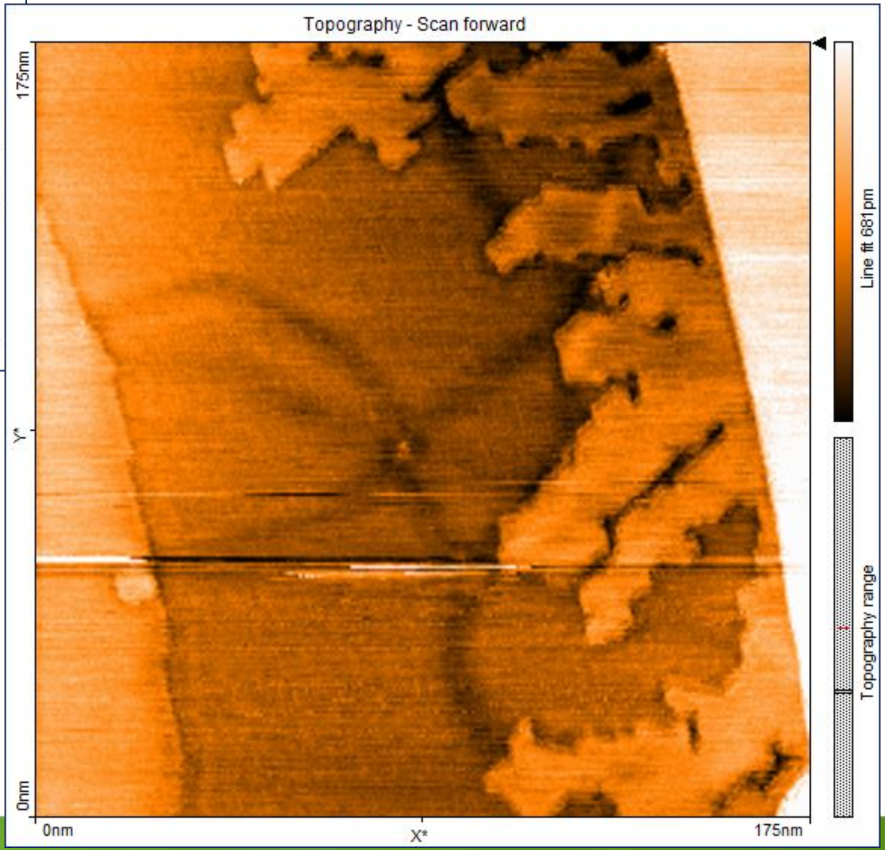

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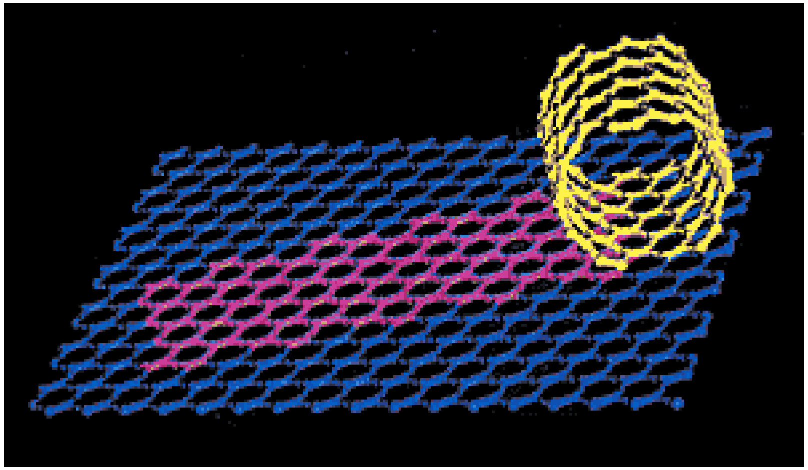
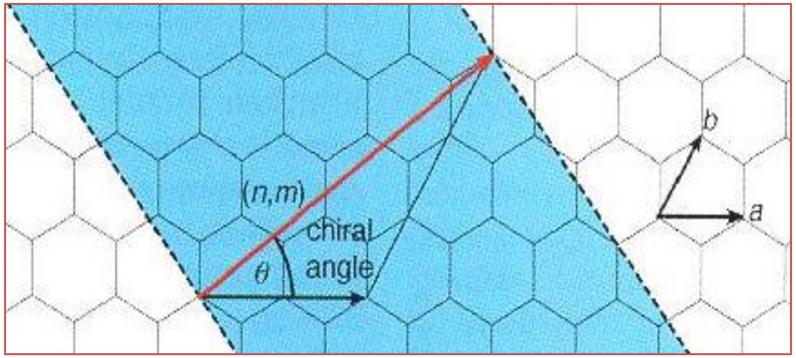
Nanotubes

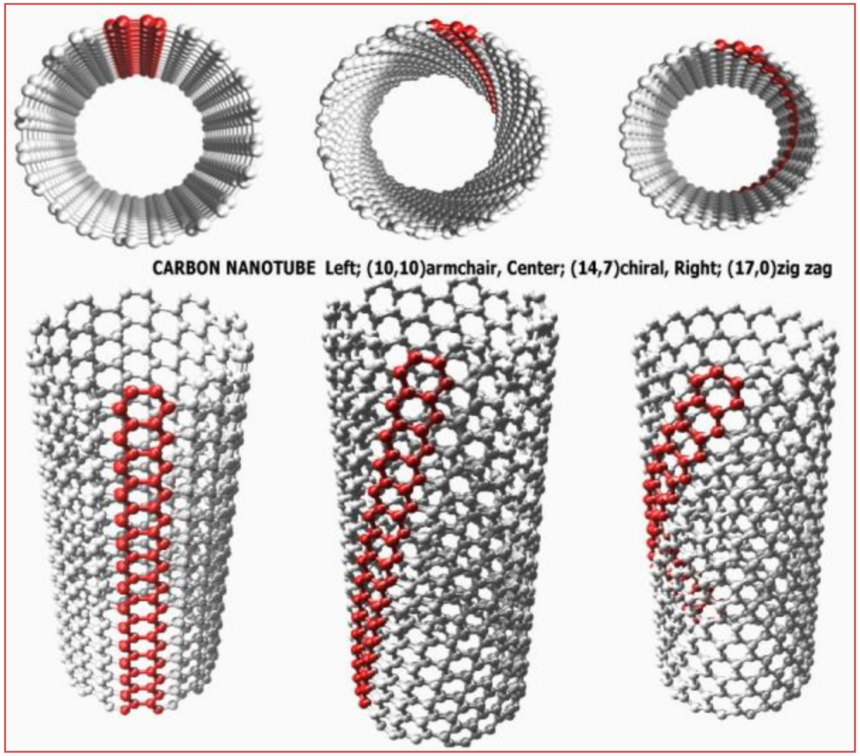




Orientation is defined by the chiral vector (n, m): $c_h = n\,a + m\,b$

Different orientations:

- **Armchair**
- **Zig-zag**
- **Chiral**

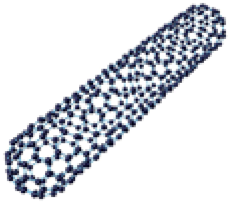


CARBON NANOTUBE Left; (10,10)armchair, Center; (14,7)chiral, Right; (17,0)zig zag

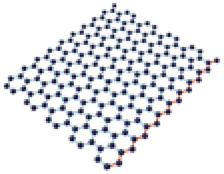
J.Basak, D.Mitra, S.Sinha „*Carbon nanotube: the next generation sensors*” presentation

Paweł Tomasz Pęczkowski

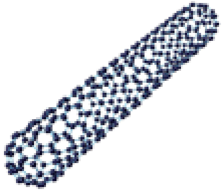
Nanotubes



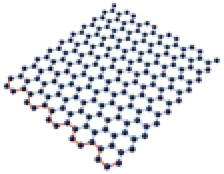
Single Wall Nanotube
(Zig-Zag Type)



Uprolling a Graphene
(Zig-Zag Type)



Single Wall Nanotube
(Arm-Chair Type)



Uprolling a Graphene
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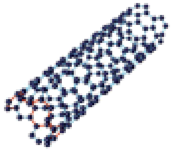
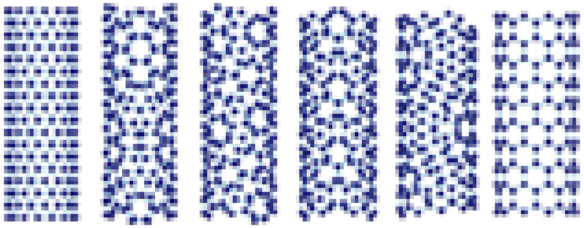
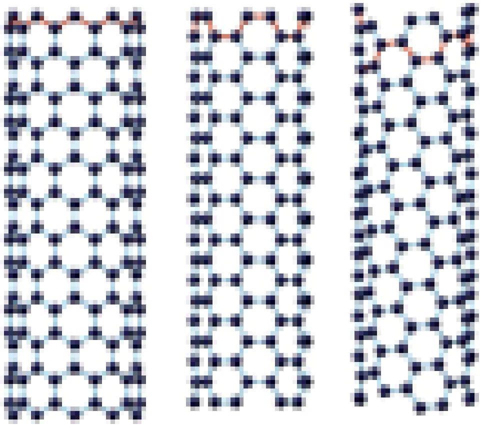
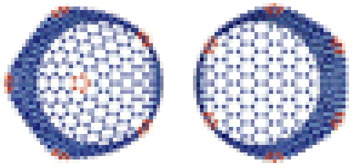
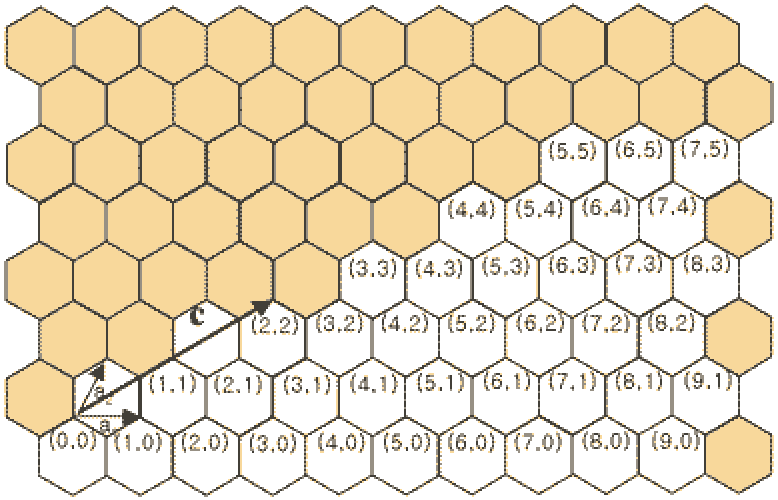


Single Wall Nanotube
(Chiral Type)





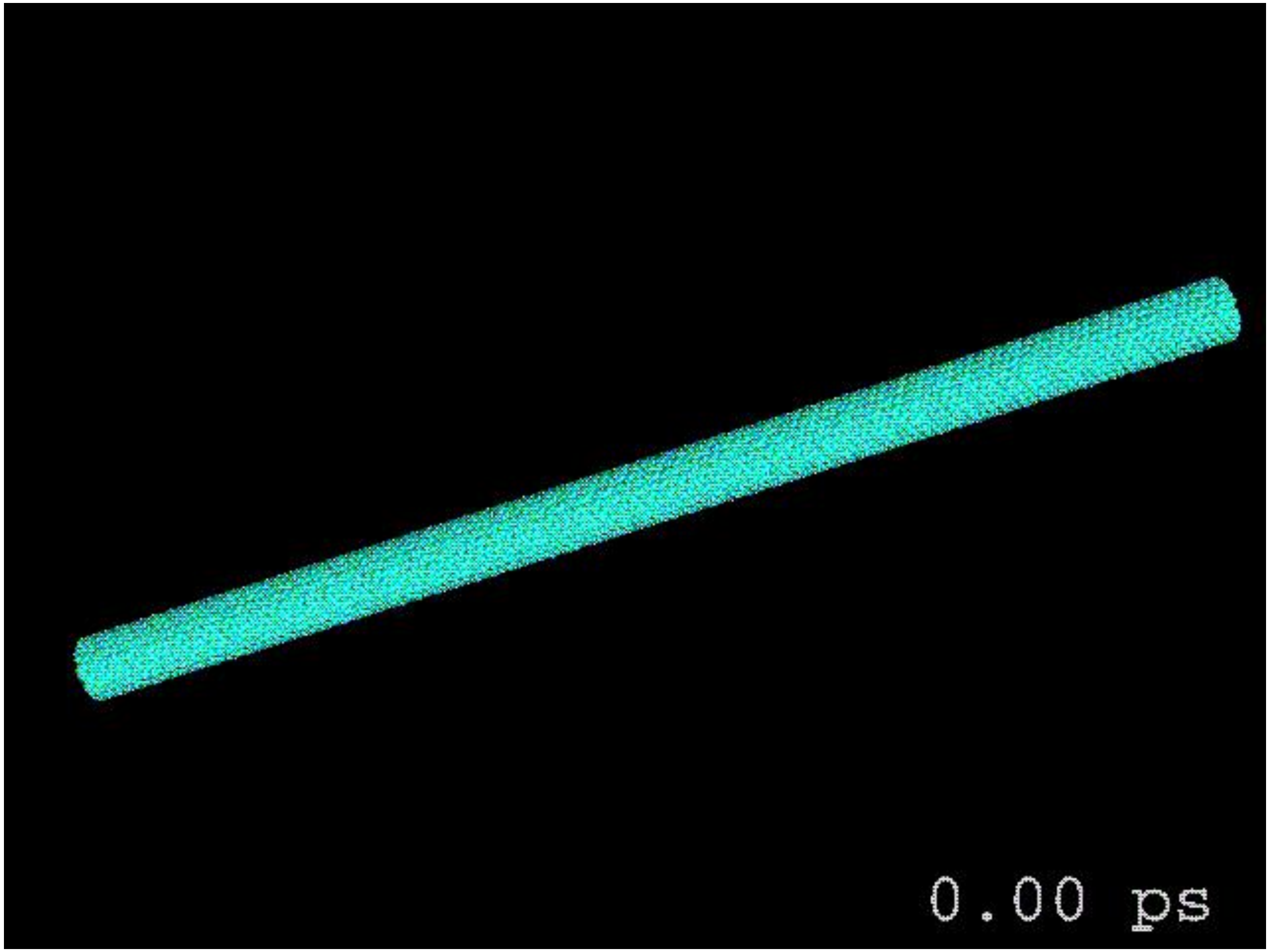




$$\phi = 0.246\,(n^2+nm+m^2)^{1/2} / \pi \text{ (nm)}$$

www.surf.nuqe.nagoya-u.ac.jp/nanotubes/omake/nanotubes/nanotubes.html

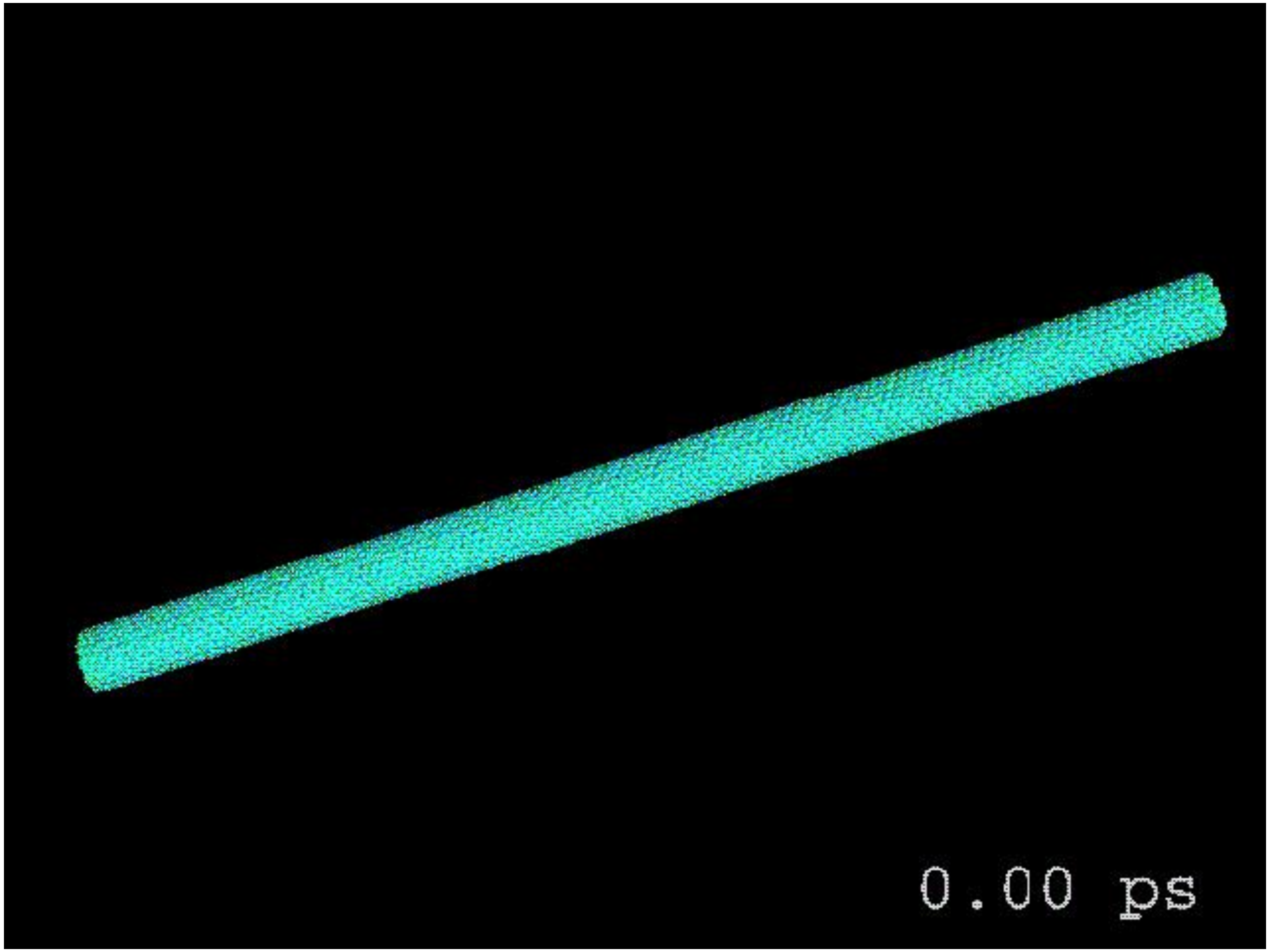
Nanomachines



Single – twist

http://www.ipt.arc.nasa.gov

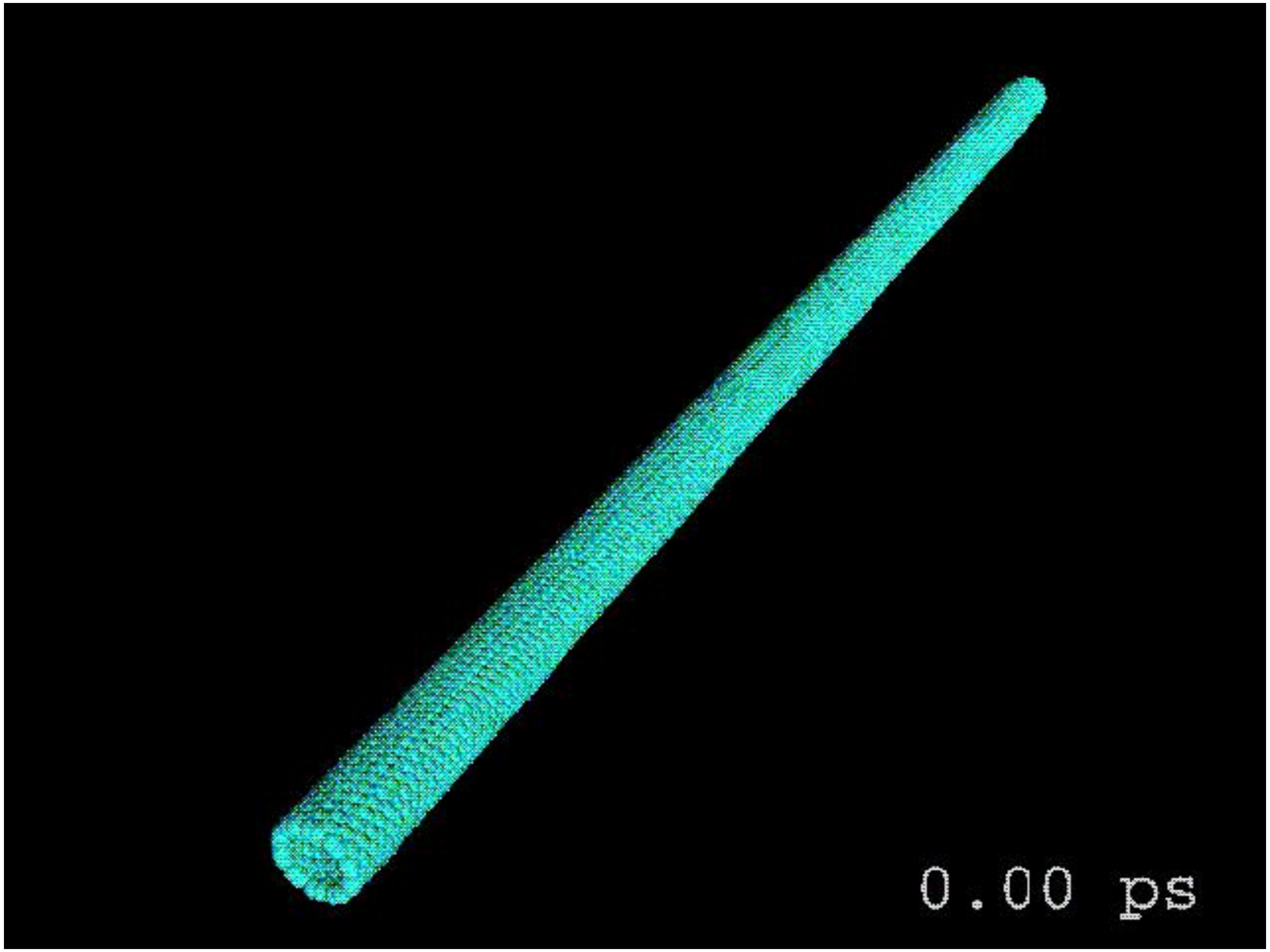
Nanomachines



Single – bend

http://www.ipt.arc.nasa.gov

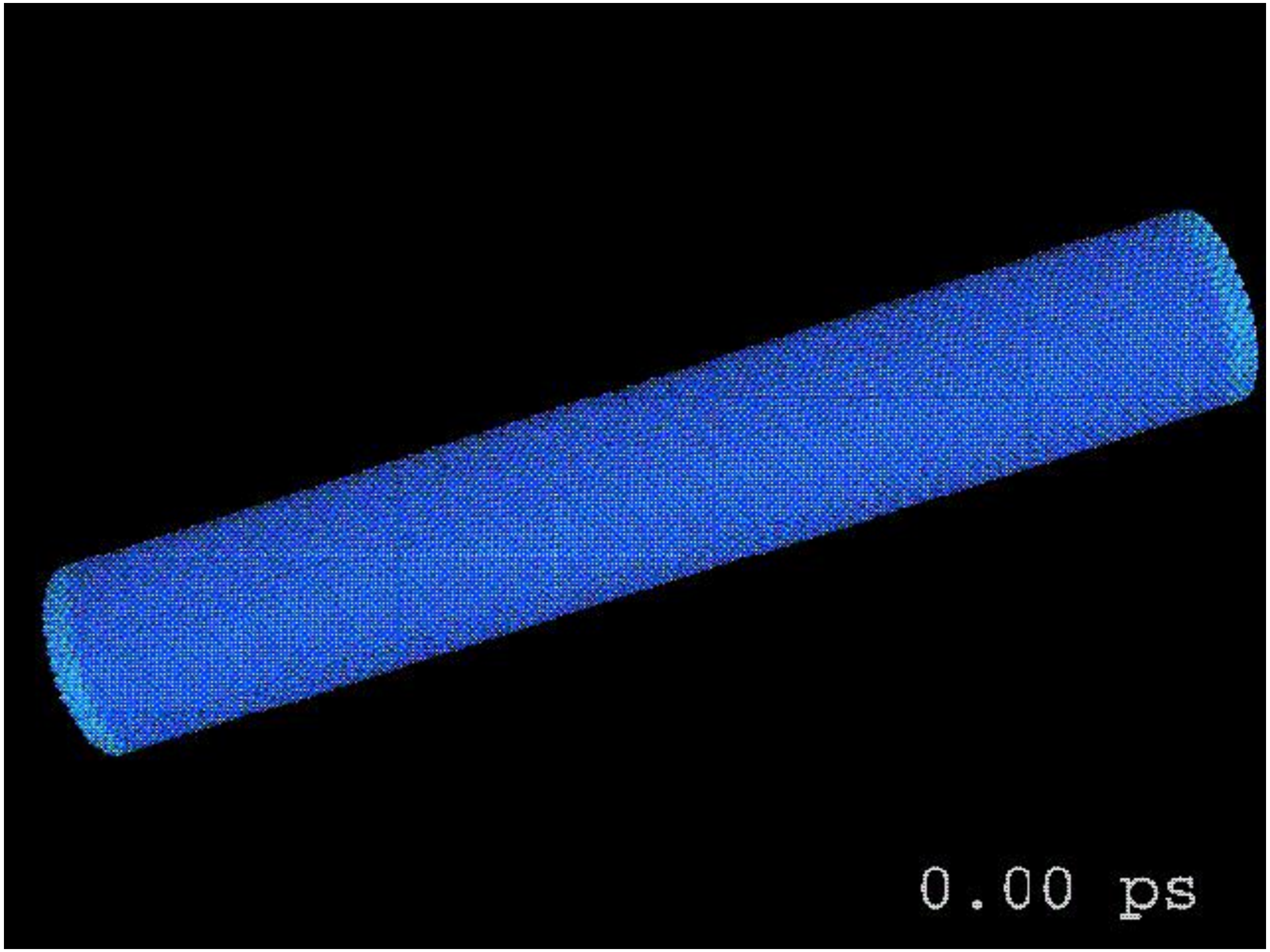
Nanomachines



Single – compress

http://www.ipt.arc.nasa.gov

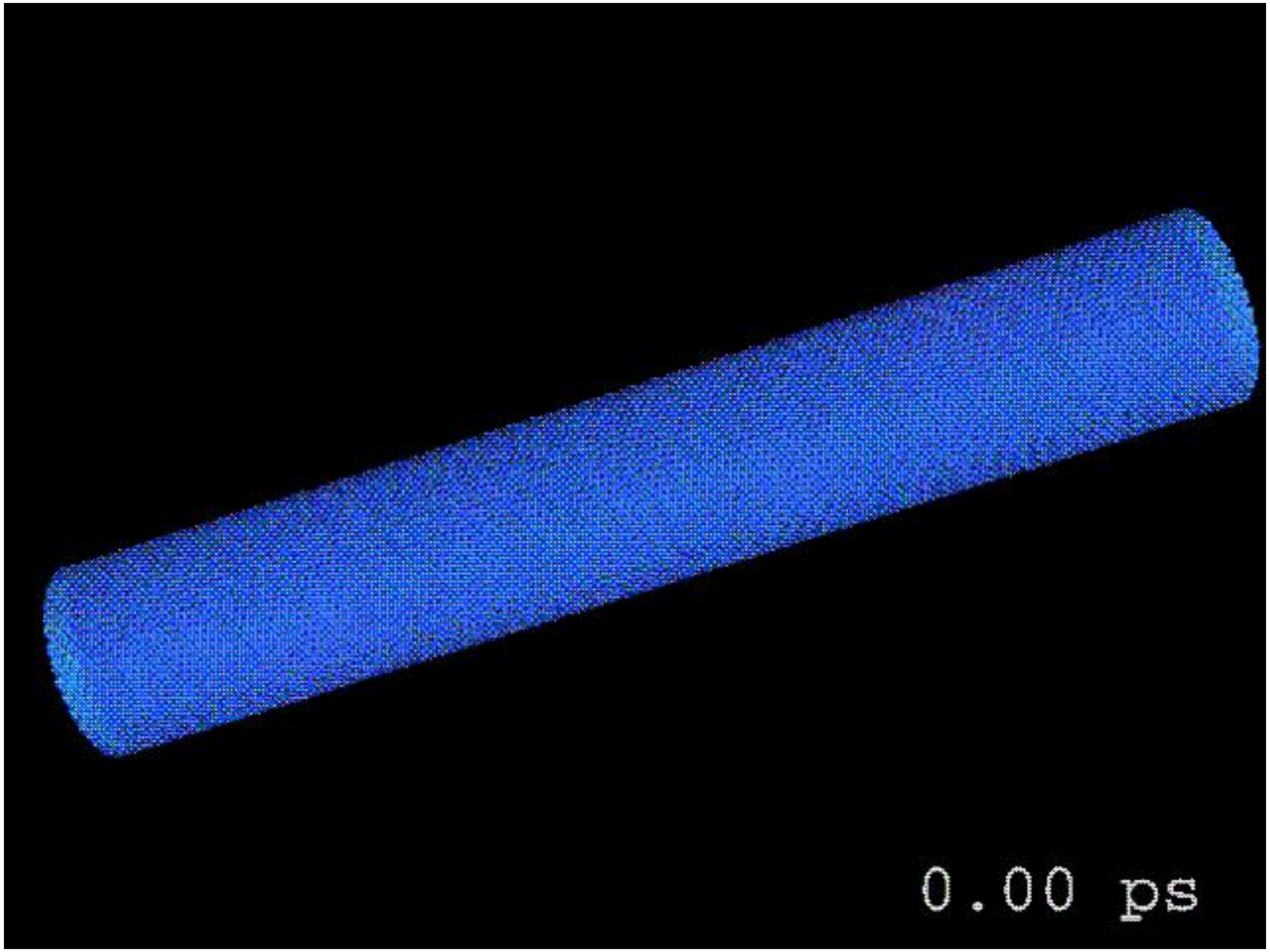
Nanomachines



Multi – twist

http://www.ipt.arc.nasa.gov

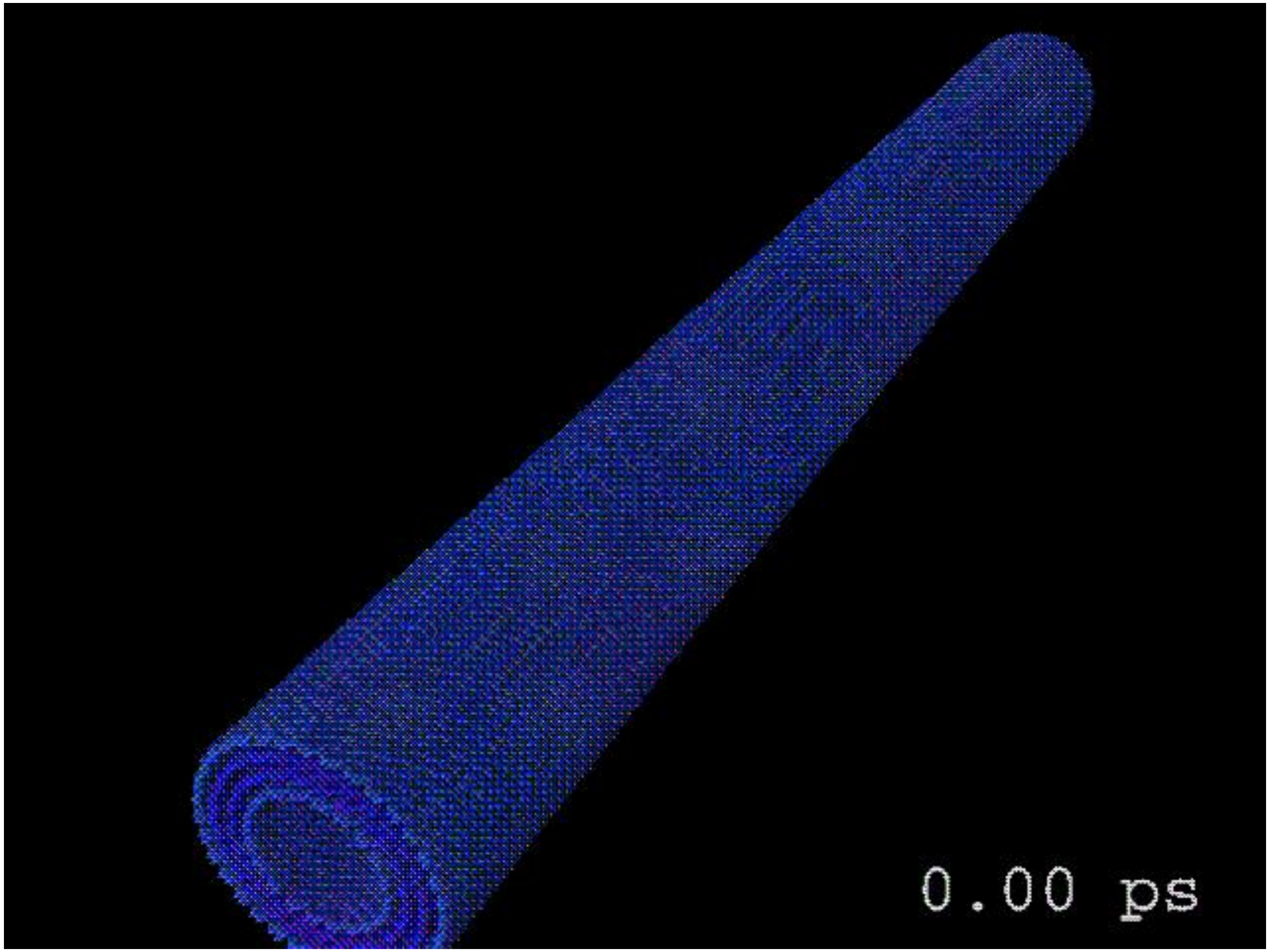
Nanomachines



Multi – bend

http://www.ipt.arc.nasa.gov

Nanomachines



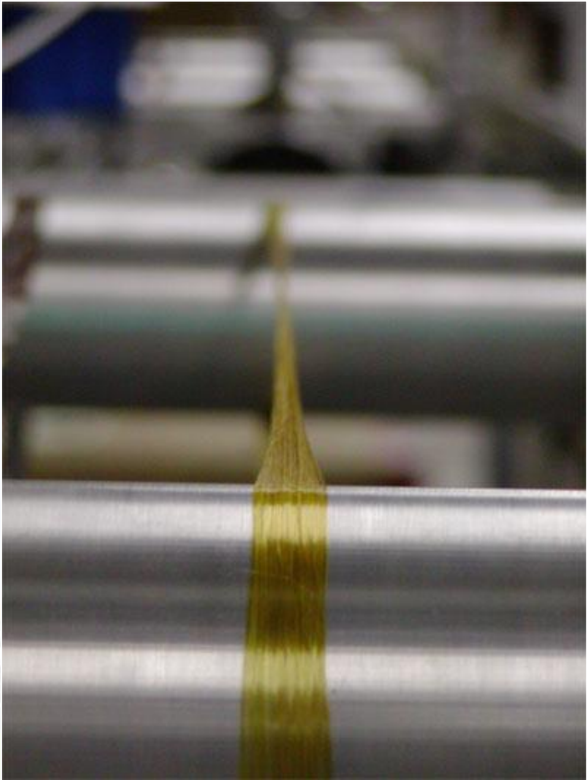
Multi – compress

http://www.ipt.arc.nasa.gov

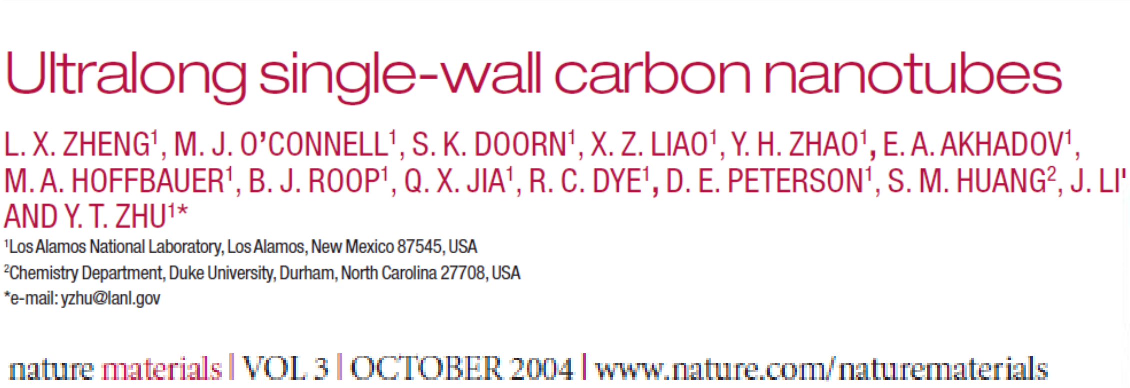
Space elevator

Space elevator

http://www.spaceelevator.com/



Space elevator



LETTERS

Ultralong single-wall carbon nanotubes

L. X. ZHENG[1], M. J. O'CONNELL[1], S. K. DOORN[1], X. Z. LIAO[1], Y. H. ZHAO[1], E. A. AKHADOV[1],
M. A. HOFFBAUER[1], B. J. ROOP[1], Q. X. JIA[1], R. C. DYE[1], D. E. PETERSON[1], S. M. HUANG[2], J. LI
AND Y. T. ZHU[1]*

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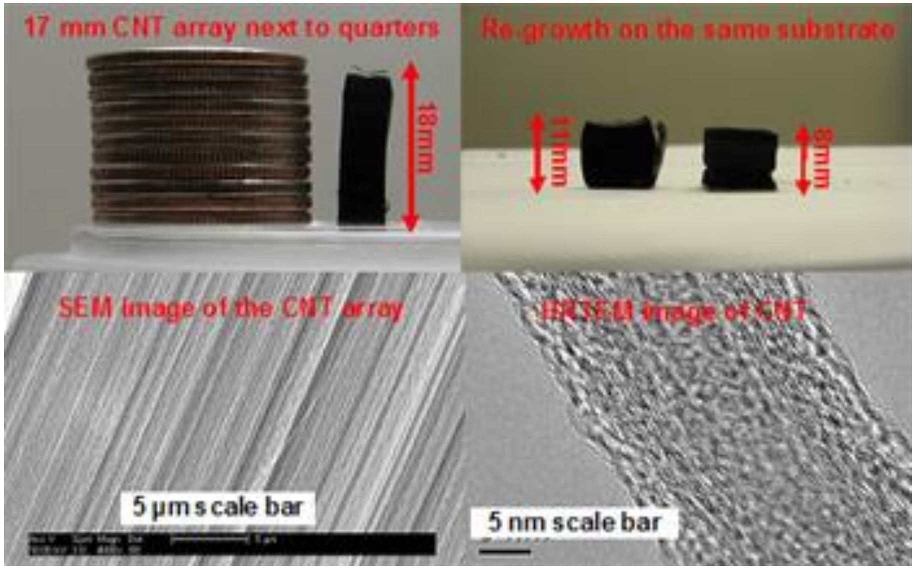
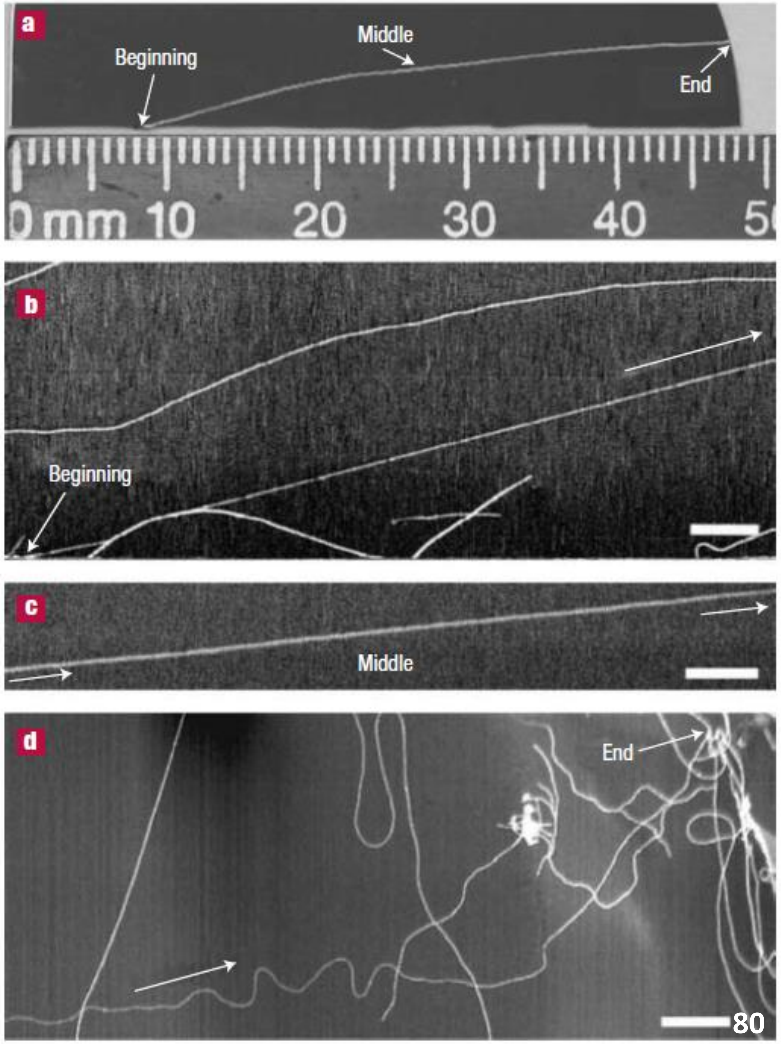
[2]Chemistry Department, Duke University, Durham, North Carolina 27708, USA
*e-mail: yzhu@lanl.gov

nature materials | VOL 3 | OCTOBER 2004 | www.nature.com/naturematerials

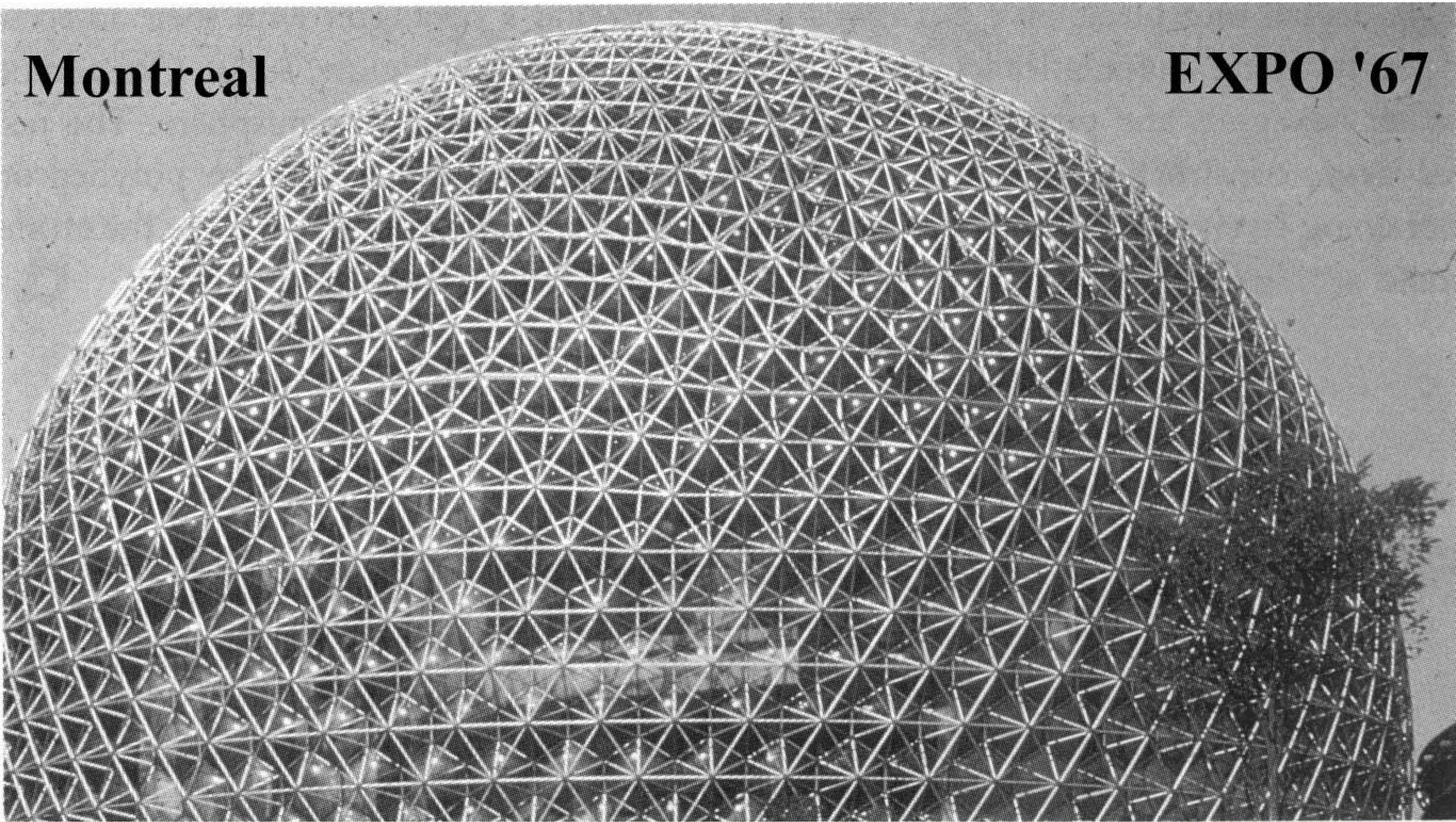


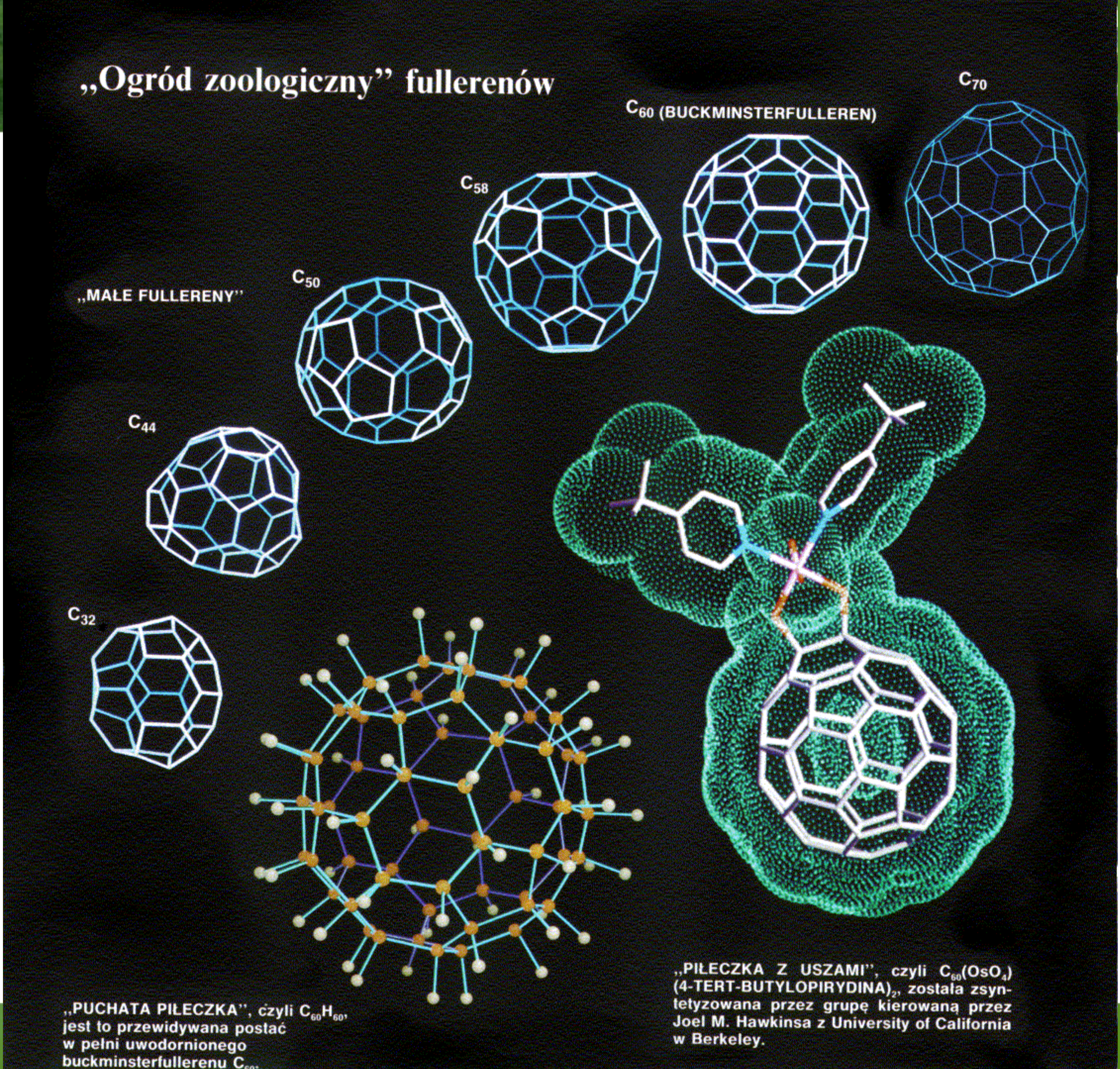
http://www.uc.edu/news/NR.asp?id=5700



Fullerenes

Buckminster Fuller pour un exposition en 1967 à Montréal



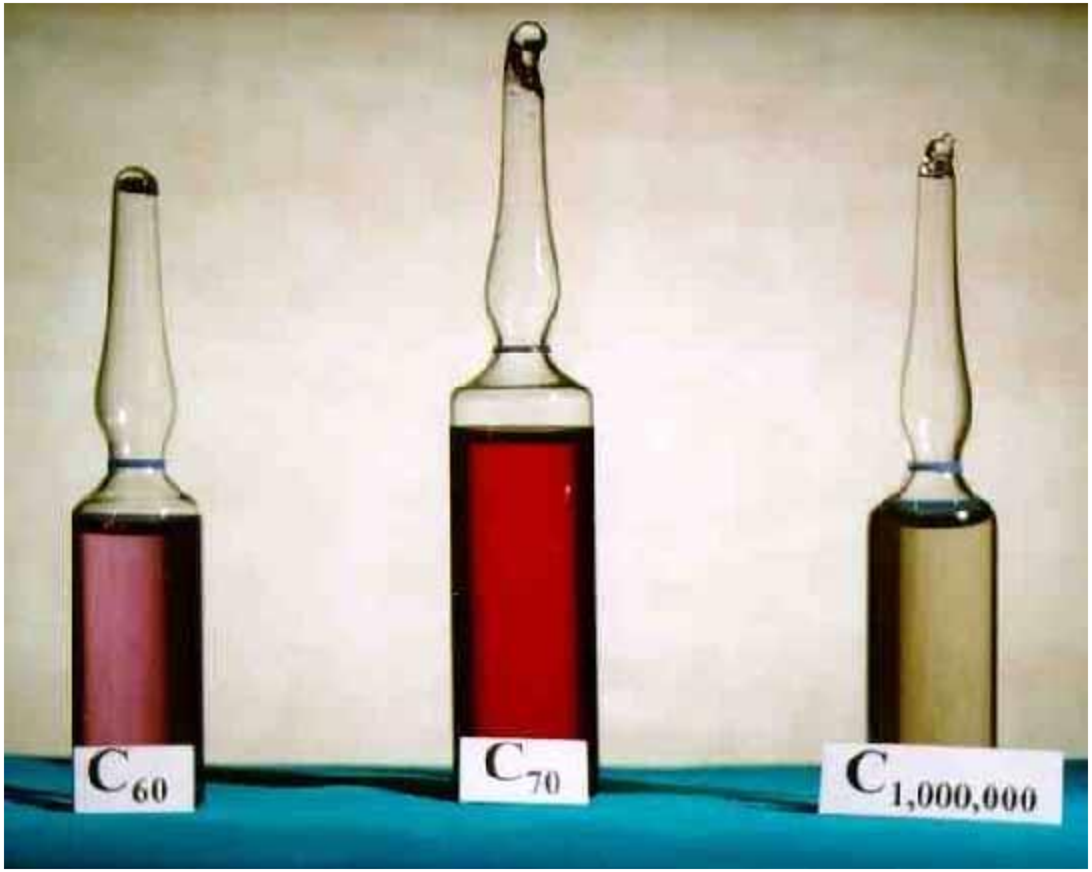


„Ogród zoologiczny” fullerenów

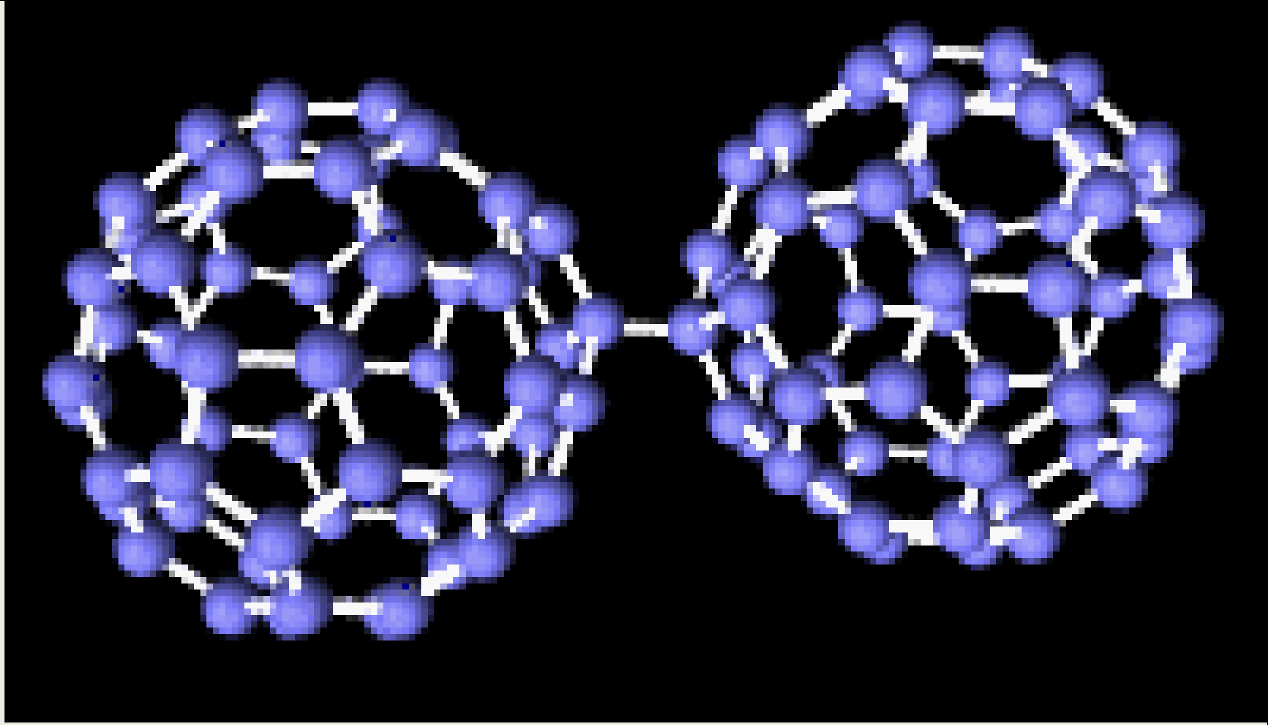
„PUCHATA PIŁECZKA”, czyli $C_{60}H_{60}$, jest to przewidywana postać w pełni uwodornionego buckminsterfullerenu C_{60}.

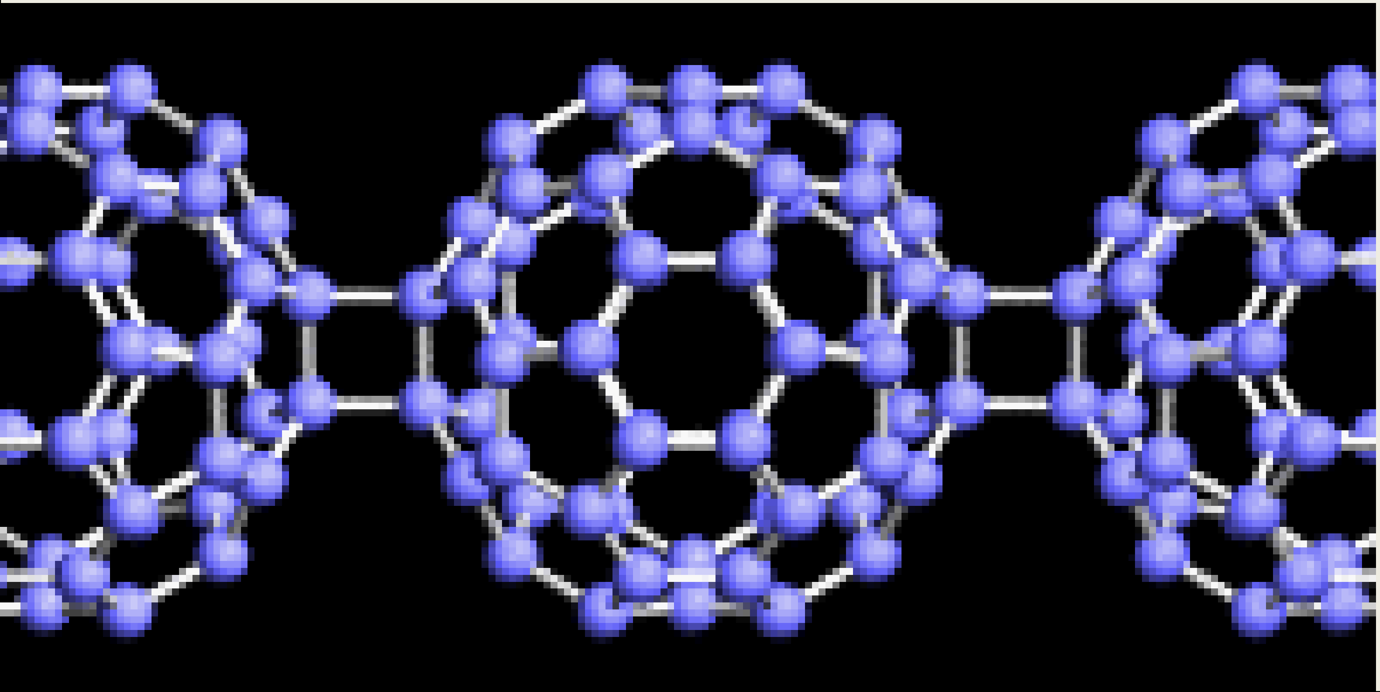
„PIŁECZKA Z USZAMI”, czyli $C_{60}(OsO_4)$(4-TERT-BUTYLOPIRYDINA)$_2$, została zsyntetyzowana przez grupę kierowaną przez Joel M. Hawkinsa z University of California w Berkeley.

Fullerenes

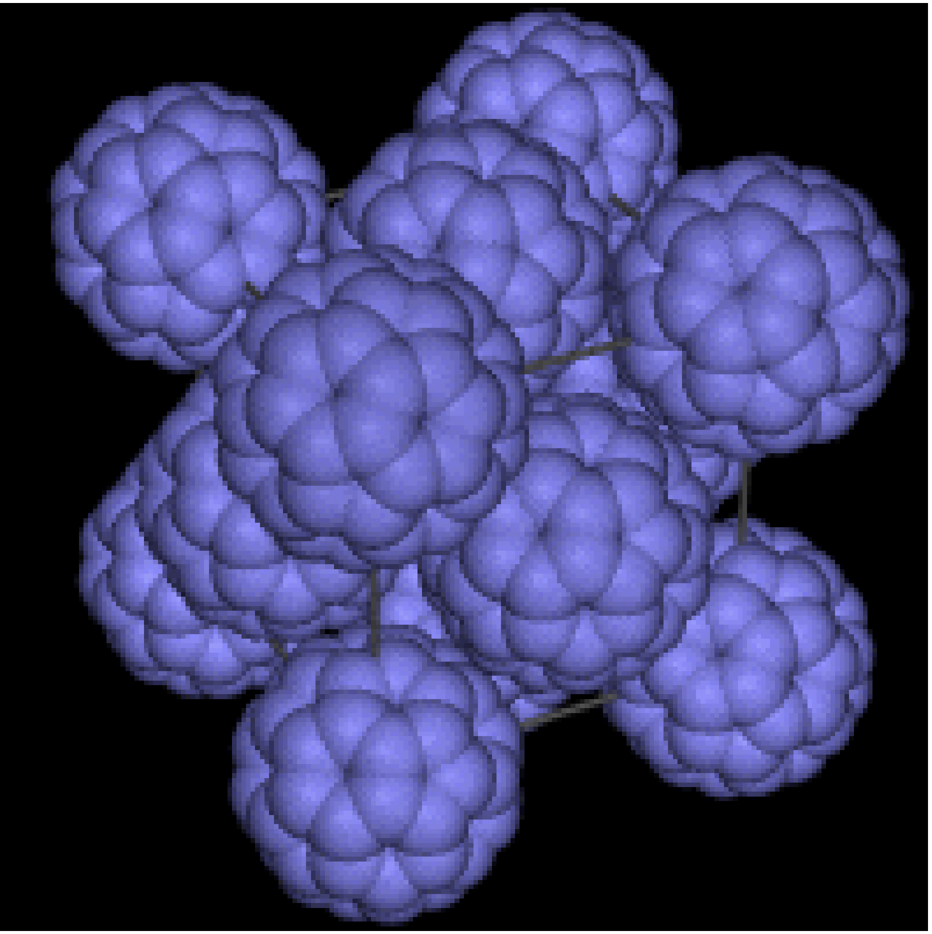


Solutions in toluene

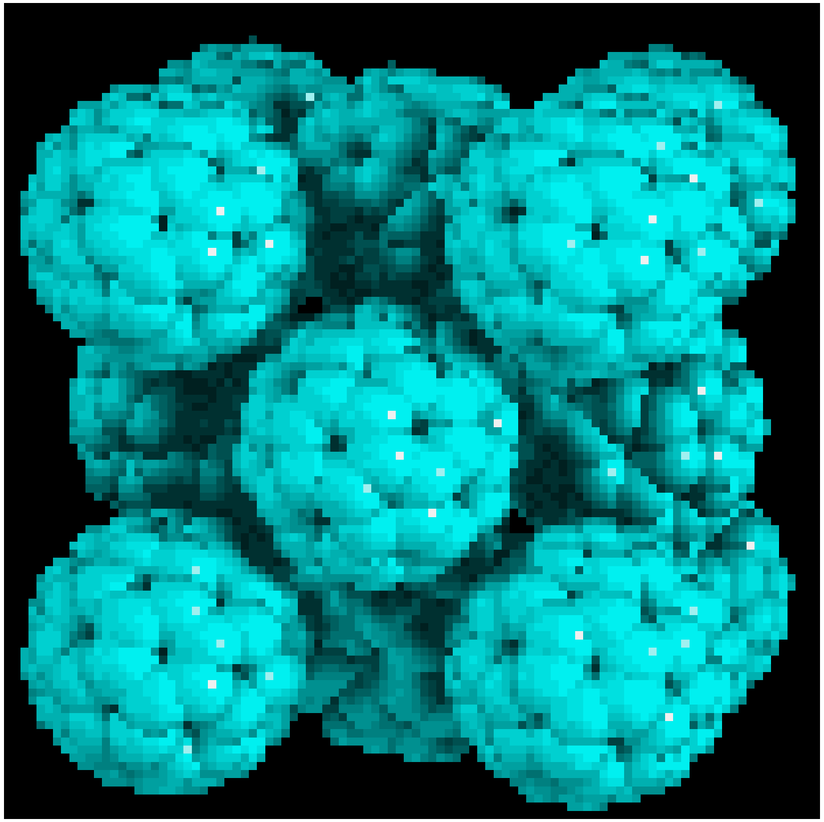




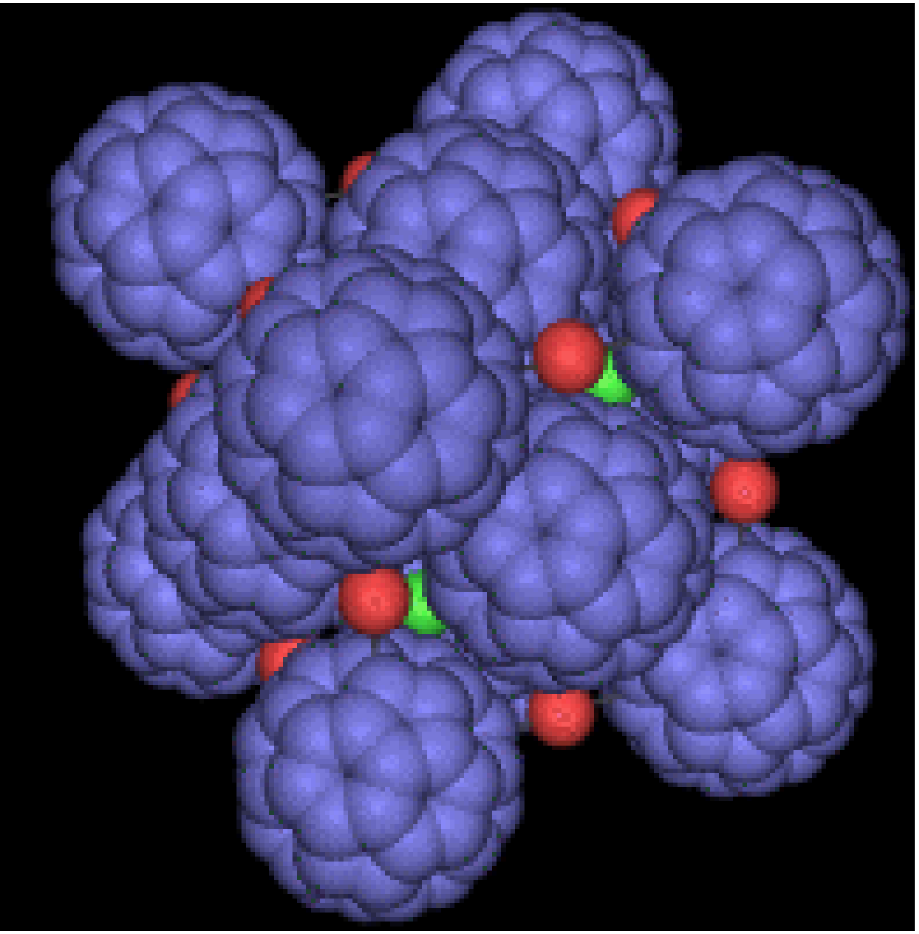
Fullerenes

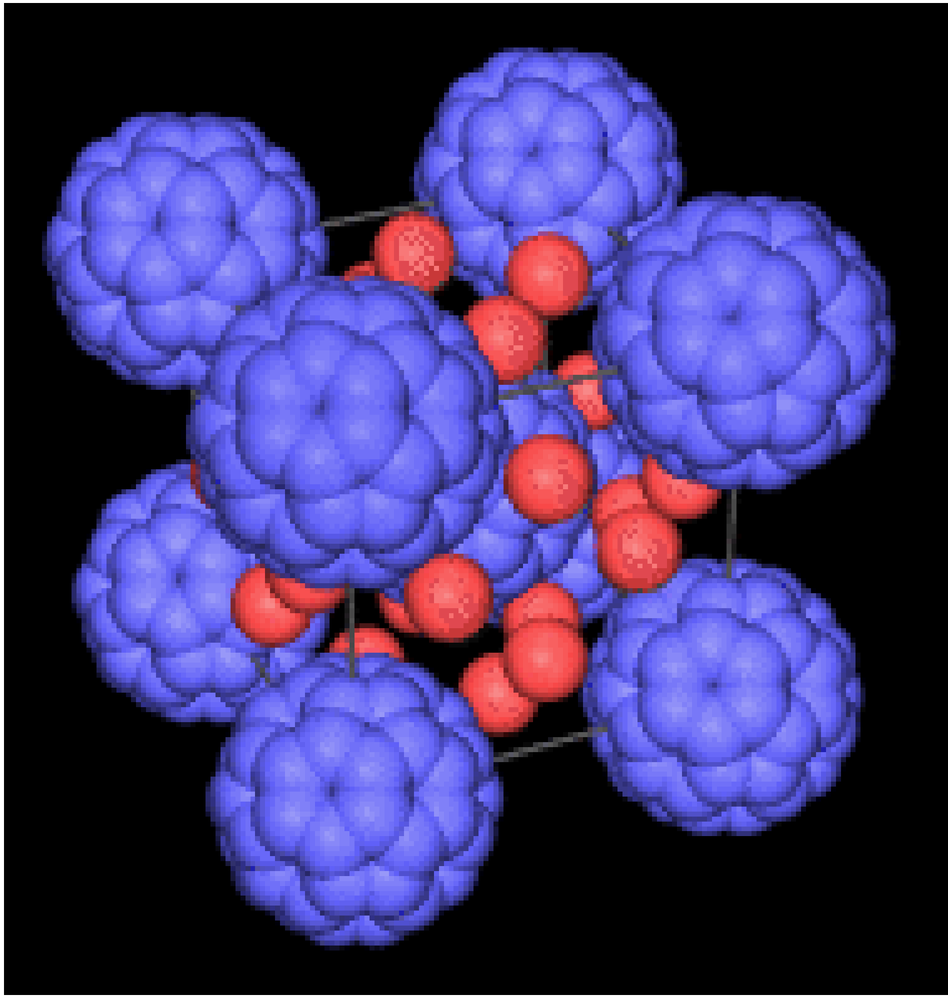


fcc C_{60} crystals



Fullerenes

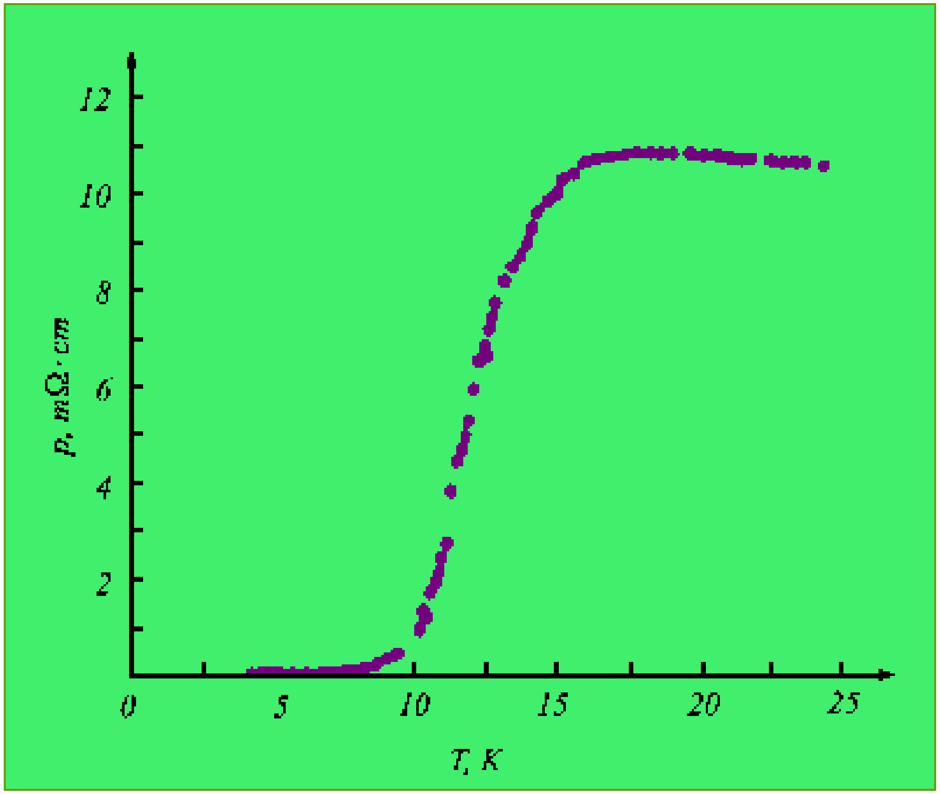




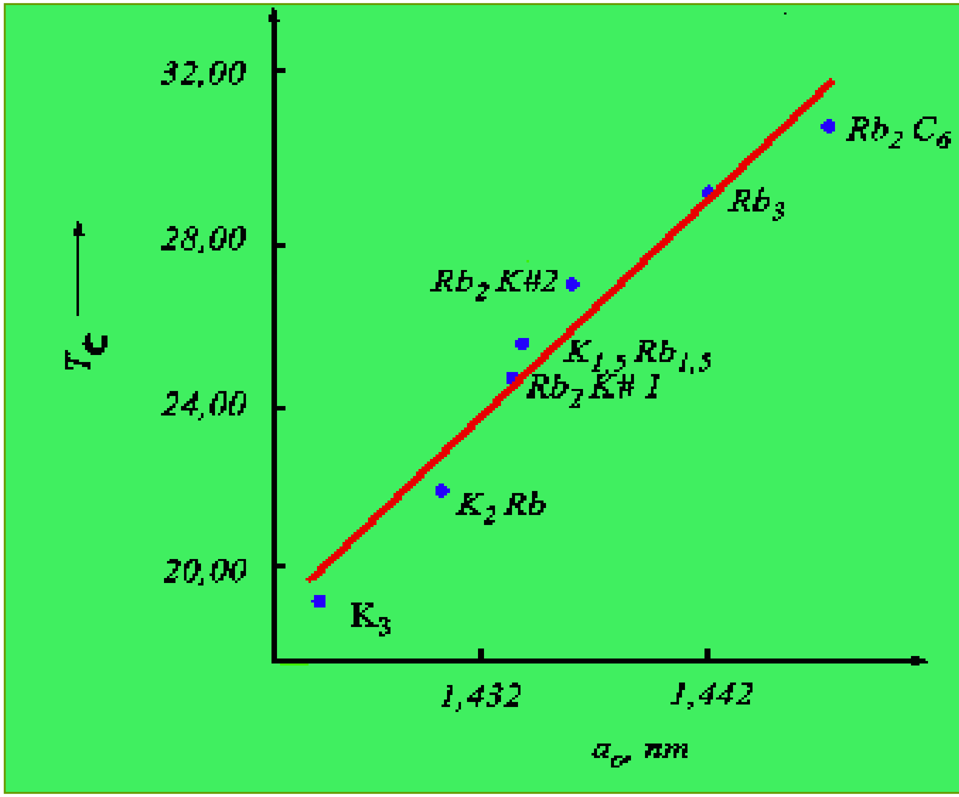
Superconductivity K_3C_{60}

X.D. Xiang, J.G. Hou, et al. Nature 361, 54, 1993

Zależność oporu właściwego K_3C_{60} od temperatury

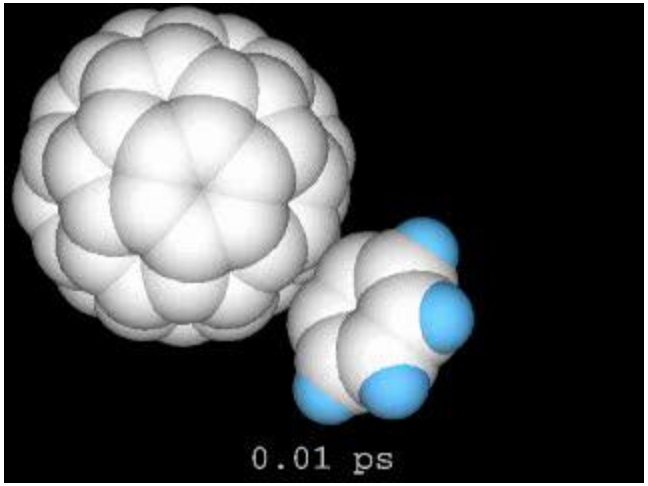


Zależność Tc od stałej sieci

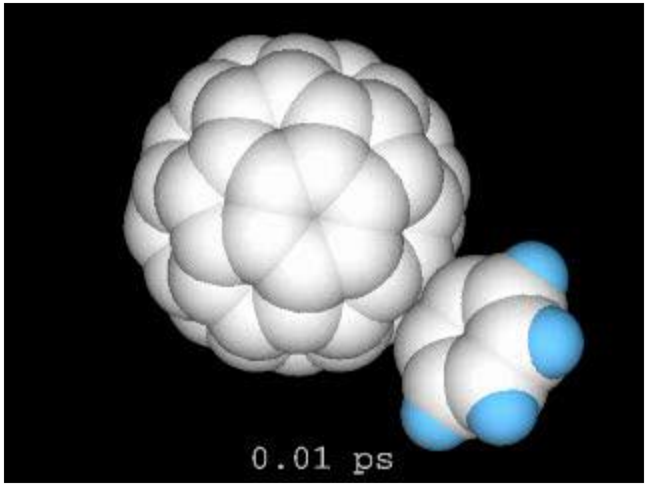


Nanomachines

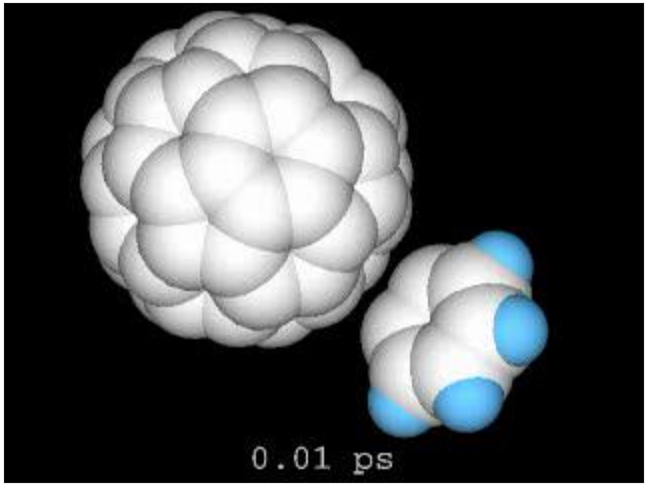
Benzene + C_{60}



Za wolno



Za szybko



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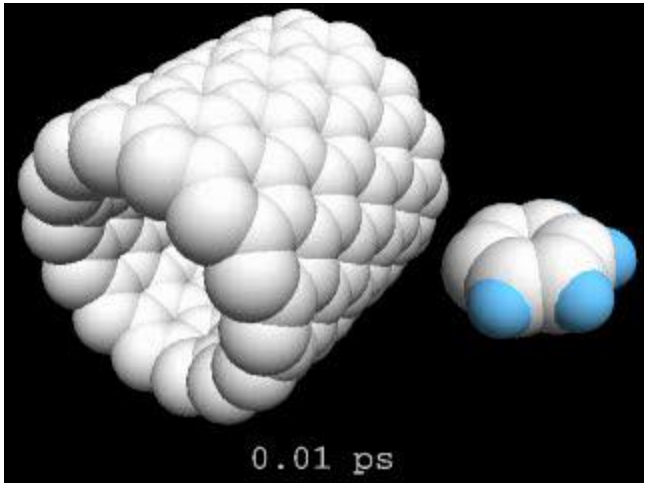
Benzen + CN



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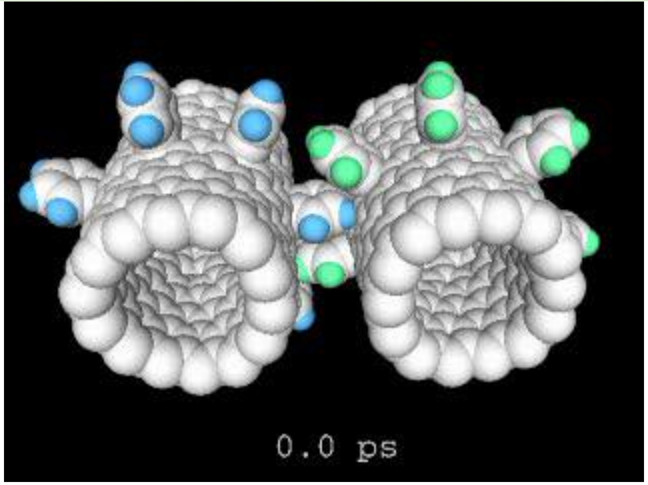
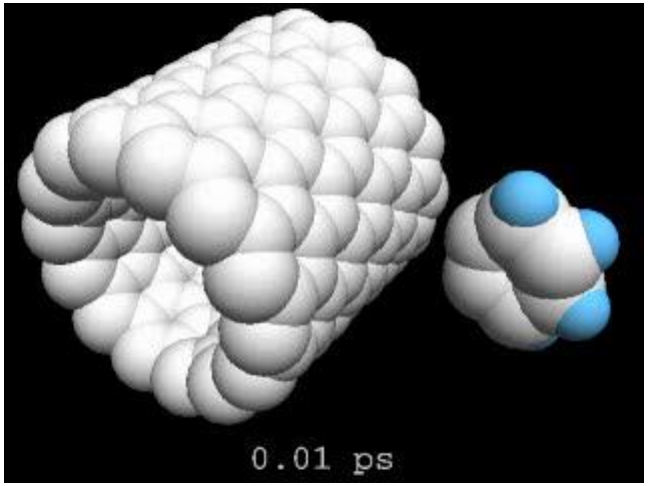
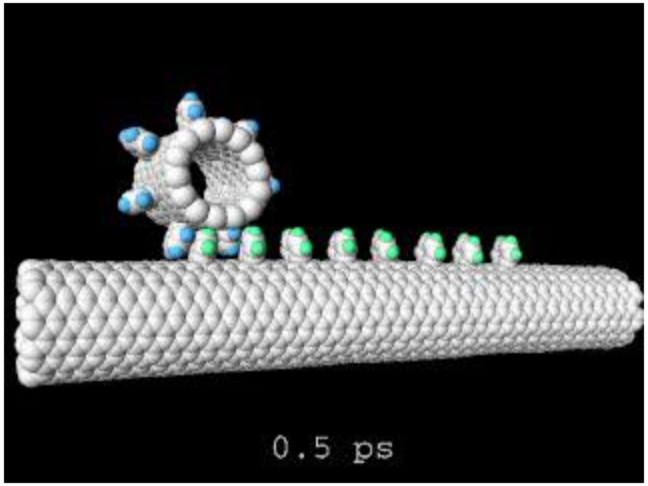


Gear Rotation in a Vacuum 200 rot/ns



W sam raz



Powered Shaw

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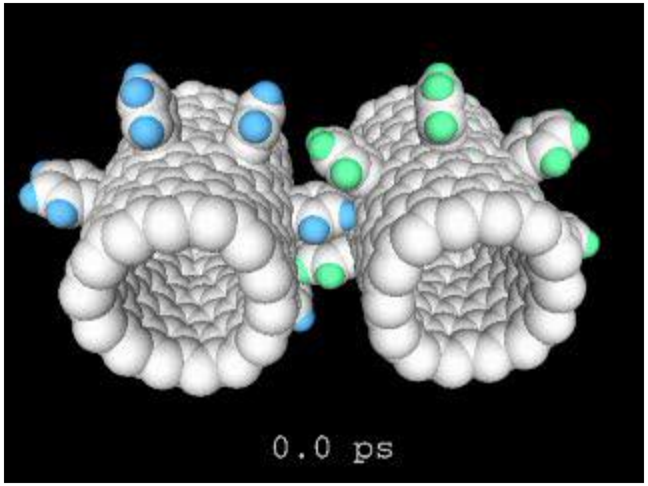
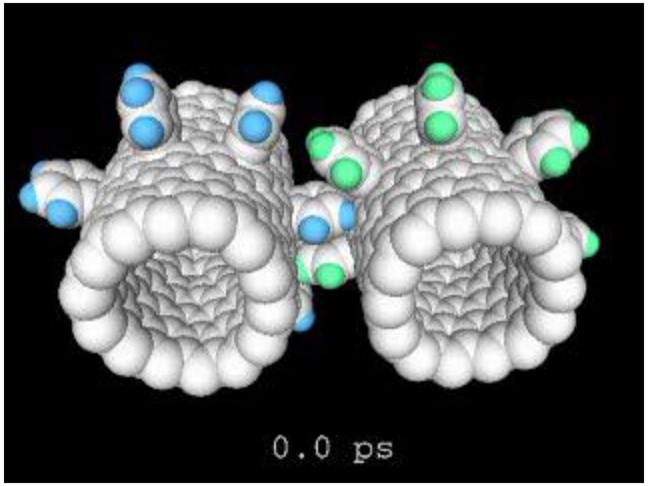
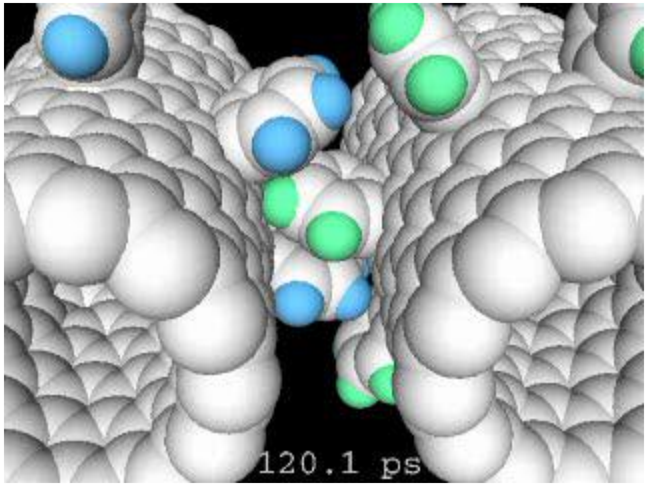


Gear Rotation at RT 50/70/100 rot/ns



Gear Rotation at RT 50 rot/ns



Too fast > 100 rot/ns

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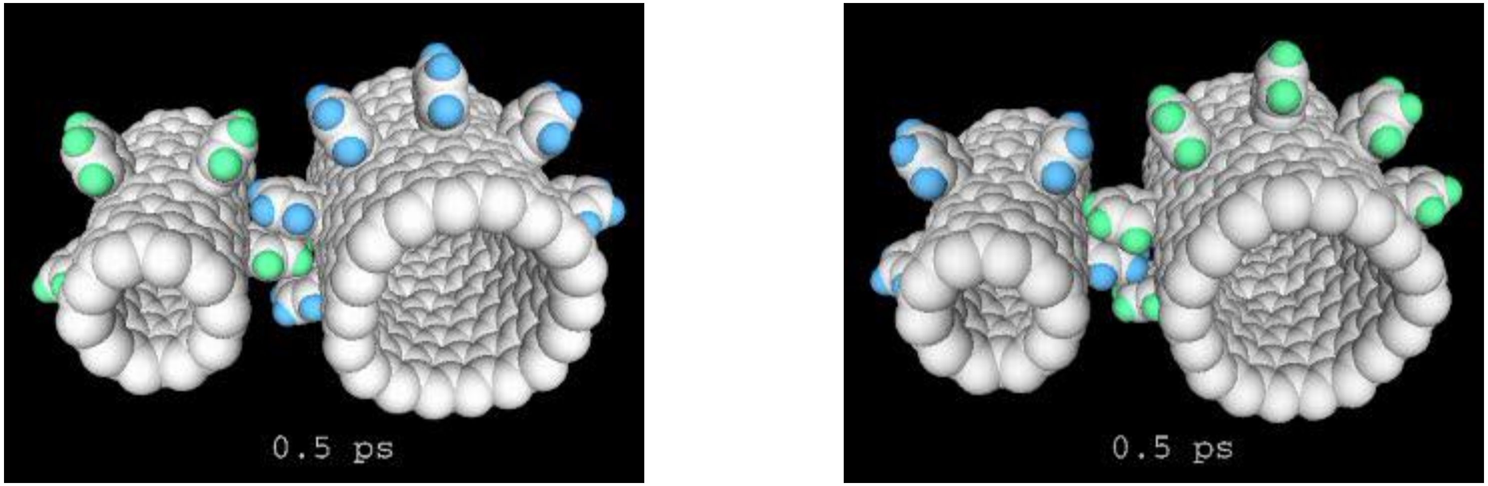
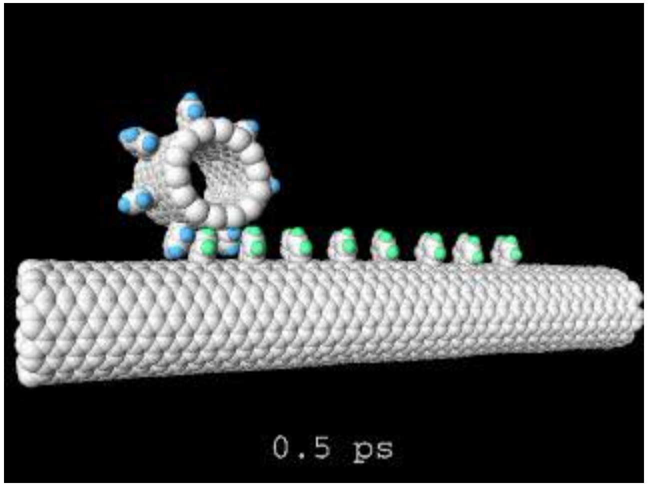
Large Gear Drives Small Gear



Gear and Shaft Operation



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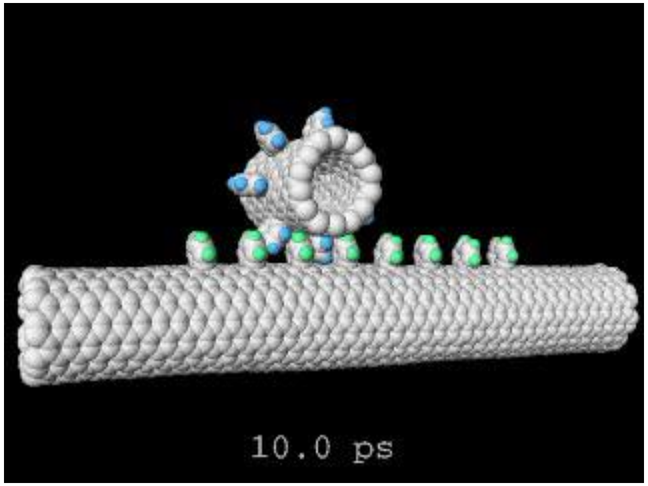

Powered Gear

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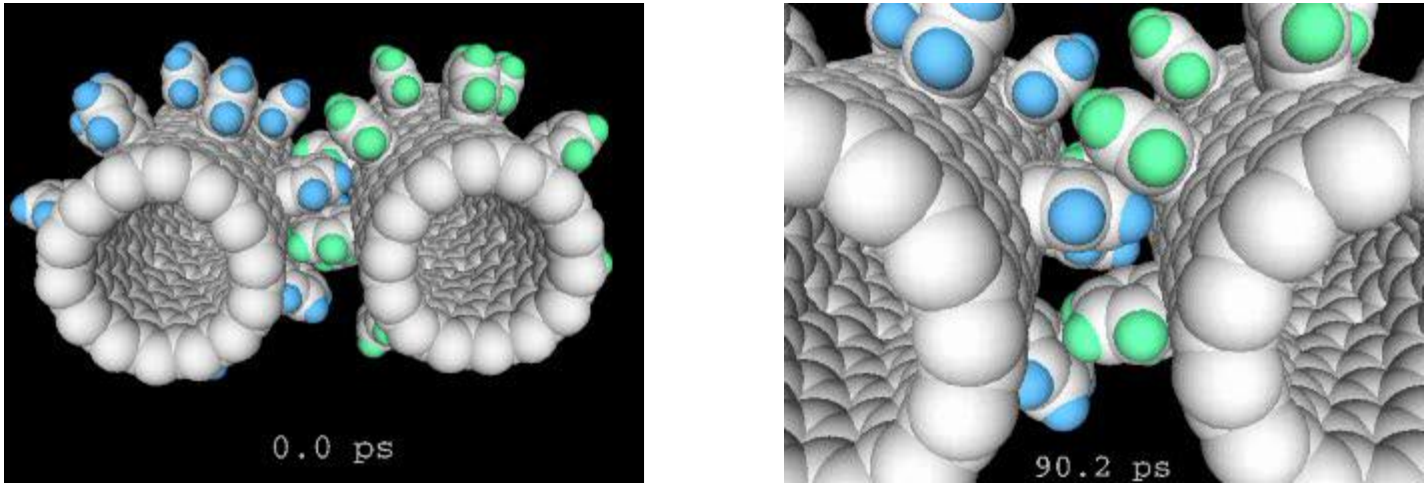
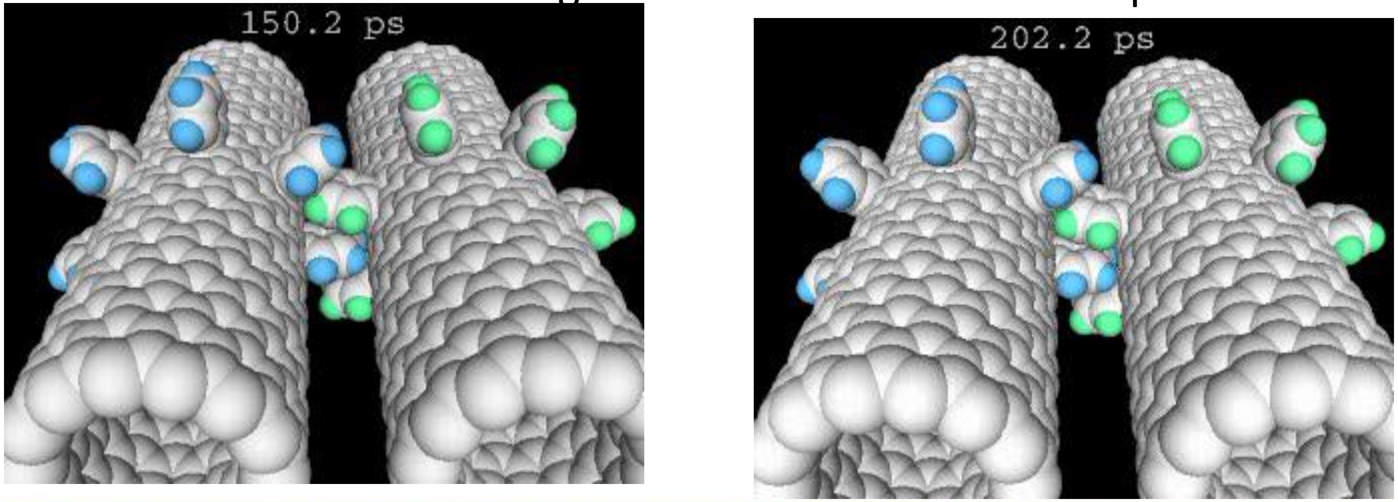
Nanomachines

Rotation of Gears with Two Off-line Rows of Teeth



Zbyt szybko

Long Gear Rotation at Room Temperature



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Startup

Rotating

VOLUME 69, NUMBER 6 PHYSICAL REVIEW LETTERS 10 AUGUST 1992

Negatively Curved Graphitic Sheet Model of Amorphous Carbon

S. J. Townsend,(a) T. J. Lenosky,(a) D. A. Muller,(a) C. S. Nichols,(b) and V. Elser(a)
Cornell University, Ithaca, New York 14853

(Received 9 April 1992)

„plumber's nightmare"

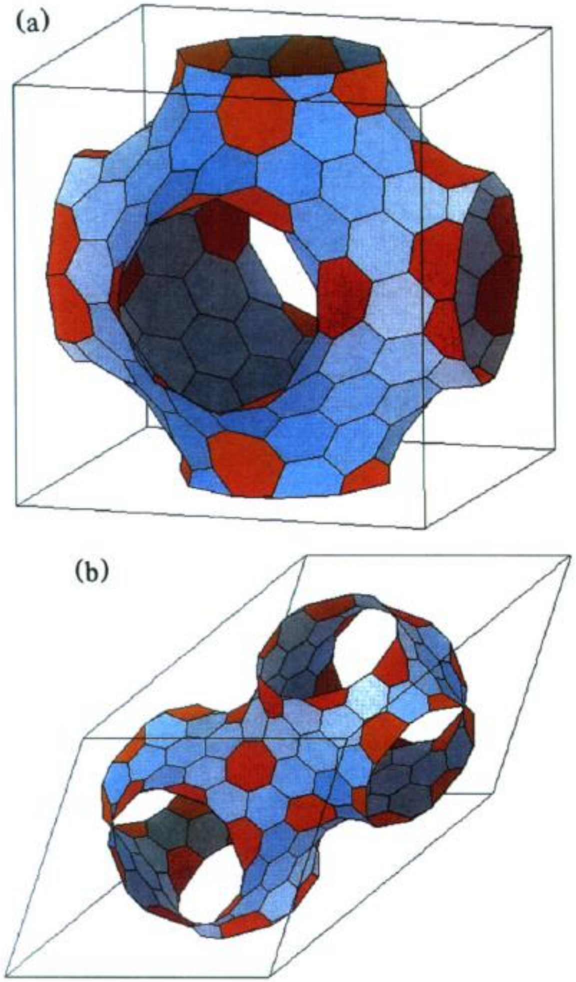

FIG. 1. Views of two new crystalline schwarzites. Each has 216 carbon atoms per primitive unit cell with 80 six-membered rings (blue) and 24 seven-membered rings (orange). The structure in (a) lies on a *P* minimal surface in a cubic cell 15.7 Å on a side. The structure in (b) lies on a *D* minimal surface in an fcc cell whose cubic lattice constant is 24.6 Å.

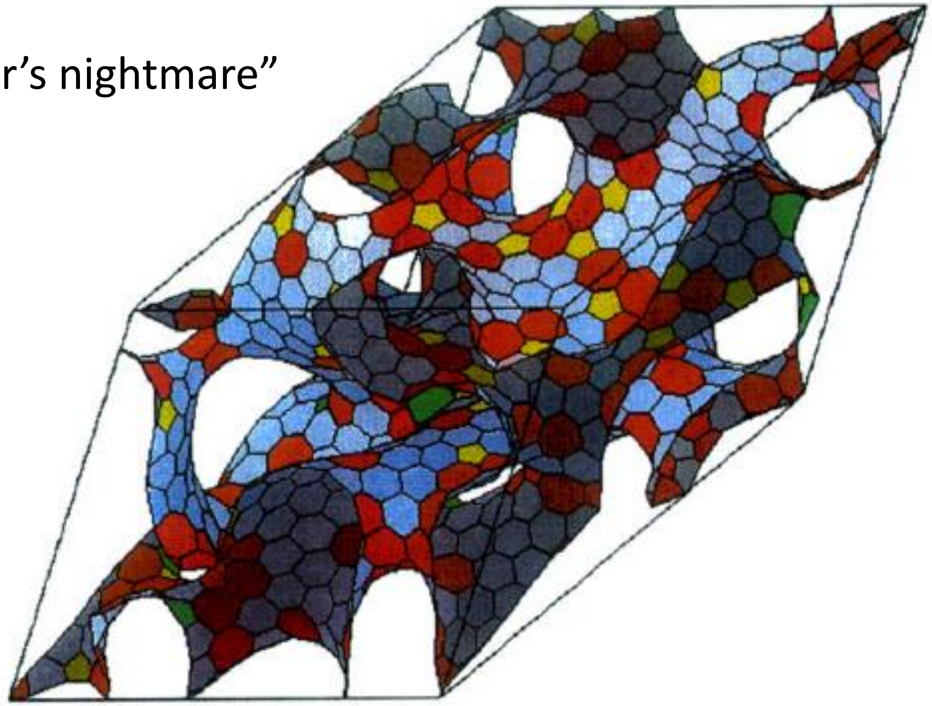

FIG. 2. View of a random schwarzite model on a surface of genus 12 per fcc supercell. The structure has 1248 carbons arranged into 38 five-membered rings (yellow), 394 six-membered rings (blue), 155 seven-membered rings (orange), 12 eight-membered rings (green), and 1 nine-sided ring (pink). Slower annealing produces a structure with many fewer five-membered rings. The cubic unit cell (4 times the volume of the fcc cell shown) is 42.9 Å on a side.

Modern Physics Letters B, Vol. 9, No. 22 (1995) 1461–1470
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OK,

Schwartzite

IMAGE ANALYSIS OF A NEGATIVELY CURVED GRAPHITIC SHEET MODEL FOR AMORPHOUS CARBON

L. A. BURSILL AND LAURE N. BOURGEOIS
School of Physics, The University of Melbourne, Parkville,
Vic. 3052 Australia

Received 4 September 1995

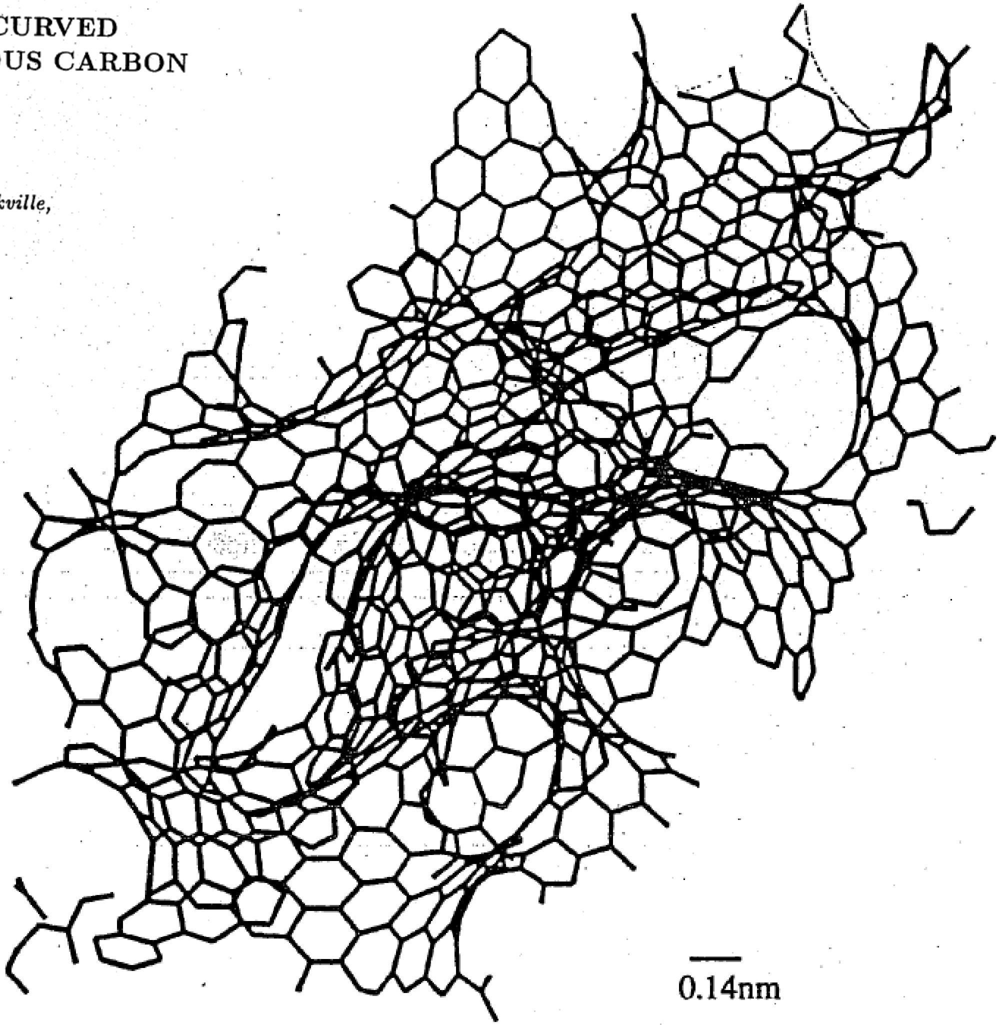

Fig. 2. Random schwartzite model of a surface of genus 12; the volume shown has the shape of a primitive f.c.c cell.

VOLUME 91, NUMBER 23 PHYSICAL REVIEW LETTERS week ending 5 DECEMBER 2003

Magnetism in All-Carbon Nanostructures with Negative Gaussian Curvature

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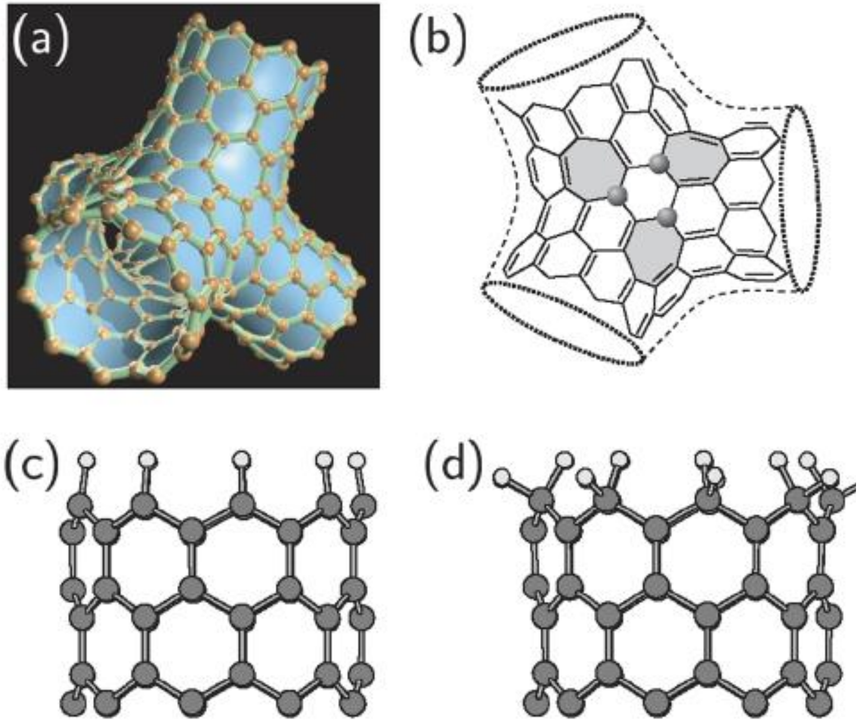
(Received 8 July 2003; published 5 December 2003)



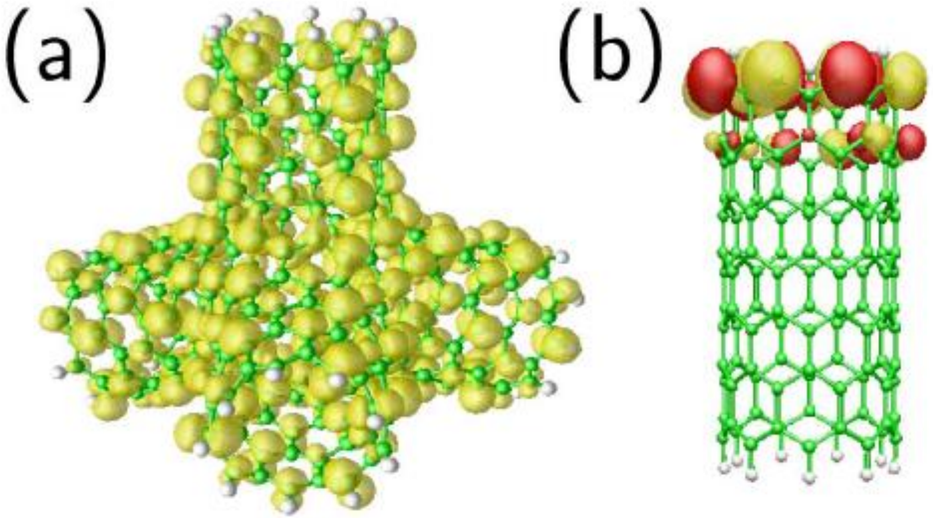


FIG. 3 (color online). (a) Charge density associated with the four unpaired spins, which are unrelated to the edge states in an sp^2 terminated tetrapod. (b) The wave function of a spin-polarized edge state in an sp^2 terminated (9, 0) nanotube. We use color shading to represent the phase of the wave function.