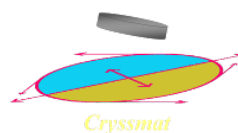


Introducción a la Nanotecnología

Simulación de NanoMateriales

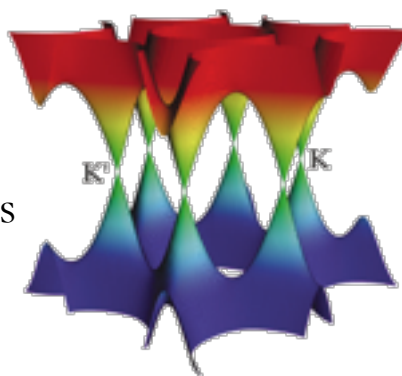


Dr. Ricardo Faccio
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Facultad de Química, Udelar



Contenido

- Introducción a DFT
- Propiedades Mecánicas
- Propiedades Estructurales



0 Introducción: Resolviendo un sistema de muchas partículas

□ Sistemas de Muchas Partículas

$$\Psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

$$\hat{H}\Psi_0(\vec{r}) = \varepsilon_0 \Psi_0(\vec{r})$$

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{R}_i}^2}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} + \dots \\ & \dots + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} \end{aligned}$$

0 Introducción: Primera aproximación

□ Aproximación adiabática Born-Oppenheimer

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2} \sum_i \underbrace{\frac{\nabla_{\vec{R}_i}^2}{M_i}}_0 - \frac{\hbar^2}{2} \sum_i \underbrace{\frac{\nabla_{\vec{r}_i}^2}{m_e}}_{\hat{T}} - \underbrace{\frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|}}_{\hat{V}_{\text{ext}}} + \dots \\ & \dots + \underbrace{\frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\hat{V}} + \underbrace{\frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}}_{\text{constante}} \\ = & -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + cte. \end{aligned}$$

0 Introducción: Segunda aproximación

▣ Teoría del Funcional de la Densidad (DFT)

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2} \sum_i \underbrace{\frac{\nabla_{\vec{R}_i}^2}{M_i}}_0 - \underbrace{\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e}}_{\hat{T}} - \underbrace{\frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|}}_{\hat{V}_{ext}} + \dots \\ &\quad \dots + \underbrace{\frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\hat{V}} + \underbrace{\frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}}_{\text{constante}} \\ &= -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + cte. \\ \hat{H} &= \hat{T} + \hat{V} + \hat{V}_{ext}\end{aligned}$$

0 Introducción: Ecuaciones de Hartree Fock

▣ Ecuación Central

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + \hat{V}_{ext} + \Phi_i \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

▣ Partículas no interactuantes

$$\psi_i(\vec{r}_1, \dots, \vec{r}_N) = \psi_1(\vec{r}_1) \psi_2(\vec{r}_2) \dots \psi_N(\vec{r}_N)$$

▣ ¿Comportamiento Fermiónico?

■ Función de Onda Antisimétrica: Determinante de Slater

▣ Intercambio exacto

▣ No hay correlación

$$\psi_i(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{r}_1) & \dots & \chi_N(\vec{r}_1) \\ \vdots & \ddots & \vdots \\ \chi_N(\vec{r}_1) & \dots & \chi_N(\vec{r}_N) \end{vmatrix}$$

0 Introducción: Teoría de Funcionales de la Densidad

□ ¿Qué es un Funcional?

- Se dice que F es un “funcional” de una función $f(t)$ cuando F es un número cuyo valor depende de la “forma” de la Función $f(t)$.
- Para cada función f (definida sobre el mismo dominio, t) el funcional $F[f]$ arroja el mismo valor: $F : \mathfrak{F} \rightarrow \mathbb{R} : f \rightarrow F[f]$
- Un funcional es una “función de funciones”
- Ejemplos
 - La integral de una función es un funcional
 - La energía total de un sistema cuántico es un funcional de la densidad. La densidad es una función definida en $\mathbb{R}^3$

$$F[f] = \int_{-\infty}^{\infty} f(t) e^{-t^2} dt$$

$$F[f] = f(0)$$

0 Introducción: Teoremas de P. Hohenberg & W. Kohn

Primer Teorema: Para un sistema de muchas partículas existe una correspondencia uno a uno entre la densidad electrónica $\rho(\mathbf{r})$ del estado basal y su potencial externo V_{ext} .

Una consecuencia inmediata de este teorema establece que en estado basal el valor medio de cualquier operador es un funcional único de la densidad electrónica exacta (del estado basal).

$$\langle \psi | \hat{O} | \psi \rangle = O[\rho]$$

Segundo Teorema: Siendo $\hat{O}$ el operador Hamiltoniano $\hat{H}$, el funcional para la energía total en el estado basal toma la siguiente forma:

$$\begin{aligned} E_{\text{ext}}[\rho] &= \langle \psi | \hat{T} + \hat{V} | \psi \rangle + \langle \psi | \hat{V}_{\text{ext}} | \psi \rangle \\ &= F_{\text{HK}}[\rho] + \langle \psi | \hat{V}_{\text{ext}} | \psi \rangle \\ &= F_{\text{HK}}[\rho] + \int \rho(\vec{r}) V_{\text{ext}}(\vec{r}) d\vec{r} \end{aligned}$$

P. Hohenberg y W. Kohn, Phys. Rev. 136 (1964) B864

0 Introducción: Consecuencias

□ Invertibilidad: $\rho(\vec{r}) \leftrightarrow V_{ext}(\vec{r})$

□ Universalidad: $F_{HK}[\rho] \quad \hat{\rho}(\vec{r}) = \sum_{i=1}^N \delta(\vec{r}_i - \vec{r})$

$$\rho(\vec{r}) = \langle \psi^*(\vec{r}_1, \dots, \vec{r}_N) | \hat{\rho}(\vec{r}) | \psi(\vec{r}_1, \dots, \vec{r}_N) \rangle$$

$$\rho(\vec{r}) = \sum_{i=1}^N \int \psi^*(\vec{r}_1, \dots, \vec{r}_i = \vec{r}, \dots, \vec{r}_N) \psi(\vec{r}_1, \dots, \vec{r}_i = \vec{r}, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N$$

□ Principio Variacional: Rayleigh-Ritz

El problema sigue siendo el mismo!

0 Introducción:

Ecuaciones de Kohn y Sham (DFT)

$$E[\rho] = T_0[\rho] + V_H[\rho] + V_{xc}[\rho] + V_{ext}[\rho]$$

$$\hat{H}_{KS} = \hat{T}_0 + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext}$$

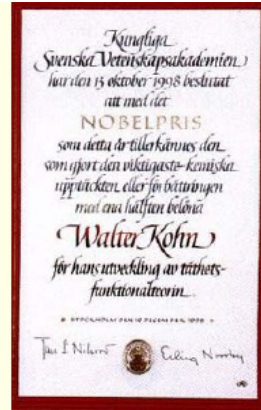
$$\hat{H}_{KS} = -\frac{\hbar^2}{2m_e} \nabla^2 + \underbrace{\frac{e^2}{4\pi\epsilon_0} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'}_{\text{Universal!}} + V_{xc} + V_{ext}$$

$$\hat{V}_{xc} = \frac{\delta V_{xc}[\rho]}{\delta \rho}$$

$$\rho(\vec{r}) = \sum_{i=1}^N \phi_i^*(\vec{r}) \cdot \phi_i(\vec{r})$$

W. Kohn y L. J. Sham, Phys. Rev. 140 (1965) A1133

0 Introducción: Premio Nobel de Química 1998



"Self-consistent Equations including Exchange and Correlation Effects"
W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

0 Introducción: Funcional Correlación-Intercambio

Aproximación de Densidad Local LDA

$$E_{xc}^{LDA} = \int \rho(\vec{r}) \epsilon_{xc}(\rho(\vec{r})) d\vec{r}$$

$$\text{LDA: } E_{xc}^{LDA} = \int f(\rho(\mathbf{r})) d^3r$$

$$\text{GGA: } E_{xc}^{GGA} = \int f(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|) d^3r$$

$$\text{MGGA: } E_{xc}^{MGGA} = \int f(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|, \nabla^2 \rho(\mathbf{r}), t(\mathbf{r})) d^3r$$

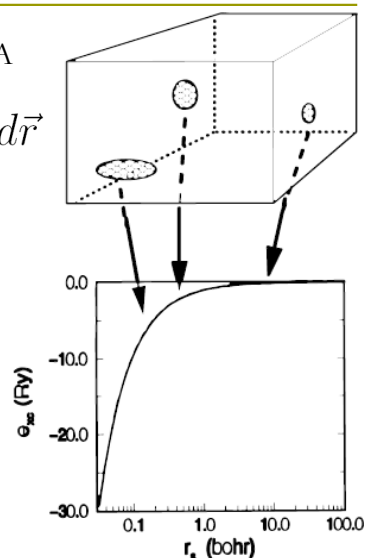
$$\text{LDA+U: } E_{xc}^{LDA+U} = E_{xc}^{LDA} + E_{ee} - E_{dc}$$

$$\text{GGA+U: } E_{xc}^{GGA+U} = E_{xc}^{GGA} + E_{ee} - E_{dc}$$

$$\text{hybrid: } E_{xc}^{\text{hybrid}} = E_{xc}^{\text{DFT}} + \alpha (E_{xc}^{\text{HF}} - E_{xc}^{\text{DFT}})$$

where

$$E_{xc}^{\text{HF}} = -\frac{1}{2} \sum_{\sigma} \sum_{\mathbf{k}, \mathbf{k}'} w_{\mathbf{k}} w_{\mathbf{k}'} \iint \frac{\psi_{\mathbf{k}\mathbf{k}'}^{\sigma*}(\mathbf{r}) \psi_{\mathbf{k}\mathbf{k}'}^{\sigma}(\mathbf{r}') \psi_{\mathbf{k}\mathbf{k}'}^{\sigma*}(\mathbf{r}) \psi_{\mathbf{k}\mathbf{k}'}^{\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$



0 Introducción: Funcionales vs. Experimentos

Lattice parameters (Å)

	Exp.	LDA	PBE	WC
Co	2.51	2.42	2.49	2.45
Ni	3.52	3.42	3.52	3.47
Cu	3.61	3.52	3.63	3.57
Ru	2.71	2.69	2.71	2.73
Rh	3.80	3.76	3.83	3.80
Pd	3.88	3.85	3.95	3.89
Ag	4.07	4.01	4.15	4.07
Ir	3.84	3.84	3.90	3.86
Pt	3.92	3.92	4.00	3.96
Au	4.08	4.07	4.18	4.11

■ 3d elements:

- PBE superior, LDA much too small

■ 4d elements:

LDA too small, PBE too large

- New functional Wu-Cohen (WC)

Z.Wu, R.E.Cohen, PRB 73, 235116 (2006)

■ 5d elements:

- LDA superior, PBE too large

0 Introducción: Resolviendo la Función de Onda

□ Confección del Hamiltoniano:

$$\hat{H}_{KS} = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc} + V_{ext}$$

□ Definición de la Base:

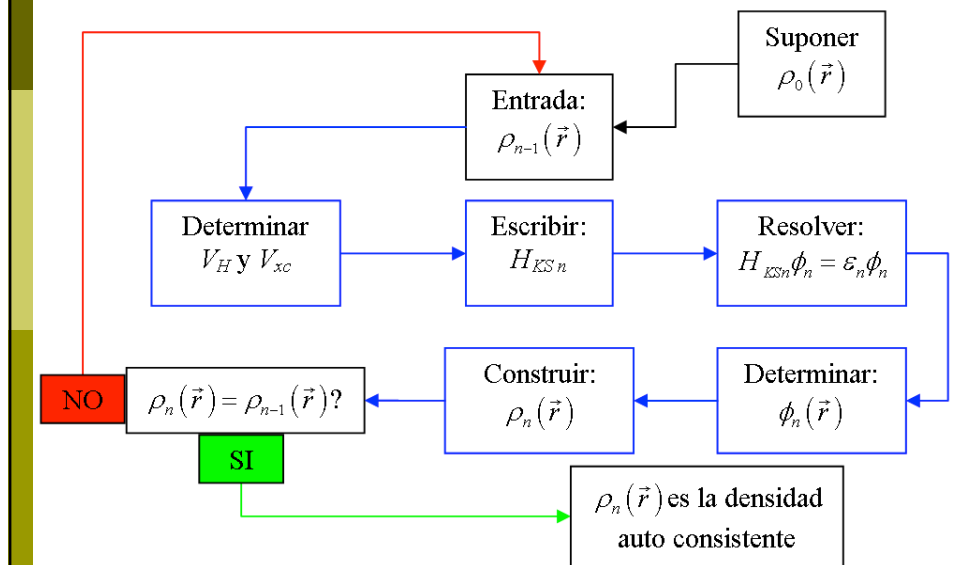
$$\phi_m = \sum_{p=1}^P c_p^m \phi_p^b$$

□ Ecuación Secular:

$$\begin{bmatrix} \dots & \dots & \dots \\ \vdots & \langle \phi_i^b | \hat{H}_{sp} | \phi_j^b \rangle - \epsilon_m \langle \phi_i^b | \phi_j^b \rangle & \vdots \\ \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} c_1^m \\ \vdots \\ c_P^m \end{bmatrix} = \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix}$$

Pero $\phi(\mathbf{r})$ final no tiene porque ser igual a $\phi(\mathbf{r})$ inicial

0 Introducción: Solución Auto-consistente SCF

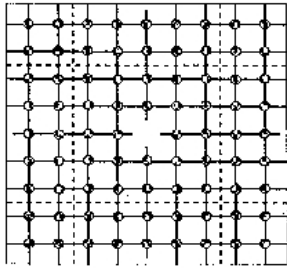


0 Introducción: Funciones de Base & Estructura de Códigos

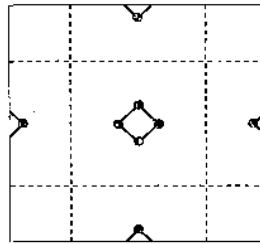
- ❑ Ondas Planas
 - Pseudopotenciales
 - Ondas planas aumentadas
 - **Códigos: VASP y Quantum Espresso**
- ❑ Métodos particionados (aumentados)
 - LMTO
 - ASW
 - LAPW
 - **Códigos: WIEN2k**
- ❑ Combinación Lineal de Orbitales Atómicos
 - Bases Gaussianas localizadas, en este caso numéricas.
 - **Códigos: Gaussian y SIESTA**

0 Introducción Potencialidades

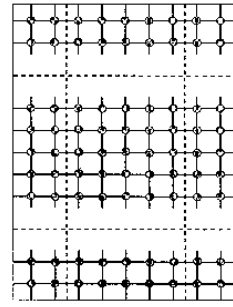
- PBC: Periodic Boundary Conditions
- Sistemas periódicos: Muestras cristalinas
- Sistemas no periódicos: *Superceldas*



Defectos



moléculas



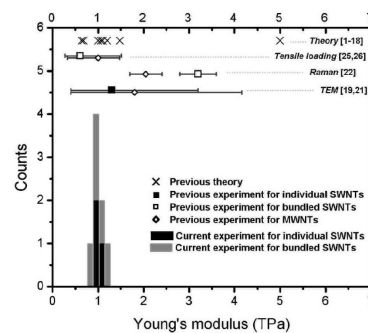
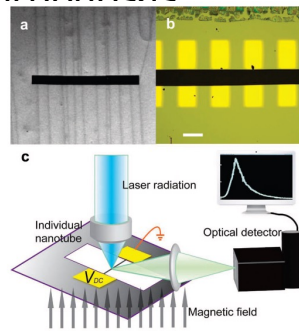
superficies

2. Propiedades Mecánicas

Propiedades Elásticas de
nanocintas de Grafeno

2. Propiedades Mecánicas

▣ Propiedades mecánicas de nanoestructuras carbonosas

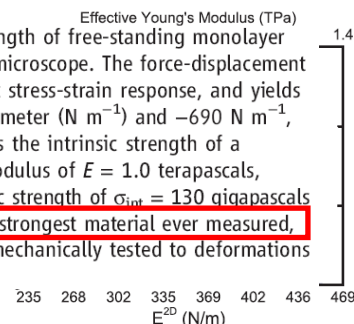
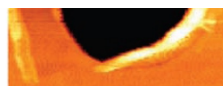
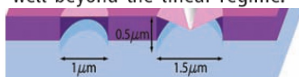


Determination of the Young's Modulus of Structurally Defined Carbon Nanotubes Yang Wu *et al*, *Nano Lett.* **8 (12)**, 4158-4161 (2008)

2. Propiedades Mecánicas



We measured the elastic properties and intrinsic breaking strength of free-standing monolayer graphene membranes by nanoindentation in an atomic force microscope. The force-displacement behavior is interpreted within a framework of nonlinear elastic stress-strain response, and yields second- and third-order elastic stiffnesses of 340 newtons per meter (N m^{-1}) and -690 N m^{-1} , respectively. The breaking strength is 42 N m^{-1} and represents the intrinsic strength of a defect-free sheet. These quantities correspond to a Young's modulus of $E = 1.0$ terapascals, third-order elastic stiffness of $D = -2.0$ terapascals, and intrinsic strength of $\sigma_{\text{int}} = 130$ gigapascals for bulk graphite. **These experiments establish graphene as the strongest material ever measured,** and show that atomically perfect nanoscale materials can be mechanically tested to deformations well beyond the linear regime.



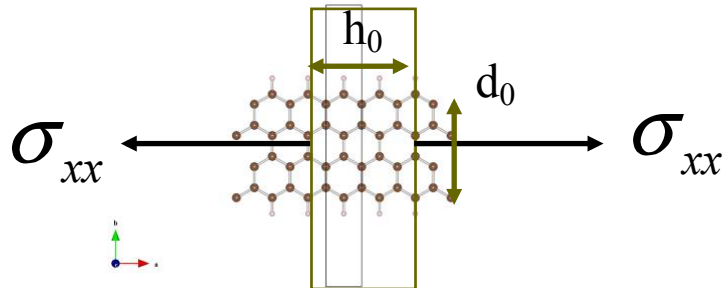
“Strength of Monolayer Graphene Measurement of the Elastic Properties and Intrinsic”

Lee *et al*. *Science* **321**, 385 (2008)

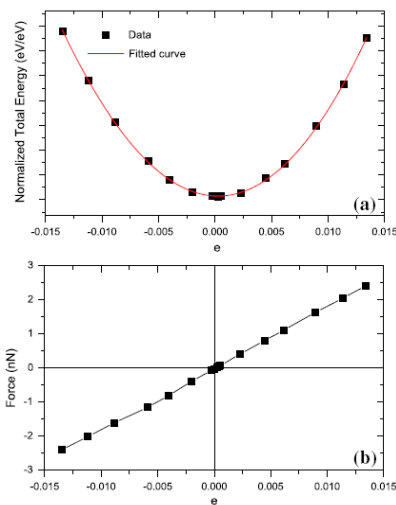
2. Propiedades Mecánicas

■ Simulación Computacional.

- Propiedades mecánicas de: H-ZGNR.
- Curvas esfuerzo vs deformación.
- Cambios de E_{gap} .
- Campo Eléctrico Crítico.
- Modulo de Young equivalente.



2. Propiedades Mecánicas

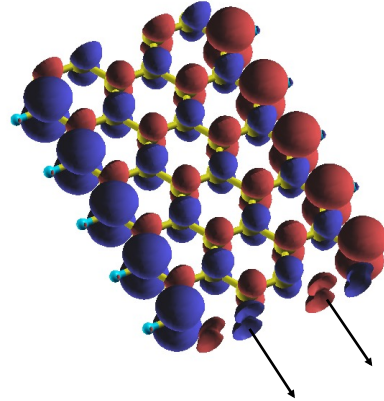


Force nN	E_{gap} eV	Mom. Mag. μ_B	E_{total} eV	a Å
-5.67	0.60	0.251	-5123.29053	9.78
-3.68	0.60	0.257	-5123.48784	9.85
-1.92	0.61	0.261	-5123.59075	9.91
-0.97	0.62	0.263	-5123.61926	9.94
-0.10	0.63	0.265	-5123.6293	9.97
0.00	0.63	0.265	-5123.62951	9.97
0.01	0.63	0.265	-5123.62849	9.97
0.87	0.63	0.267	-5123.62166	10.00
1.75	0.63	0.269	-5123.59939	10.03
3.72	0.65	0.275	-5123.47918	10.10
5.80	0.66	0.28	-5123.26005	10.18
8.04	0.67	0.288	-5122.90206	10.26
9.90	0.68	0.295	-5122.51931	10.33
16.07	0.72	0.316	-5120.6051	10.58
20.48	0.76	0.337	-5118.60822	10.77
25.17	0.81	0.36	-5115.84421	10.98
34.71	0.94	0.428	-5107.1579	11.50
40.59	1.11	0.507	-5097.44148	11.98

2. Propiedades Mecánicas

Reference	E^{3D} (TPa)	ν	Remarks
<i>Graphene</i>			
[10]	0.799	—	Graphene (force field)
[17]	1.02	0.149	Graphene (<i>ab initio</i>)
[18]	1.11	—	Graphene (<i>ab initio</i>)
[19]	1.012	0.245	Graphene (Brenner ^a)
[19]	0.669	0.416	Graphene (Brenner ^b)
[20]	0.694	0.412	Graphene (Brenner)
[24]	1.11	0.45	Graphene (truss model)
Present work	0.96	0.17	Graphene (<i>ab initio</i>)
<i>Carbon nanotubes</i>			
[21]	0.694	—	SWNT (Brenner)
[23]	0.97	0.28	SWNT (empirical model)
[25]	0.213–2.08	0.16	SWNT (MM)
[26]	0.32–1.47	—	SWNT (experiments)
[27]	0.7	—	SWNT (MD)
[28]	1.0	0.25	DWNT (vibrations)
[29]	0.81–1.13	—	SWNT (experiments)
[30] ^c	0.8–1.05	—	SWNTS (<i>ab initio</i>)
[30]	1.05	—	SWNT (5, 5)-(<i>ab initio</i>)
Present work	1.01	—	SWNT (5, 5)-(<i>ab initio</i>)

^a Non-minimized potential; ^b minimized potential; ^c this result was converted to E^{3D} for comparison purposes, using:
 $E^{3D} = E^{2D} c_0$.



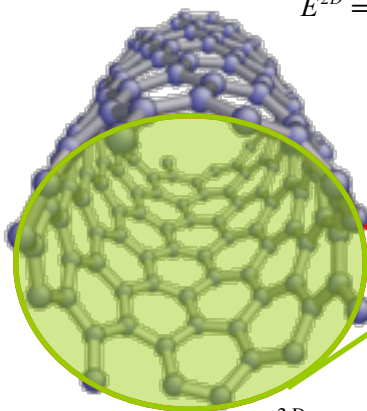
Faccio *et al*, J. Phys.: Condens. Matter 21 (2009) 285304

2. Propiedades Mecánicas

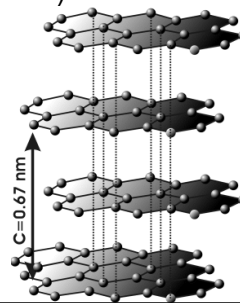
▣ Módulo de Young equivalente

$$E^{2D} = \frac{1}{A_0} \left(\frac{\partial^2 E_s}{\partial \epsilon_x^2} \right)_{E_0} = E^{3D} c_0 \quad \& \quad \nu = -\frac{\epsilon_y}{\epsilon_x} = -\frac{l_0}{w_0} \frac{\partial w}{\partial l}$$

$$E_{nanotubes}^{3D} = E_{nanotubes}^{2D} \left(\frac{2\pi r}{A} \right)$$

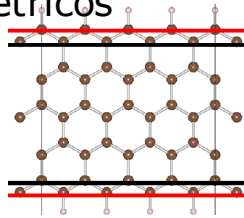


$$E_{graphene}^{3D} = E_{graphene}^{2D} * 0.335 \text{ nm}$$

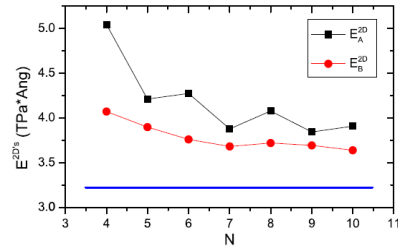
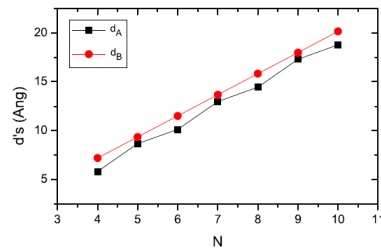


2. Propiedades Mecánicas

▣ Módulo de Young equivalente y parámetros geométricos



N	d_A	d_B (Å)	E_A^{3D} (TPa Å)	E_B^{3D}
4	05.80	07.19	5.04	4.07
5	08.66	09.35	4.21	3.90
6	10.12	11.51	4.27	3.76
7	12.98	13.68	3.88	3.68
8	14.45	15.83	4.08	3.72
9	17.30	18.00	3.84	3.69
10	18.77	20.16	3.91	3.64
∞	—	—	3.23	—

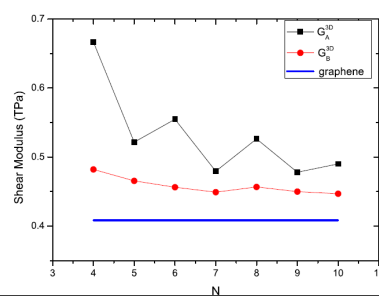
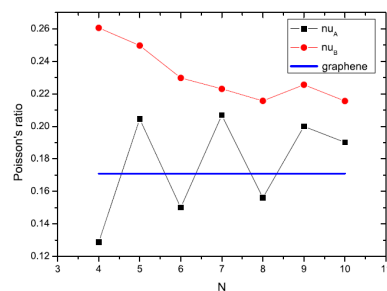


2. Propiedades Mecánicas

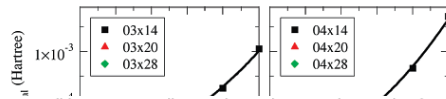
▣ Poisson's Ratio and Shear Stress

$$G^{3D} = \frac{E^{3D}}{2(1+\nu)}$$

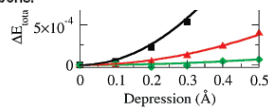
N	ν_A	ν_B	G_A	G_B
4	0.129	0.261	0.667	0.482
5	0.204	0.250	0.522	0.466
6	0.150	0.230	0.555	0.456
7	0.207	0.223	0.480	0.449
8	0.156	0.216	0.526	0.457
9	0.200	0.226	0.478	0.450
10	0.190	0.216	0.490	0.447
∞	0.179	—	0.408	—



2. Propiedades Mecánicas



Graphene nanoribbons present diverse electronic properties ranging from semiconducting¹⁻³ to half-metallic,⁴ depending on their geometry dimensions, and chemical composition.^{5,6,7} Here we present a route to control these properties via externally applied mechanical deformations. Using state-of-the-art density functional theory calculations combined with classical elasticity theory considerations, we find a remarkable Young's modulus value of ~ 7 TPa for ultranarrow graphene strips and a pronounced electromechanical response toward bending and torsional deformations. Given the current advances in the synthesis of nanoscale graphene derivatives, our predictions can be experimentally verified opening the way to the design and fabrication of miniature electromechanical sensors and devices based on ultranarrow graphene nanoribbons.



“Electromechanical Properties of Suspended Graphene Nanoribbons”
O. Hod, G. E. Scuseria, Nano Letters **9** (2009) 2619

2. Propiedades Mecánicas

□ Conclusiones

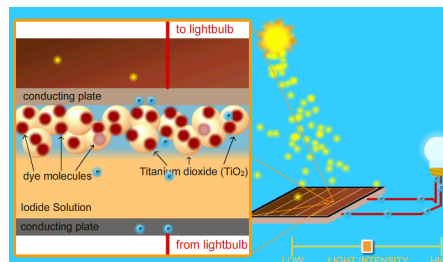
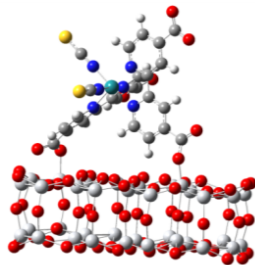
- Se reportan las propiedades mecánicas para nanocintas de carbono.
- Se generalizan los resultados a través del módulo de Young equivalente E^{3D} y E^{2D} .
- Las propiedades mecánicas dependen del ancho de la cinta.
- Se reportan E^{2D} equivalentes superiores al del Grafeno.

R. Faccio, P. Denis, H. Pardo, C. Goyenola & A. W. Mombrú,
“Mechanical properties of graphene nanoribbons” J. Phys.: Condens.
Matter **21** (2009) 285304

3. Propiedades Estructurales

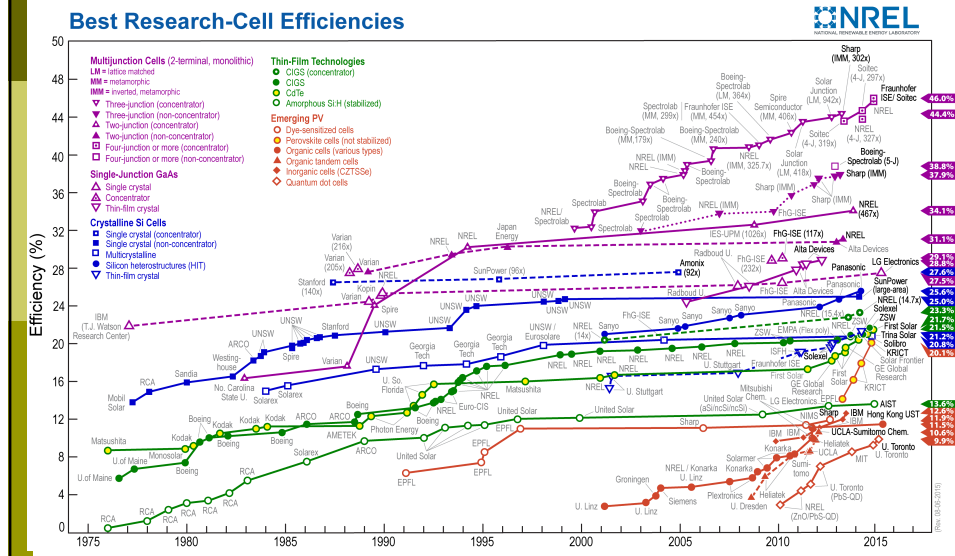
3. Celdas Solares

- Los electrones se arrancan del colorante y se inyectan en TiO_2 para transportarlo fuera de la celda
- Los “huecos” permanecen en la tinta
- La separación hueco-electrón genera un voltaje y corriente.

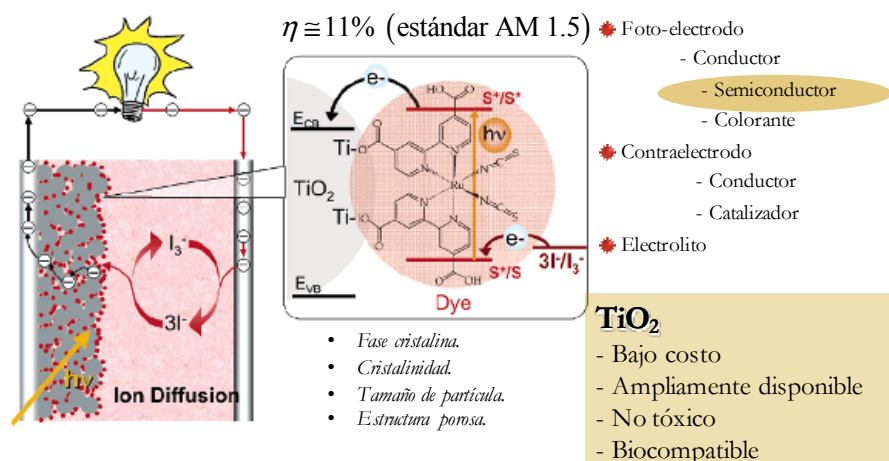


fuelle: <http://nanosense.org/activities/cleanenergy/solarcellanimation.html>

3. Eficiencias para cada Tecnología



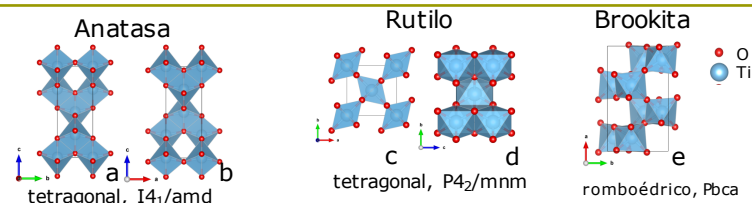
3. Celdas Solares de Sensibilización Espectral (DSSC)



• Grätzel M, *Inorg. Chem.* 2005, 44, 6841

• Faccio, R et al, *A. Recent Patents on Nanotechnology* 2011, 5(1), 46-61.

3. Polimorfos del TiO_2



Celda unidad de la fase anatasa vista según las direcciones $[100]$ (a) y $[010]$ (b),
Celda unidad correspondiente a rutilo vista según las direcciones $[001]$ (c) y $[100]$ (d).
Estructura del polimorfo brookita según la dirección $[001]$ (e).

Rutilo es la fase más estable a altas temperaturas, pero **anatasa** y brookita son los polimorfos más comunes en muestras naturales y sintéticas de **tamaño nanométrico**.

Síntesis

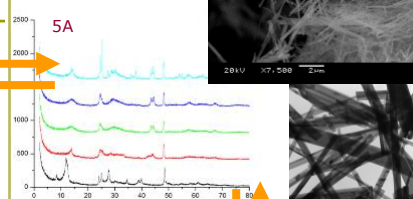
*Método hidrotérmal
bajo presión endógena*



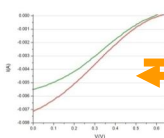
$\text{NaOH(ac)} \ 10\text{M}$
 $120^\circ \text{C} < T_r < 150^\circ \text{C}$
 $24\text{h} < t_r < 68\text{h}$

(A, R, o A/R 50% p/p)

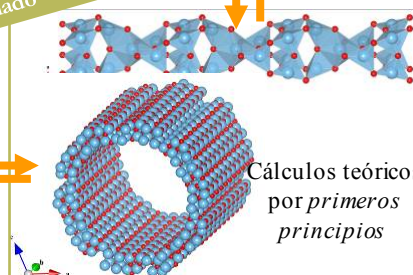
Caracterización



Prototipos



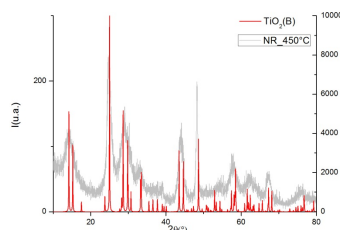
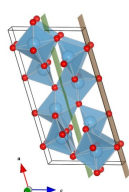
Modelado



3. Modelado de Nanoestructuras

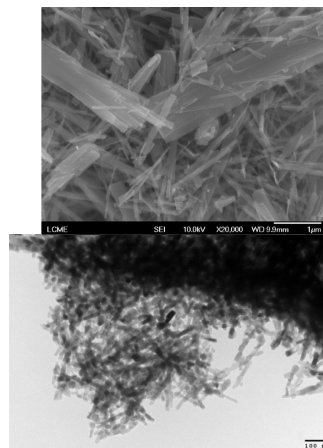
Énfasis en el polimorfo $\text{TiO}_2(\text{B})$

Aparece como fase meta estable al calentar las estructuras de *alta relación de aspecto* de bajo contenido sódico (tanto en el caso de NR como NT) a temperaturas del orden o inferiores a las empleadas en el proceso de sinterizado de los fotoelectrodos.



La conversión a anatasa en el caso de NTs se ve acompañada de la pérdida de morfología (y por lo tanto área específica y porosidad).

Estructura laminar



3. Polimorfo $\text{TiO}_2(\text{B})$

	PW-GGA(eV)	PW-mBJ (eV)	Exp. (eV)
R	2.1	2.7	3.0[1]
A	2.3	3.0	3.2 [1]
TB	3.1	3.4	3.22[3][2]

Celda unidad de $\text{TiO}_2(\text{B})$ luego de la optimización.

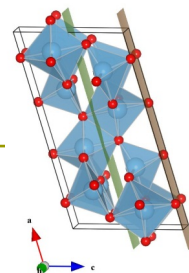
[1] Chen X. et al *Chem. Rev.* **2007**, 107, 2891-2959.

[2] Feist T. P. et al *Journal of Solid State Chemistry* **1992**, 101, 275-295

[3] Procházka J. et al *Chem Mater* **2009**, 21, 1457–1464

Modelos considerados

- Modelos bidimensionales (estabilidad, reactividad)
- Modelos unidimensionales (nanotubos e hilos atómicos)
- Clúster



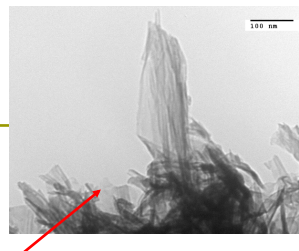
Parámetros de red optimizados

	Base	a (Å)	b (Å)	c (Å)	β (°)
Anatasa	PW	3.818	3.818	9.617	-
	Exp [1]	3.784	3.784	9.515	-
Rutilo	PW	4.594	4.594	2.959	-
	Exp [1]	4.593	4.593	2.959	-
$\text{TiO}_2(\text{B})$	PW	12.302	3.763	6.632	106.97
	Exp [2][3]	12.179	3.741	6.525	107.10

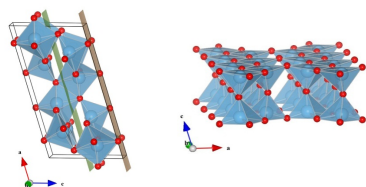
3. Modelos de Superficies

Estudio de Estabilidad de Superficies Ultrafinas

- Aproximación a paredes de nanotubos ($e \sim 2-3\text{nm}$)
- Evidencia experimental de mecanismo de enrollamiento
- Sintetizadas para varios polimorfos ($e \sim 6-12\text{\AA}$)



$$E_S = \frac{E_{slab} - N_{Ti} E_{TiO_2-bulk}}{2S}$$



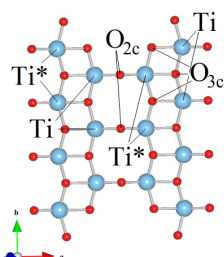
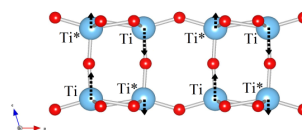
TB(001)

Slabs	# átomos Ti	# capas TiO ₂	SE (J/m ²)
A(101)	8	2	0.40
A(100)	12	2	0.64
A(001)	5	4	0.90
R(110)	6	3	0.77
R(101)	6	3	1.14
R(100)	27	3	0.77
TB(001)	24	2	0.33
TB(100)	8	4	0.69

Energía de superficie (SE) para los slabs simulados.
Los modelos resaltados (A(101) y TB(001)) son los que muestran menor energía de superficie.

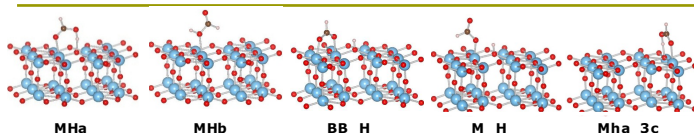
3. Nanohojas ultrafinas de TB(001)

- Reordenamiento tal que se alcanza una configuración muy simétrica
- Coordinación del tipo pirámide de base cuadrada
- Similitudes con «penta-coordinated-nanosheet» derivada de A(101)
- Todos los átomos superficiales se encuentran insaturados permitiendo la unión con especies donoras de electrones



- Se estudia reactividad, HCOOH
- Anclaje e interacción con N719
- Se emplea como bloque constructor de nanotubos y nanohilos (hilos atómicos)

3. Nanohoja TB(001): Reactividad



$$E_{form} = -(E_f - E_{ni})$$

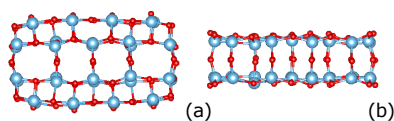
Energías de adsorción, distancias de enlace y ángulos de enlace para las diferentes configuraciones de adsorción sobre TB(001).

Config.	E _{ads} (eV)	C-O1 (Å)	C-O2 (Å)	θ (°)	O1-Ti(5c) (Å)	O2-Ti(5c) (Å)	H-O(2c) (Å)
MHa	0.51	1.31	1.24	125.3	---	2.35	1.57
MHb	0.09	1.37	1.21	124.0	2.64	---	2.65*
MHa_3c	0.35	1.32	1.24	125.2	---	2.35	1.63
M_H_2	-0.28	1.33	1.22	124.8	2.00	---	0.99
BB_H_1	0.38	1.27	1.27	127.2	2.17	2.14	0.98

Energías de Adsorción similares a las obtenidas para HCOOH sobre anatasa.

Buenas perspectivas de uso de superficies de TiO₂(B) para sensibilización con colorantes

3. Interacción TiO₂-N719



Clúster de Ti₃₆O₆₄ optimizado basado en la superficie TB(001)
(proyección superior (a) y lateral (b))

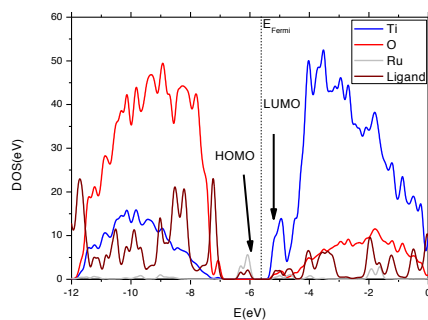
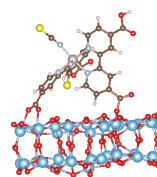
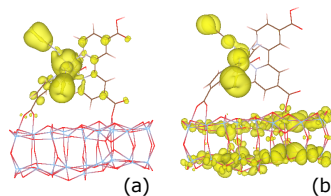


Diagrama de densidad de estados local (LDOS) proyectado sobre Ti, O, Ru y ligando N719.
Nota: el nivel de Fermi se encuentra en E=-5.62 eV.

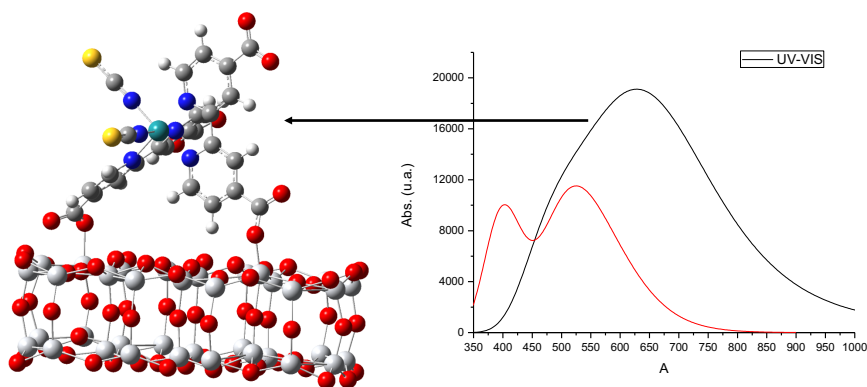


Estructura final optimizada N719-Ti₃₆O₆₄



Densidad de estados local proyectada para HOMO (a) y LUMO (b)

3. Propiedades Ópticas TiO₂(B)-N719



3. Conclusiones

- Energías de Formación para TB(001) similar a A(101)
- Energías de Adsorción de HCOOH similares para ambas superficies.
- Distancias Ti...Ti ~ 10 Å, ideal para el anclaje de moléculas tipo N3 y N719.
- Propiedades ópticas razonables para aplicaciones en DSSC (alineamiento de niveles).

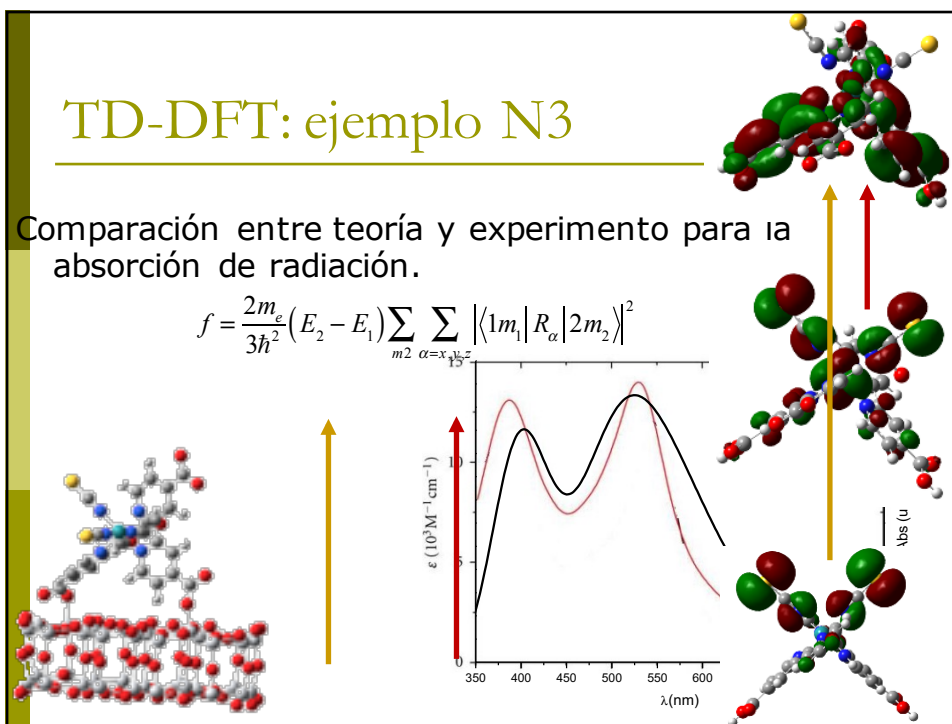
L. Fernández-Werner, R.Faccio*, A. Juan, H.Pardo, B. Montenegro, A. W. Mombrú
“Ultrathin (0 0 1) and (1 0 0) TiO₂(B) sheets: Surface reactivity and structural properties”.
Applied Surface Science 290 (2014) 180–187

4. Propiedades Ópticas

TD-DFT: ejemplo N3

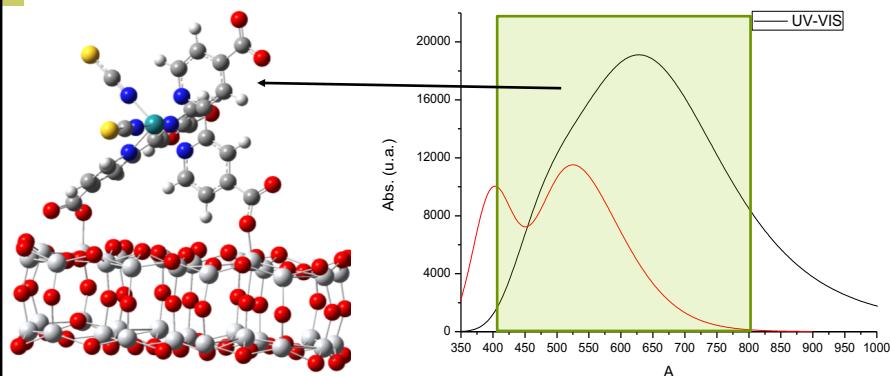
Comparación entre teoría y experimento para la absorción de radiación.

$$f = \frac{2m_e}{3\hbar^2} (E_2 - E_1) \sum_{m_2} \sum_{\alpha=\lambda, \mu, \nu} \left| \langle 1m_1 | R_\alpha | 2m_2 \rangle \right|^2$$

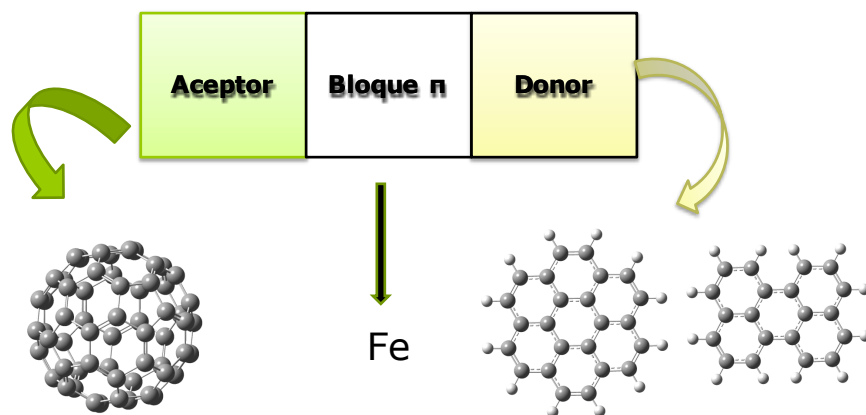


Sensibilización de Nanopartículas

- **Simulación:** Si el colorante se absorbe sobre la nanopartícula TiO_2 anatasa ocurre:

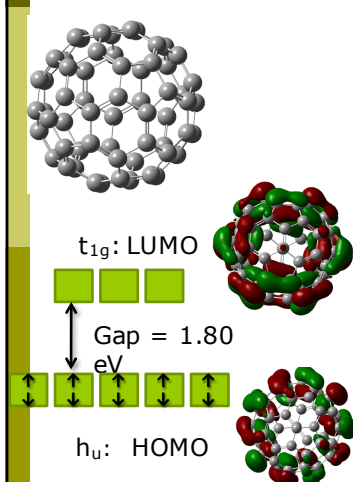


Sistema Propuesto

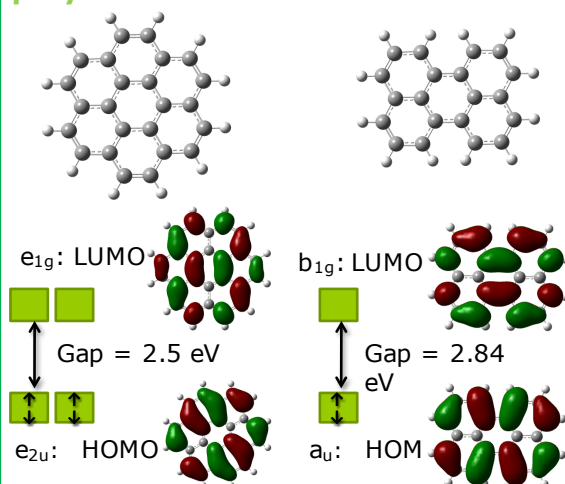


Descripción de Funciones

Sistema Aceptor: C_{60}

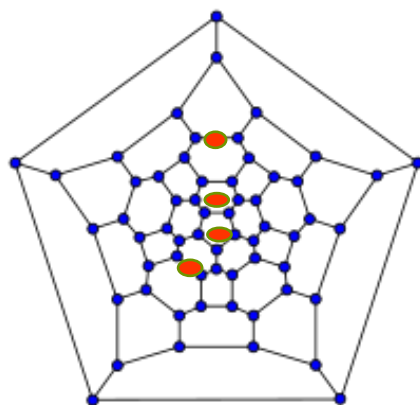


Sistemas Donor: coroneno y peryleno



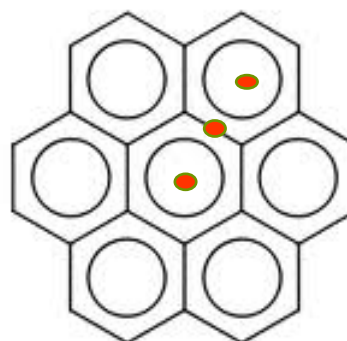
Posiciones Características

C_{60} : tipos de enlace



P, H, L, S

Coronene: tipo de enlace



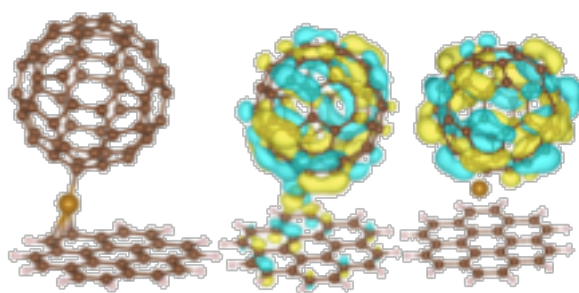
H(I), B, H(II)

Energías de formación y geometría final

Caso, PAH	Sitio	Energía de Formación (eV)	ΔE (eV)	H-L TDDFT (eV)
(I), Peryleno	S	-0.736	0.000	0.168
	L	-0.251	0.485	-
	P	-0.622	0.114	-
	H	-0.251	0.485	-
(I), Coroneno	S	-0.029	0.327	-
	L	-0.306	0.050	-
	P	-0.356	0.000	0.192
	H	-0.035	0.321	-
(II), Peryleno	L	-1.157	0.006	-
	P	-0.746	0.417	-
	H	-1.163	0.000	0.559
	L	-0.758	0.349	-
(II), Coroneno	P	-0.761	0.337	-
	H	-1.098	0.000	0.495

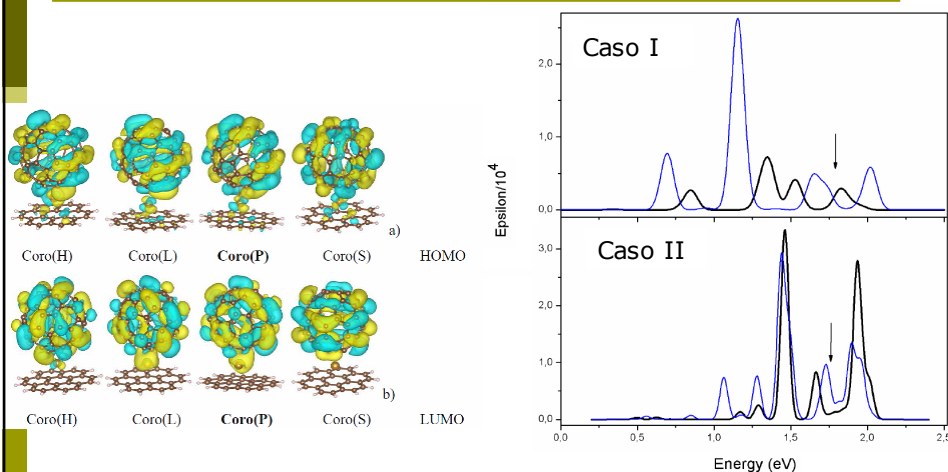
Geometrías Caso(II)
más estables que
Caso (I)

Coroneno H(II)

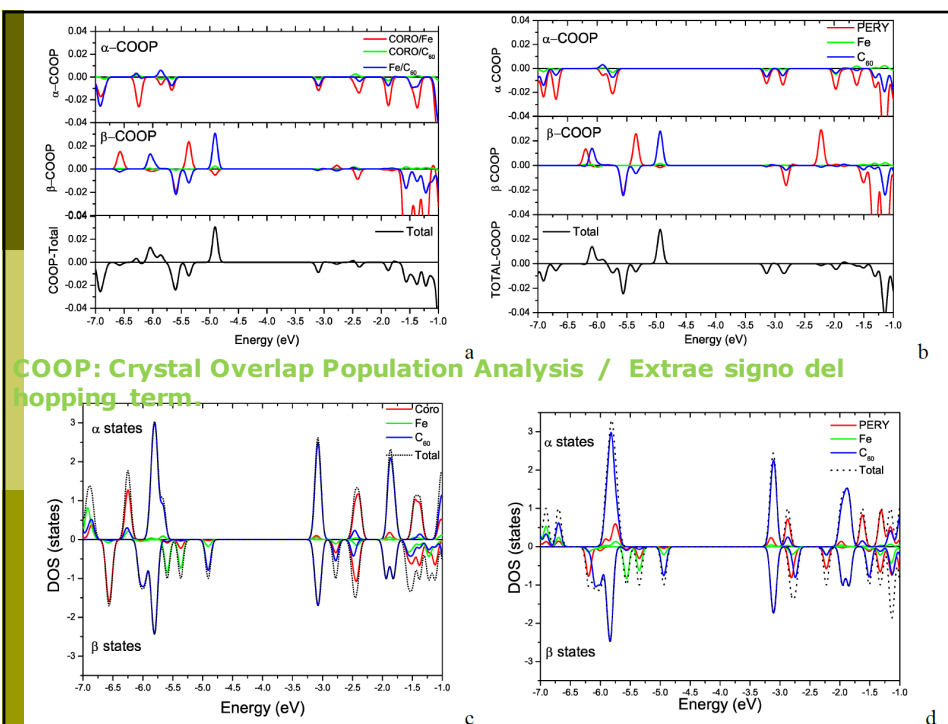


Geometría más estable, HOMO y LUMO
respectivo

HOMO-LUMO (caso I)

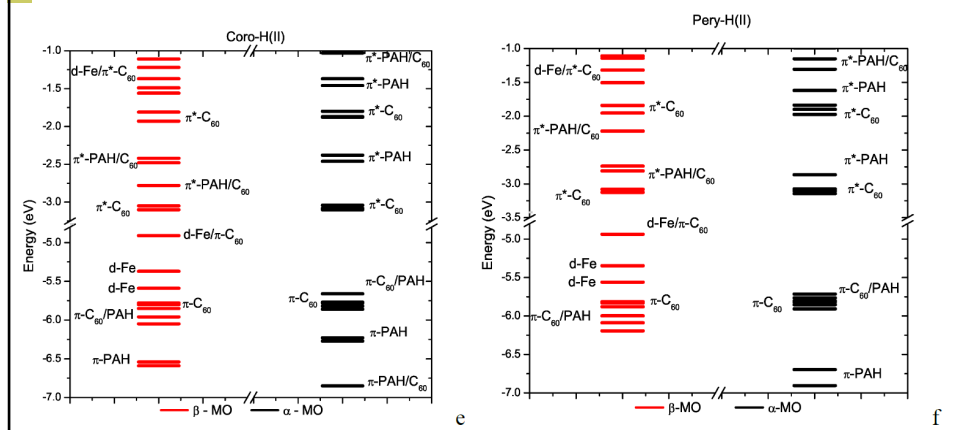


Se muestra que es posible obtener sistemas con absorción NIR-VIS en ambos casos: (I) y (II).

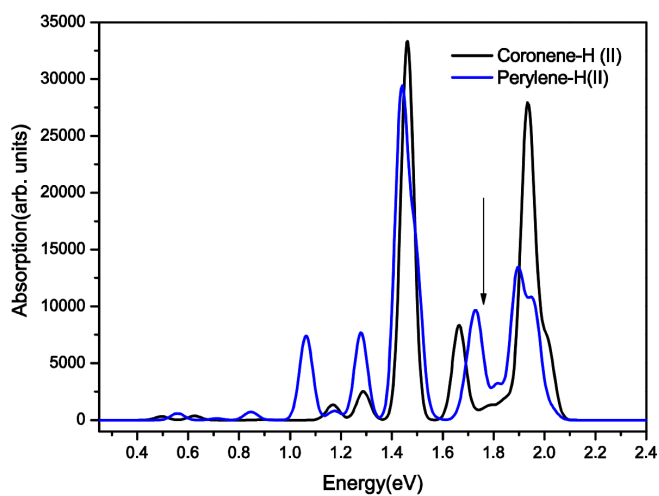


COOP: Crystal Overlap Population Analysis / Extrae signo del hopping term.

Caracterización de niveles energéticos, caso(II):



Propiedades Ópticas



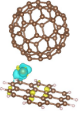
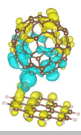
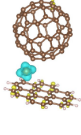
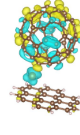
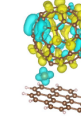
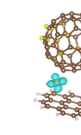
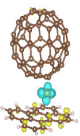
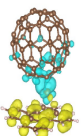
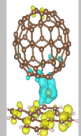
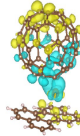
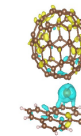
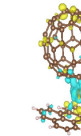
System	Energy (eV)	f	Configuration Interaction*	Transition	<S ² >
Coronene H (II)	1.389	0.0056	H-1(β) $\rightarrow$ L+7(β) (24%) H-1(β) $\rightarrow$ L+10(β) (22%) H-1(β) $\rightarrow$ L+4(β) (13%)	MLCT	2.60
	1.461	0.0743	HOMO(β) $\rightarrow$ L+2(β) (78%)	MLCT/LLCT	2.20
	1.663	0.0154	H-2(β) $\rightarrow$ L+2(β) (15%) H-1(β) $\rightarrow$ L+2(β) (11%)	MLCT	2.35
	1.931	0.0549	HOMO(α) $\rightarrow$ LUMO(α) (47%) H-4(β) $\rightarrow$ L+1(β) (13%)	ILCT	2.33
	1.961	0.0115	H-2(α) $\rightarrow$ L+2(α) (37%) H-4(β) $\rightarrow$ L+1(β) (27%)	ILCT	2.33
	2.008	0.0056	H-2(β) $\rightarrow$ LUMO(β) (54%)	MLCT	2.52
Perylene H (II)	1.063	0.0165	H-1(β) $\rightarrow$ L+2(β) (20%) H-2(β) $\rightarrow$ L+2(β) (19%) H-2(β) $\rightarrow$ L+3(β) (15%)	MLCT	2.23
	1.279	0.0171	HOMO(β) $\rightarrow$ L+2(β) (51%) H-2(β) $\rightarrow$ L+2(β) (15%) H-1(β) $\rightarrow$ L+2(β) (10%)	MLCT/LLCT	2.28
	1.438	0.0624	H-1(β) $\rightarrow$ L+2(β) (37%) HOMO(β) $\rightarrow$ L+2(β) (19%)	MLCT/LLCT	2.38
	1.494	0.0306	HOMO(β) $\rightarrow$ L+3(β) (56%)	MLCT/LLCT	2.48
	1.739	0.0135	H-1(β) $\rightarrow$ LUMO(β) (15%) H-4(α) $\rightarrow$ L+2(α) (11%)	MLCT	2.22
	1.892	0.0263	HOMO(β) $\rightarrow$ L+4(β) (20%) HOMO(α) $\rightarrow$ LUMO(α) (17%) H-1(β) $\rightarrow$ L+3(β) (15%)	MLCT/LLCT	2.22

* Main contributions to the configuration interaction

** total spin square mean value, which should be equal to S(S+1)=2

EEDM y caracterización de transiciones

Table 5.- Electronic density differences maps (EEDM) between the ground state and the corresponding excited state with iso-density surface at 0.0002 au, including its oscillation strength and transition classification.

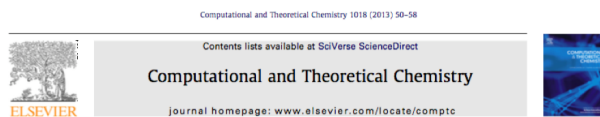
Energy	1.389 eV	1.461 eV	1.663 eV	1.931 eV	1.961 eV	2.008 eV
Coronene-H (II)						
	MLCT 1.063 eV	MLCT/LLCT 1.279 eV	MLCT 1.438 eV	ILCT 1.493 eV	ILCT 1.739 eV	MLCT 1.891 eV
Perylene-H (II)						
	MLCT	MLCT/LLCT	MLCT/LLCT	MLCT/LLCT	MLCT	MLCT

Note 1: Excited charge density is represented in cyan and the ground state density is represented in yellow

Note 2: The most intense oscillator strength is shaded.

Conclusiones:

- ▣ Sería posible preparar C_{60} -Fe-PAH
- ▣ Energía de gap en el NIR-Vis
- ▣ f no despreciable en dicho rango, para ambas configuraciones (i) y (ii)
- ▣ Mayor f para transiciones MLCT
- ▣ Perspectivas C_{60} -Fe-graphene

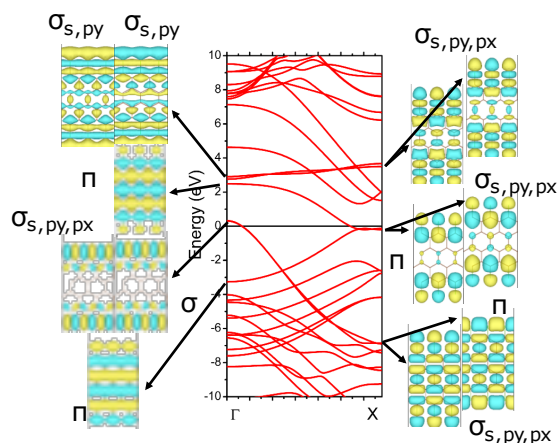


Hybrid compounds based on fullerene and polycyclic aromatic hydrocarbons with absorption in the near infrared region

Ricardo Faccio, Helena Pardo, Alvaro W. Mombrú *



Muchas Gracias!



3. Ejemplo

▣ Rutilo:

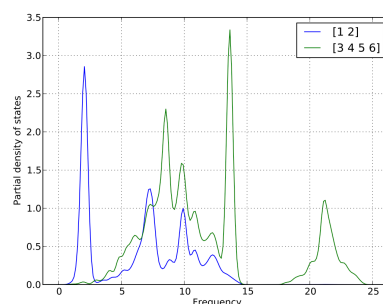
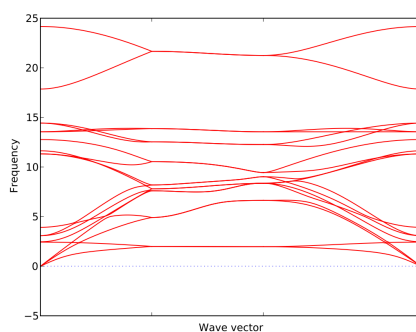
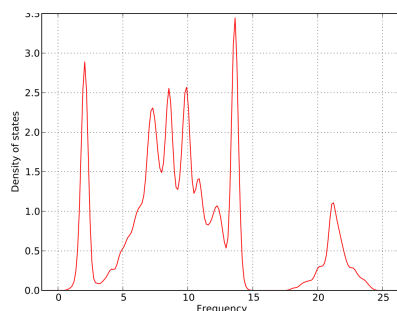
Grupo Espacial $P 4_2/m n m$

$a=b= 4.5977(4)\text{\AA}$ y $c=2.9564(2)\text{\AA}$

Átomo Wyckoff $x\ y\ z$

$\text{Ti}^{4+}\ 2a\ 0.0\ 0.0\ 0.0$

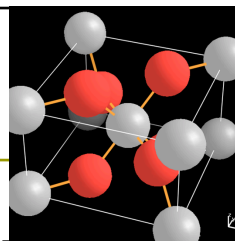
$\text{O}^{2-}\ 4f\ 0.3023(3)\ 0.3023(3)$



4. Ejemplo:

▣ Frecuencias

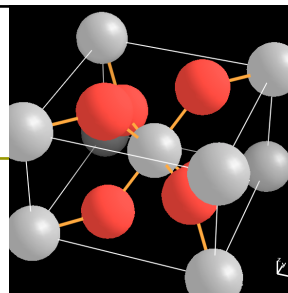
1 f =	24.163760 THz	151.825382 2PiTHz	806.016250 cm-1	99.933315 meV
2 f =	17.858403 THz	112.207657 2PiTHz	595.692194 cm-1	73.856446 meV
3 f =	14.425855 THz	90.640323 2PiTHz	481.194726 cm-1	59.660564 meV
4 f =	14.425855 THz	90.640323 2PiTHz	481.194726 cm-1	59.660564 meV
5 f =	13.549475 THz	85.133864 2PiTHz	451.961834 cm-1	56.036146 meV
6 f =	13.549475 THz	85.133864 2PiTHz	451.961834 cm-1	56.036146 meV
7 f =	12.767136 THz	80.218282 2PiTHz	425.868805 cm-1	52.800649 meV
8 f =	11.630951 THz	73.079419 2PiTHz	387.966746 cm-1	48.101763 meV
9 f =	11.320651 THz	71.129750 2PiTHz	377.616271 cm-1	46.818467 meV
10 f =	11.320651 THz	71.129750 2PiTHz	377.616271 cm-1	46.818467 meV
11 f =	3.917258 THz	24.612861 2PiTHz	130.665672 cm-1	16.200484 meV
12 f =	3.075099 THz	19.321416 2PiTHz	102.574256 cm-1	12.717591 meV
13 f =	3.075099 THz	19.321416 2PiTHz	102.574256 cm-1	12.717591 meV
14 f =	2.461587 THz	15.466605 2PiTHz	82.109687 cm-1	10.180307 meV
15 f =	2.416689 THz	15.184503 2PiTHz	80.612056 cm-1	9.994625 meV
16 f/i=	0.016908 THz	0.106236 2PiTHz	0.563988 cm-1	0.069926 meV
17 f/i=	0.021903 THz	0.137620 2PiTHz	0.730600 cm-1	0.090583 meV
18 f/i=	0.021903 THz	0.137620 2PiTHz	0.730600 cm-1	0.090583 meV



4 Ejemplo:

□ Autovectores

□ Ejemplo: Modo N° 2



2 f = 17.858403 THz 112.207657 2PiTHz 595.692194 cm-1 73.856446 meV

X	Y	Z	dx	dy	dz
0.000000	0.000000	0.000000	-0.000000	0.000000	0.000000
2.294651	2.294651	1.476306	0.000000	-0.000000	-0.000000
1.594810	1.594810	0.000000	-0.353553	-0.353553	-0.000000
3.194493	3.194493	0.000000	0.353553	0.353553	0.000000
0.899841	3.689461	1.476306	0.353553	-0.353553	-0.000000
3.689461	0.899841	1.476306	-0.353553	0.353553	-0.000000

4. Ejemplo: Rutilo

□ Clasificación de los modos

freq(cm-1) Irrep

1 (-0.025):	A _{2u}
2 (-0.022):	E _u
4 (2.428):	B _{1u}
5 (2.464):	A _{2u}
6 (3.075):	E _u
8 (3.918):	B _{1g}
9 (11.322):	E _u
11 (11.631):	B _{1u}
12 (12.767):	A _{2g}
13 (13.550):	E _g
15 (14.427):	E _u
17 (17.859):	A _{1g}
18 (24.164):	B _{2g}

IR, Raman and Hyper-Raman Active Modes

IR Active Modes

WP	A _{1g}	A _{1u}	A _{2g}	A _{2u}	B _{1g}	B _{1u}	B _{2g}	B _{2u}	E _u	E _g
4f	.	.	.	1	.	.	.	.	2	.
2a	.	.	.	1	.	.	.	.	2	.

Infrared active modes: A_{2u} + 3E_u (Acoustic modes not included)

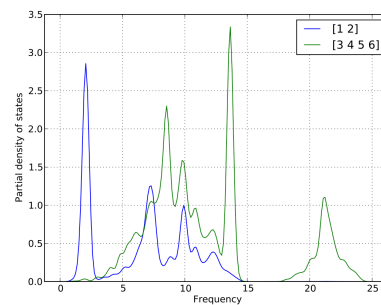
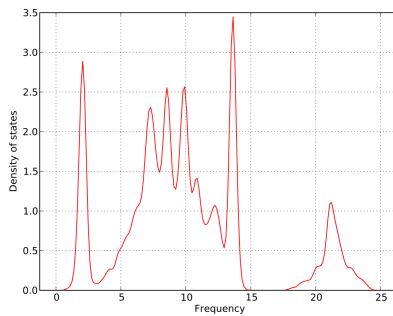
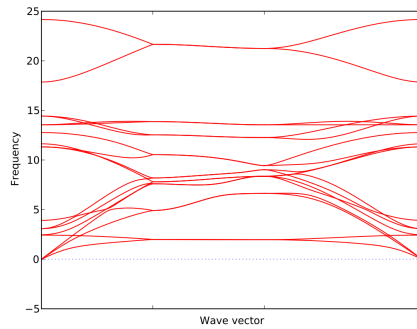
Raman Active Modes

WP	A _{1g}	A _{1u}	A _{2g}	A _{2u}	B _{1g}	B _{1u}	B _{2g}	B _{2u}	E _u	E _g
4f	1	.	.	.	1	.	1	.	.	1
2a	.	.	.	.	.	.	.	.	.	.

Raman active modes: A_{1g} + B_{1g} + B_{2g} + E_g

4. Ejemplo: Rutilo

- ▣ Rutilo:
- ▣ Grupo Espacial $P 4_2/m n m$
- ▣ $a=b= 4.5977(4)\text{\AA}$ y $c=2.9564(2)\text{\AA}$
- Ti⁴⁺ 2a 0.0 0.0 0.0
- O²⁻ 4f 0.3023(3) 0.3023(3)



4. Ejemplo: Rutilo

- ▣ Tensor Dieléctrico: ϵ_{ij}
- ▣ MACROSCOPIC STATIC DIELECTRIC TENSOR
(including local field effects in DFT)

7.423904	0.000000	0.000000
0.000000	7.423904	0.000000
0.000000	0.000000	8.849335

4. Ejemplo: Rutilo

□ Cargas de Born

$$Z_{k,\alpha\beta}^* = \frac{\Omega}{|e|} \frac{\partial P_\alpha}{\partial \epsilon_{k\beta}}$$

BORN EFFECTIVE CHARGES (e)

ion 1			
1	6.35763	1.04091	0.00000
2	1.04090	6.35765	0.00000
3	0.00000	0.00000	7.68997
ion 2			
1	6.35763	-1.04091	0.00000
2	-1.04090	6.35765	0.00000
3	0.00000	0.00000	7.68997
ion 3			
1	-3.16931	-1.82350	0.00000
2	-1.82348	-3.16930	0.00000
3	-0.00077	-0.00077	-3.84183
ion 4			
1	-3.16968	-1.82377	0.00000
2	-1.82381	-3.16974	0.00000
3	0.00077	0.00077	-3.84183
ion 5			
1	-3.16968	1.82377	0.00000
2	1.82348	-3.16930	0.00000
3	0.00077	-0.00077	-3.84183
ion 6			
1	-3.16931	1.82350	0.00000
2	1.82381	-3.16974	0.00000
3	-0.00077	0.00077	-3.84183

4. Ejemplo: Rutilo

□ Actividad Raman

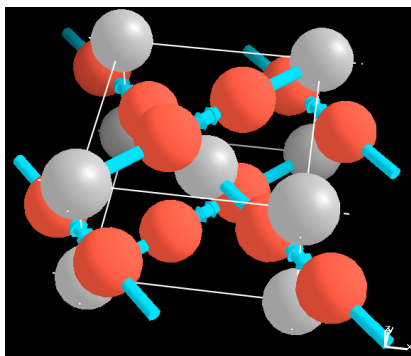
mode	freq(cm-1)	alpha	beta2	activity	Irrep.
001	806.01625	0.0111139	0.119	0.842	B2g
002	595.69219	3.6897265	126.828	1500.431	A1g
003	481.19473	0.0093502	0.000	0.005	Eu
004	481.19473	0.0017736	0.000	0.001	Eu
005	451.96183	-0.0246816	43.201	302.435	Eg
006	451.96183	0.0092582	43.239	302.678	Eg
007	425.86581	0.0028455	0.000	0.001	A2g
008	387.96675	0.0016885	0.000	0.000	B1u
009	377.61627	0.0072289	0.000	0.002	Eu
010	377.61627	0.0039901	0.000	0.001	Eu
011	130.66567	0.0017733	0.042	0.300	B1g
012	102.57426	0.0134835	0.000	0.008	Eu
013	102.57426	0.0080623	0.000	0.004	Eu
014	82.10969	0.0392713	0.000	0.071	A2u
015	80.61206	-0.0024535	0.000	0.000	B1u

$$\frac{d\sigma_i}{d\Omega} = \left(\frac{2\pi\nu_s}{c} \right)^4 \frac{I^{Ram}}{45} \frac{h(n_i^b + 1)}{8\pi^2\nu_i}$$

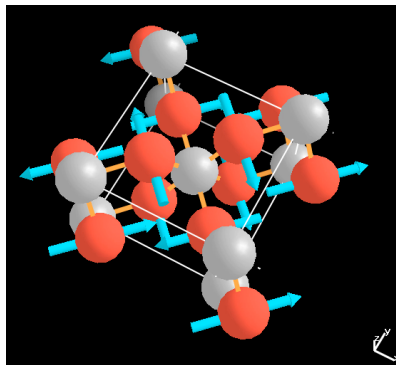
$$\frac{I^{Ram}}{45} = 45 \left(\frac{d\alpha}{dQ} \right)^2 + 7 \left(\frac{d\beta}{dQ} \right)^2 = 45\alpha'^2 + 7\beta'^2$$

4. Ejemplo: Rutilo

▣ Modos Raman Activos



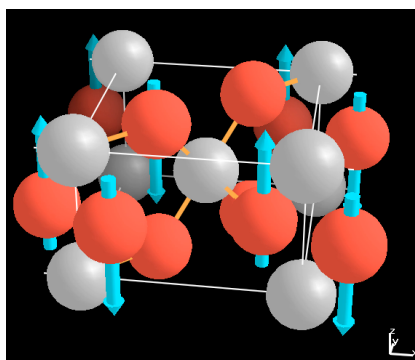
A_{1g}



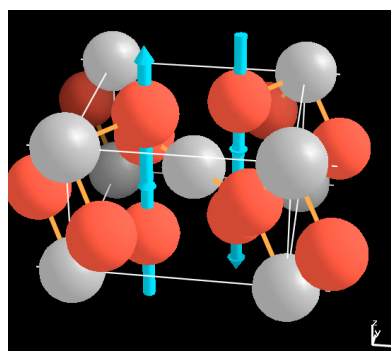
B_{1g}

4. Ejemplo: Rutilo

▣ Modos Raman Activos



E_g



E_g

3. Ejemplo

■ Rutilo:

Grupo Espacial $P 4_2/m n m$

$a=b= 4.5977(4)\text{\AA}$ y $c=2.9564(2)\text{\AA}$

Átomo Wyckoff $x\ y\ z$

$\text{Ti}^{4+}\ 2a\ 0.0\ 0.0\ 0.0$

$\text{O}^{2-}\ 4f\ 0.3023(3)\ 0.3023(3)$

