

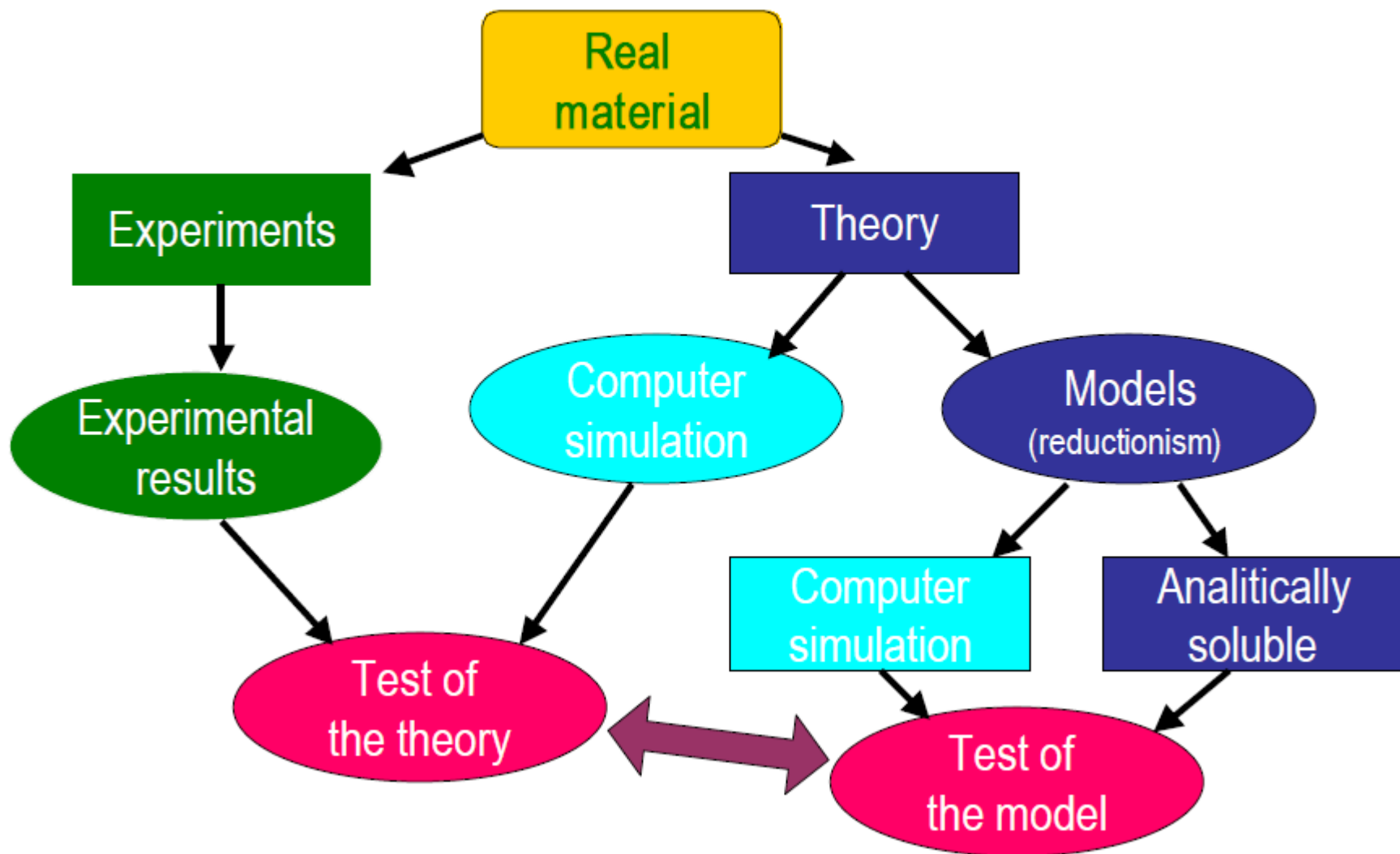


Cálculos ab initio de propiedades estructurales, electrónicas y magnéticas de sólidos.

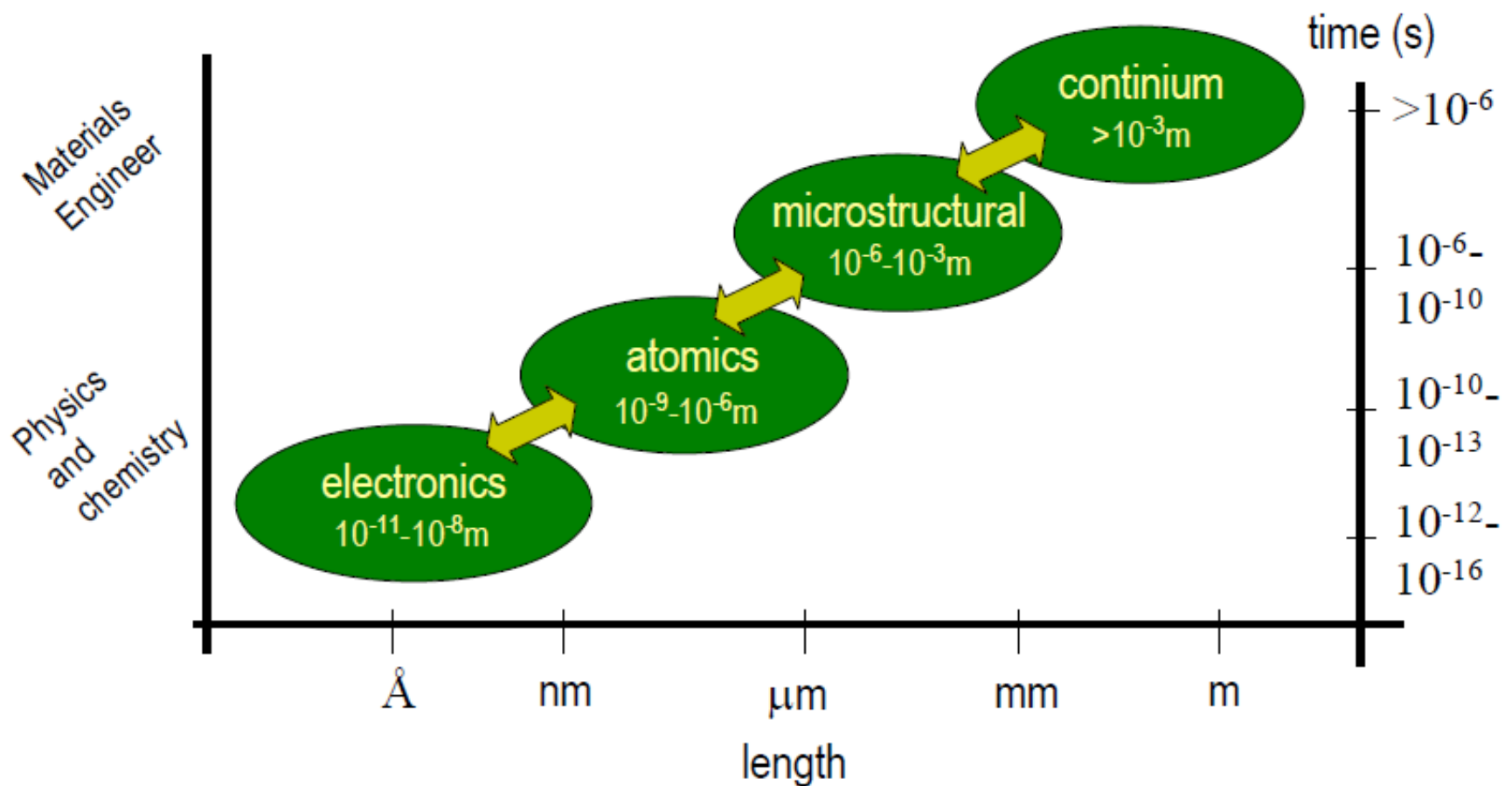
Leonardo A. Errico

Universidad Nacional de La Plata
Facultad de Ciencias Exactas
Departamento de Física

Computer simulation



Space and time in materials



Una posibilidad para estudiar sistemas que contienen muchos átomos (“sistemas complejos”) es emplear simulaciones computacionales.

Modelos clásicos: basados en esquemas semiempíricos.

Interacción entre los átomos se modela de forma tal de reproducir ciertos datos experimentales.

Alto grado de sofisticación

Muy útiles a nivel de ingeniería y cuando diferentes parámetros experimentales son conocidos con mucha precisión *en un conjunto de materiales estructural y electrónicamente similares.*

Si estos parámetros no son conocidos o el material en estudio presenta comportamientos anómalos o no bien comprendidos, este tipo de métodos no son adecuados, y es preferible una aproximación de

primeros principios.

Desventaja: demandante desde el punto de vista de requerimientos y tiempos computacionales.

Ventaja: no requieren ningún tipo de parámetro externo o conocimiento experimental del sistema en estudio.

Dos tipos de aproximaciones dentro del tratamiento cuántico :

Hartree Fock (HF)

Teorema de la Funcional Densidad (DFT).

HF: esquema tradicional, descripción de funciones de onda. En esta aproximación el intercambio exacto, correlación no es tenida en cuenta.

DFT: densidad electrónica, correlación e intercambio ambos en forma aproximada.

Aproximación universal al problema cuántico de un sistema de partículas cargadas (electrones) interactuantes en un potencial externo (el generado por los núcleos).


- Equation of the system

$$H|\Psi\rangle = E|\Psi\rangle$$

- Solid state physics hamiltonian:

$$(T_{ion} + T_e + V_{e-e} + V_{e-ion} + V_{ion-ion})\Psi(r_1, \dots, r_N; R_1, \dots, R_M) = E\Psi(r_1, \dots, r_N; R_1, \dots, R_M)$$

- Aproximación adiabática: separación de los grados de libertad iónicos y electrónicos.



 electron

$$(T_e + V_{e-e} + V_{e-ion} + V_{ion-ion})\Phi(r_1, \dots, r_N; \{R\}) = \varepsilon(\{R\})\Phi(r_1, \dots, r_N; \{R\})$$

Electrons $(T_e + V_{e-e} + V_{e-ion} + V_{ion-ion})\Phi(r_1, \dots, r_N; \{R\}) = \mathcal{E}(\{R\})\Phi(r_1, \dots, r_N; \{R\})$

• **knowing $\mathcal{E}(R)$ we can have:**

- Ground state ($T=0$)
- Crystalline structure and PV diagram
- Elastic, optics, magnetics, etc, properties

- Potential energy surface
- Interatomic potential
- \Rightarrow **interatomic forces**

Electrons : solution of the Schrödinger Eq.

- Hamiltonian of a many electrons system:

$$\left(\sum_{j=1}^N -\frac{\hbar^2}{2m} \nabla_j^2 + V_{e-e} + V_{ext} \right) \Phi(\vec{r}_1, \dots, \vec{r}_N) = E \Phi(\vec{r}_1, \dots, \vec{r}_N)$$

- To look for the GS by means of a variational method:

$$E_0[\Phi_0] = \text{Min}_{\tilde{\Phi}} \langle \tilde{\Phi} | H | \tilde{\Phi} \rangle$$

$$\tilde{\Phi}(\vec{r}_1, \dots, \vec{r}_N) \quad 3N \text{ dimensions trial function}$$

- **Approximate Methods** : one electron selfconsistent equations

Hartree: $\Phi(\vec{r}_1, \dots, \vec{r}_N) = \phi_1 \dots \phi_N$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Z}{r} + \int \frac{n(r')}{|r-r'|} dr' \right) \phi_i = \varepsilon_i \phi_i, \quad \text{con } n(r) = \sum_i |\phi_i|^2$$

Hartree-Fock: $\Phi(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \det[\phi_1 \dots \phi_{N_i}]$

Density Functional Theorem (DFT)

1927: Thomas y Fermi: Modelo semiclásico para átomos pesados aislados en términos de la densidad electrónica $\rho(r)$ del estado fundamental del átomo.

1930: Dirac: Generalización de la teoría: “Thomas-Fermi-Dirac Theory”.

1964: Hohenberg y Kohn

Hohenberg and Kohn Theorem: La energía total de un sistema de N electrones en un potencial externo se puede escribir como una funcional de $\rho(r)$

$$E = E[\rho(r)]$$

$$E = E[\rho(r)_{\uparrow}, \rho(r)_{\downarrow}]$$

La “buena” $\rho(r)$ es aquella que minimiza $E[\rho(r)]$

Pero:

Forma explícita de $E[\rho(\mathbf{r})]$?



Approximaciones!!

$$E = E^{\text{hartree}} + E^{\text{exchange and correlation}}$$

$$E[\rho(r)] = T[\rho(r)] + E_H[\rho(r)] + E_{nn}[\rho(r)] + E_{xc}[\rho(r)]$$

$$E_H[\rho(r)] = \frac{e^2}{2} \int d^3r d^3r' \frac{\rho(r)\rho(r')}{|r-r'|}$$

- Remember, DFT is a great theory
- Highly accurate structures
- Sufficient accuracy for a huge range of problems
- Efficient!

- But it is not perfect

- DFT is an exact theory
- KS is an exact way of doing DFT
- The problem comes from our choice of $E_{xc}[\rho]$

Exchange and correlation

SCIENCE'S COMPASS



PERSPECTIVES

PERSPECTIVES: DENSITY FUNCTIONAL THEORY

In Pursuit of the "Divine" Functional

Ann E. Mattsson

Paul Dirac reputedly said that the Schrödinger equation (SE) marked the end of chemistry: All answers could be calculated from the SE. The SE can indeed be solved exactly for some systems, such as the hydrogen atom, and numerically to arbitrary precision for systems with a small number of electrons. However, the many-body character of the SE sets a fundamental limit on the size of solvable systems (1).

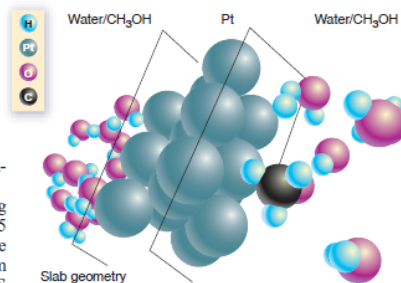
In a seminal paper, Hohenberg and Kohn (2) showed in 1964 that the SE, formulated as an equation of an N -electron wave function of $3N$ variables, could be reformulated as an equation of the electron density with only three variables. Thanks to this tremendous simplification, density-functional theory (DFT) has become an invaluable alternative to the SE in most areas of physics and chemistry, as demonstrated at a recent workshop in Albuquerque, New Mexico (3).

An important step toward applying DFT to real systems was taken in 1965 when Kohn and Sham (4) published the Kohn-Sham (KS) equations, derived from the Hohenberg-Kohn theorem. The KS equations recast the SE problem of interacting electrons moving in an external ion potential into a problem of noninteracting electrons moving in an effective potential

lated exactly, just as the properties of small systems can be calculated from the SE.

The first step toward the divine functional was the local density approximation (LDA), where only the electron density at a point in the system is used for determining this point's contribution to the total exchange-correlation energy of the system (4, 6, 7). LDA assumes a homogeneous electron gas but also works amazingly well for inhomogeneous systems. It is still used extensively.

Attempts to determine why the LDA



DFT wins. A methanol molecule at the interface of water and platinum. Periodic boundary conditions are used, creating extended metallic surface states. Structural and

sively used in gas-phase catalysis, where the metallic character of the catalyst makes traditional SE methods inappropriate, and for determining phase diagrams (e.g., for steels).

In recognition of the importance of DFT, Walter Kohn was awarded half of the 1998 Nobel Prize in Chemistry (the other half was awarded to John Pople) (10). Today numerous approximate functionals are in use (11)—a sign of the method's utility but also an indication that none is suitable for all systems. As the complexity of systems investigated by DFT grows (see the figure), the task of choosing the right functional becomes increasingly difficult.

Although DFT is an invaluable tool in investigations of complicated systems, we cannot yet rely solely on this tool but need to combine it with, for example, some experimental data. Furthermore, recent studies involving surfaces have revealed unexpectedly poor and inconsistent energy results (12, 13). Errors are much harder to estimate for DFT than for SE contributions, making it difficult to know when DFT is likely not to give accurate results.

For many years, improved numerical techniques and faster algorithms have dominated efforts to improve the results of DFT calculations. Now a number of efficient DFT programs are available that, regardless of numerical method, give the same answer for a given functional. The remaining error stems from the exchange-correlation functional itself. To further improve the accuracy of DFT calculations, better functionals need to be developed.

To this end, a workshop was organized by Sandia National Laboratories in August of this year (3).

Exchange and correlation

DENSITY FUNCTIONAL THEORY

Fixing Jacob's ladder

Density functional theory calculations can be carried out with different levels of accuracy, forming a hierarchy that is often represented by the rungs of a ladder. Now a new method has been developed that significantly improves the accuracy of the 'third rung' when calculating the properties of diversely bonded systems.

Roberto Car

Density functional theory (DFT) is the method of choice for calculating the electronic structure of molecules and materials in applications involving large systems and/or extensive sampling of geometries. It comes in several 'flavours', each relying on various approximations, which means that although DFT methods can typically describe bonds of a similar kind reasonably well, they have difficulties dealing with diversely bonded systems. Now, writing in *Nature Chemistry*, Jianwei Sun

and co-workers have made a major contribution to overcome this limitation by devising a new functional and creating a new flavour of DFT that is computationally efficient and works equally well for covalent and metallic bonds as it does for ionic, hydrogen and even intermediate-range van der Waals bonding¹.

The electronic ground-state energy, and how it changes with nuclear positions, determines the geometries of molecules and materials as well as the relative stability

of isomers, different phases of matter, and chemical reactants and products. Knowing the quantum-mechanical energy of the electrons requires knowledge of the wavefunction, and the computational cost of calculating it grows exponentially with the number of electrons (N) in the system. Walter Kohn, the father of DFT, likened the computational cost of calculating the wavefunction to an 'exponential wall' of quantum mechanics in his 1998 Nobel Prize address²: it means that accurate

820

NATURE CHEMISTRY | VOL 8 | SEPTEMBER 2016 | www.nature.com/naturechemistry

© 2016 Macmillan Publishers Limited, part of Springer Nature. All rights reserved.

THE JOURNAL OF CHEMICAL PHYSICS 144, 204120 (2016)



Rungs 1 to 4 of DFT Jacob's ladder: Extensive test on the lattice constant, bulk modulus, and cohesive energy of solids

Fabien Tran, Julia Stelzl, and Peter Blaha
Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165-TC, A-1060 Vienna, Austria

(Received 4 March 2016; accepted 22 April 2016; published online 27 May 2016)

A large panel of old and recently proposed exchange-correlation functionals belonging to rungs 1 to 4 of Jacob's ladder of density functional theory are tested (with and without a dispersion correction term) for the calculation of the lattice constant, bulk modulus, and cohesive energy of solids. Particular attention will be paid to the functionals MGGA_MS2 [J. Sun *et al.*, *J. Chem. Phys.* **138**, 044113 (2013)], mBEEF [J. Wellendorff *et al.*, *J. Chem. Phys.* **140**, 144107 (2014)], and SCAN [J. Sun *et al.*, *Phys. Rev. Lett.* **115**, 036402 (2015)] which are meta-generalized gradient approximations (meta-GGA) and are developed with the goal to be universally good. Another goal

THE JOURNAL OF CHEMICAL PHYSICS 123, 062201 (2005)

Prescription for the design and selection of density functional approximations: More constraint satisfaction with fewer fits

John P. Perdew, Adrienn Ruzsinszky, and Jianmin Tao
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118


Viktor N. Staroverov and Gustavo E. Scuseria
Department of Chemistry, Rice University, Houston, Texas 77005

Gábor I. Csonka
Department of Inorganic Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary


(Received 18 August 2004; accepted 17 March 2005; published online 17 August 2005)

Exchange and correlation

Diferentes aproximaciones

LDA  $E_{xc} = \int \varepsilon_{xc} [\rho(r)] \rho(r) d^3r$

$\varepsilon_{xc}[\rho(r)]$ debe reproducir la energía del gas de electrones.

GGA  $\varepsilon_{xc} = \varepsilon_{xc}[\rho(r), |\nabla\rho(r)|]$

- In Hartree-Fock (and KS) theory the Coulomb energy is

$$J[\rho] = \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}$$

- Includes interaction of each electron with *all* — including itself!
- In HF theory the self-interaction is exactly cancelled by exchange

$$J[\rho] = +\frac{1}{2} \sum_{ij} \int d\vec{r}_1 \int d\vec{r}_2 \frac{\psi_i^*(\vec{r}_1)\psi_i(\vec{r}_1)\psi_j^*(\vec{r}_2)\psi_j(\vec{r}_2)}{r_{12}}$$

$$E_x^{\text{HF}} = -\frac{1}{2} \sum_{ij} \int d\vec{r}_1 \int d\vec{r}_2 \frac{\psi_i^*(\vec{r}_1)\psi_j(\vec{r}_1)\psi_j^*(\vec{r}_2)\psi_i(\vec{r}_2)}{r_{12}}$$

- Functionals in the form

$$E_{\text{xc}}[\rho] = \int d\vec{r} f(\rho(\vec{r}))$$

can never treat this correctly

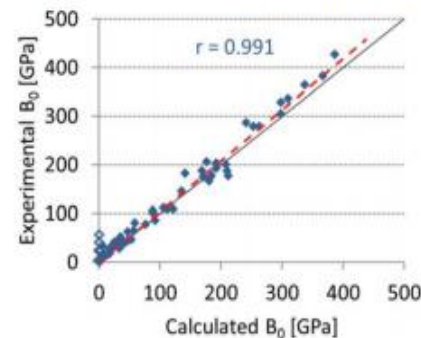
- Local information not enough
- Even semi-local functionals fail

$$E_{\text{xc}}[\rho] = \int d\vec{r} f(\rho(\vec{r}), |\vec{\nabla}\rho|(\vec{r}), \dots)$$

- Exact exchange doesn't help — this is a correlation problem

Error Estimates for Solid-State Density-Functional Theory Predictions: An Overview by Means of the Ground-State Elemental Crystals

K. Lejaeghere,¹ V. Van Speybroeck,¹ G. Van Oost,² and S. Cottenier^{1,3,4}



(r^{-3}). Moreover, the experimental uncertainties on the electric quadrupole hyperfine interaction constants B that were used to fit the b^{02} are large. Therefore, the reported error bar of 0.006 b or 5% might well be too low and the real uncertainty can amount to 10%–20% (0.01–0.02 b).¹⁰ In summary, the current knowledge on the ⁹⁹Tc ground state quadrupole moment is as follows: There are three reported values with a

ne EFG. The large sta

ue to the parabolic bel

ne $T^{3/2}$ functional dependence.

In addition, a theoretical

ncertainty of 10% for the LAPW calculation is taken into

onsideration. This is based on our previous experience

25,26], where the quadrupole moments of ⁵⁷Fe, ⁷⁷Se, and

⁹⁰Rh were determined b

tical EFG calculations a

for LSDA or GGA, respectively. Nevertheless, even the EFGs of this class fall onto the regression line, and the value for Q does not change by more than 10% if one would exclude these cases from the fit.

Comparing experimental quadrupole splittings and theoretical EFGs one can deduce $Q(^{57}\text{Fe})$ to be 0.16 b from the slope of a least square fit [22]. The resulting error of such a comparison is about 5% in Q , which might in part stem from experimental uncertainties like fitting procedures, not well determined structural parameters or temperature effects, since some experiments are done at room temperature while theory corresponds to $T = 0$ K. In any case, $Q = 0.16$ b is twice

Precision of Electric-Field Gradient Predictions by Density Functional Theory and Implications for the Nuclear Quadrupole Moment and Its Error Bar of the ¹¹¹Cd 245 keV 5/2⁺ Level

Leonardo Errico,^{†,‡} Kurt Lejaeghere,[§] Jorge Runco,[†] S. N. Mishra,[⊥] Mario Rentería,[†] and Stefaan Cottenier^{*,§,||}

[†]Departamento de Física and Instituto de Física La Plata (IFLP, CCT-La Plata, CONICET-UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Casilla de Correo 67, 1900 La Plata, Argentina

[‡]Universidad Nacional del Noroeste de la pcia. de Buenos Aires (UNNOBA), Monteagudo 2772, Pergamino, (CP 2700) Buenos Aires, Argentina

[§]Center for Molecular Modeling, and ^{||}Department for Materials Science and Engineering, Ghent University, Tech Lane Ghent Science Park – Campus A, building 903, BE-9052 Zwijnaarde, Belgium

[⊥]Tata Institute of Fundamental Research, Homi Bhabha road, Mumbai-400005, India

RESEARCH ARTICLE SUMMARY

DFT METHODS

Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere,^{*} Gustav Bihlmayer, Torbjörn Björkman, Peter Blaha, Stefan Blügel, Volker Blum, Damien Caliste, Ivano E. Castelli, Stewart J. Clark, Andrea Dal Corso, Stefano de Gironcoli, Thierry Deutsch, John Kay Dewhurst, Igor Di Marco, Claudia Draxl, Marcin Dulak, Olle Eriksson, José A. Flores-Livas, Kevin F. Garrity, Luigi Genovese, Paolo Giannozzi, Matteo Giantomassi, Stefan Goedecker, Xavier Gonze, Oscar Grånäs, E. K. U. Gross, Andris Gulans, François Gygi, D. R. Hamann, Phil J. Hasnip, N. A. W. Holzwarth, Diana Iusana, Dominik B. Jochym, François Jollet, Daniel Jones, Georg Kresse, Klaus Koepf, Emine Küçükbenli, Yaroslav O. Kvashnin, Inka L. M. Locht, Sven Lubeck, Martijn Marsman, Nicola Marzari, Ulrike Nitzsche, Lars Nordström, Taisuke Ozaki, Lorenzo Paulatto, Chris J. Pickard, Ward Poelmans, Matt L. J. Probert, Keith Refson, Mamiel Richter, Gian-Marco Rigamonti, Santanu Saha, Matthias Scheffler, Martin Schlipf, Kartheinz Schwarz, Sangeeta Sharma, Francesca Tavazza, Patrik Thunström, Alexandre Tkatchenko, Marc Torrent, David Vanderbilt, Michiel J. van Setten, Veronique Van Speybroeck, John M. Wills, Jonathan R. Yates, Guo-Xu Zhang, Stefaan Cottenier^{*}

Kohn and Sham (1965): “Kohn and Sham equations”

$$(T + V_{en}(r) + V_H(r) + V_{xc}(r))\mathcal{G}_i(r) = \varepsilon_i \mathcal{G}_i(r)$$

$\rho(r)$ dada por:

$$\rho(r) = \sum_{oc} \mathcal{G}_i^*(r) \mathcal{G}_i(r)$$

Una vez que se ha hecho la elección del potencial XC, las ecuaciones de Kohn–Sham quedan completamente determinadas.

Un código DFT resuelva estas ecuaciones numéricamente, lo que conduce (en principio) a soluciones/predicciones numéricamente exactas.

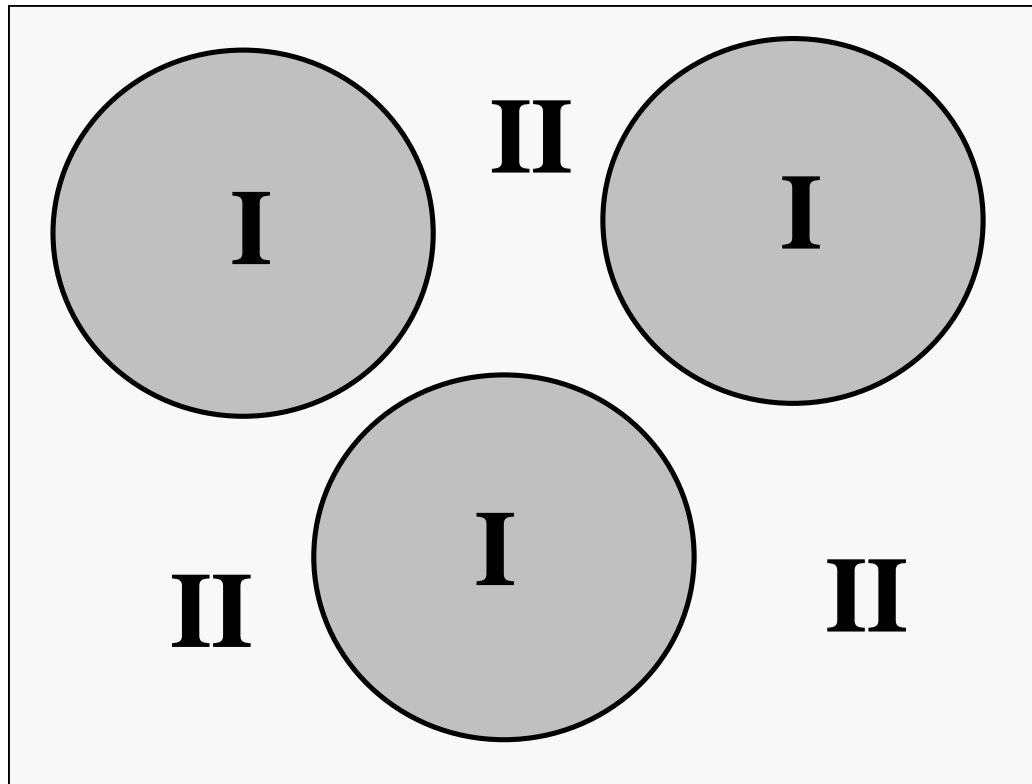
Métodos numéricos

$$g_i(\bar{r}) = \sum_{\alpha} C_{i,\alpha} \Phi_{\alpha}(\bar{r})$$

La base que “definida” por el problema a resolver.

El método APW.

J. C. Slater, *Phys. Rev.* 51, 846 (1937).



Base dual:

Esferas Atómicas:

$$\mathcal{G}(\bar{r}) = \sum_{l,m} A_{l,m} u_l(r) Y_{l,m}(\bar{r})$$

$$\left\{ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right\} r u_l(r) = 0$$

Región intersticial:

$$\mathcal{G}(\bar{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\bar{G}} C_{\bar{G}} e^{i(\bar{G}+\bar{k})\bar{r}}$$

$$A_{l,m} = \frac{4\pi i^l}{\sqrt{\Omega} u_l(E_l, R_i)} \sum_{\bar{G}} C_{\bar{G}} J_l(|\bar{G} + \bar{k}| R_i) Y_{l,m}^*(\bar{k} + \bar{G})$$

Problema: $u_l(r)$ es solución de la ecuación radial de Schrodinger sólo at E_l .

El método FP-LAPW

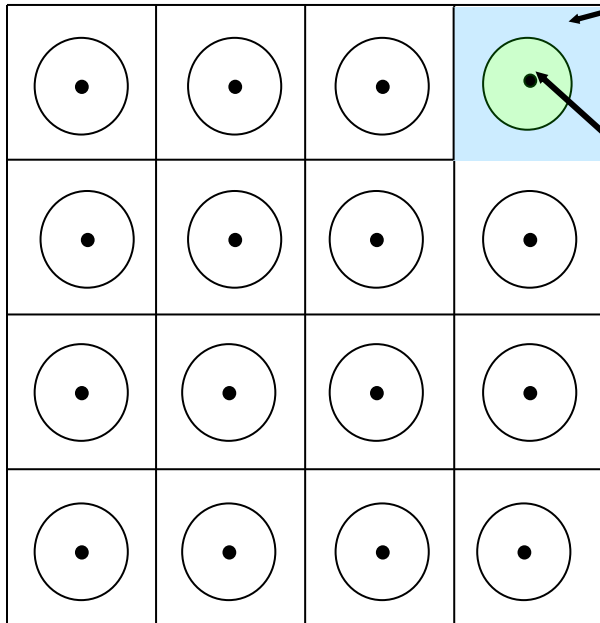
Intersticio:

$$\mathcal{G}(\bar{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\bar{G}} C_{\bar{G}} e^{i(\bar{G}+\bar{k})\bar{r}}$$

Esferas atómicas

$$\mathcal{G}(\bar{r}) = \sum_{l,m} \left[A_{l,m} u_l(r, E_l) + B_{l,m} \dot{u}_l(r, E_l) \right] Y_{l,m}(\bar{r})$$

$$\left\{ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right\} r \dot{u}_l(r) = r u_l(r)$$



$$\varphi(r) = \frac{1}{\Omega^{1/2}} \sum_G C_G e^{i(G+K)r}$$

$$\varphi(r) = \sum_{m,l} [A_{l,m} u(r) + B_{l,m} \dot{u}_l(r)] Y_{l,m}(r)$$

non-relativistic
relativistic

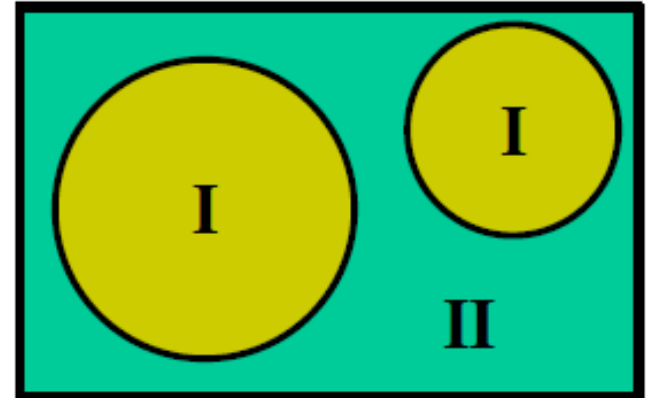
all-electron full-potential
all-electron muffin-tin
pseudopotenciales
jellium

LDA
GGA

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + v_{xc}(\vec{r}) \right] \varphi_i^k = \varepsilon_i^k \varphi_i^k$$

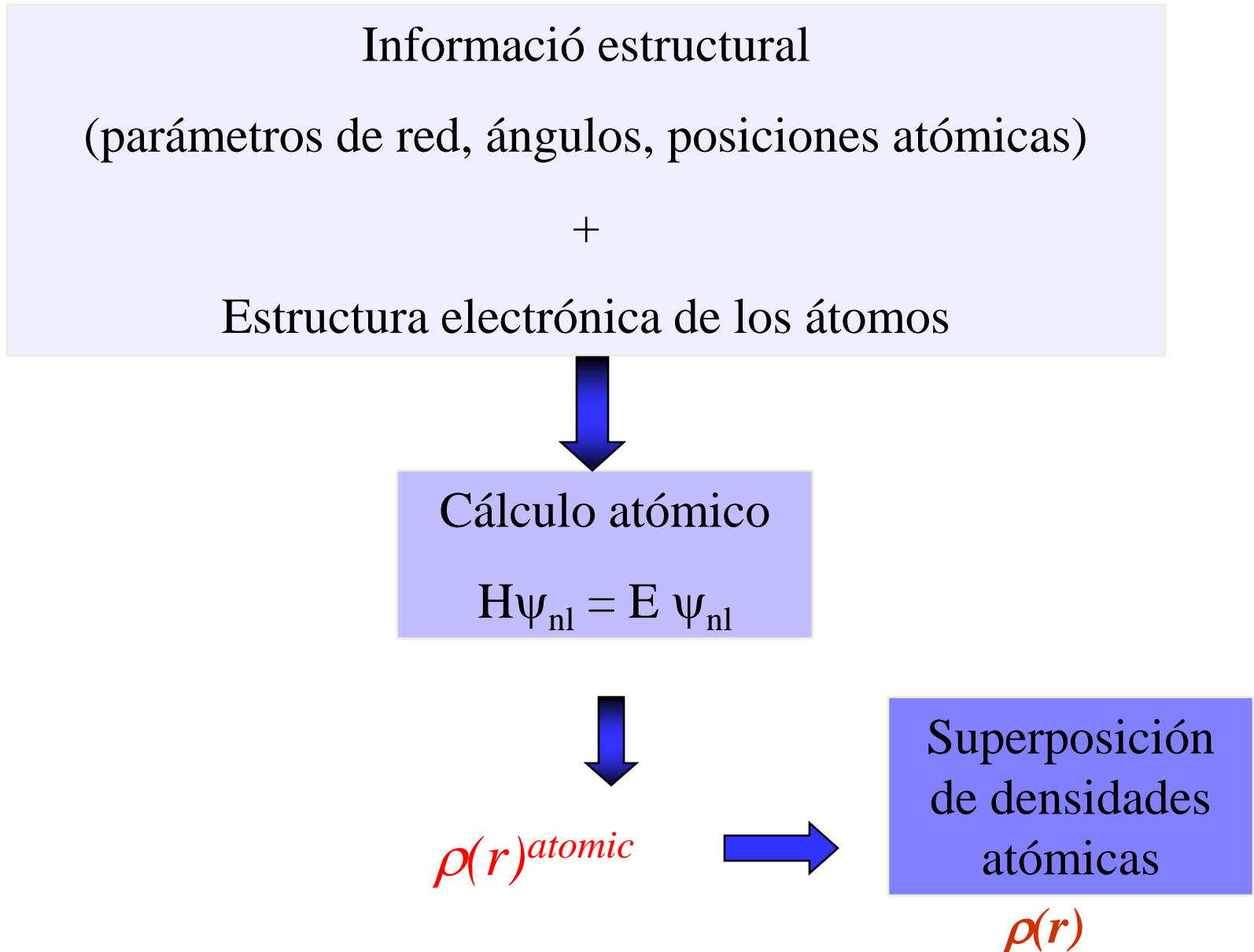
periodic
no-periodic

spin-polarized
non spin-polarized



linearized augmented
plane wave: LAPW
scattering functions
(ex.: Hankel): LMTO
plane wave
LCAO

Esquema General



$$\rho(r) \longrightarrow \nabla^2 V_C = -8\pi \rho(r)$$

$$V = V_C + V_{EXC}$$

$$[-\nabla^2 + V]\psi_k = E_k \psi_k$$

$$E_k, \psi_k$$

$$\rho(r)_{val} = \sum_{E_k < E_F} \psi_k^* \psi_k \quad \rho(r)_{core}$$

$$\rho(r)_{new} = \rho_{old} \otimes (\rho_{val} + \rho_{core})$$

Terminamos el cálculo ¿Qué tenemos?

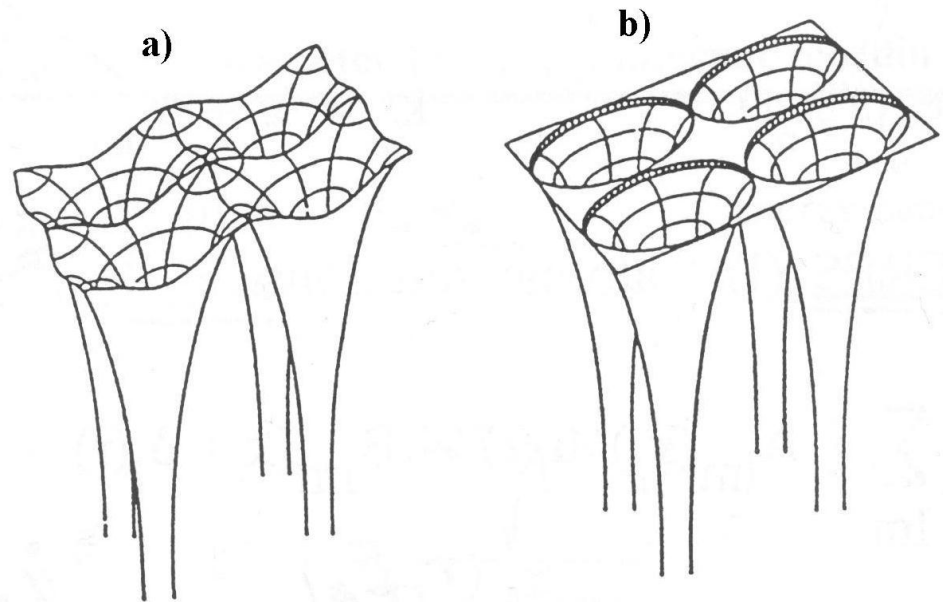
Por supuesto, $\rho(r)$.

A partir de $\rho(r)$ podemos obtener el potencial electrostático y la energía del estado fundamental del sistema en estudio.

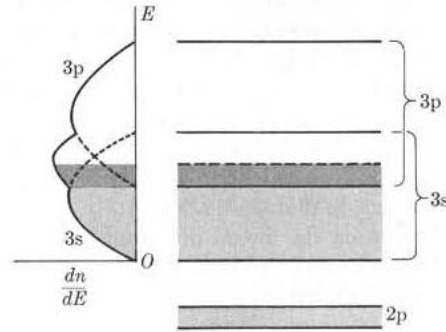
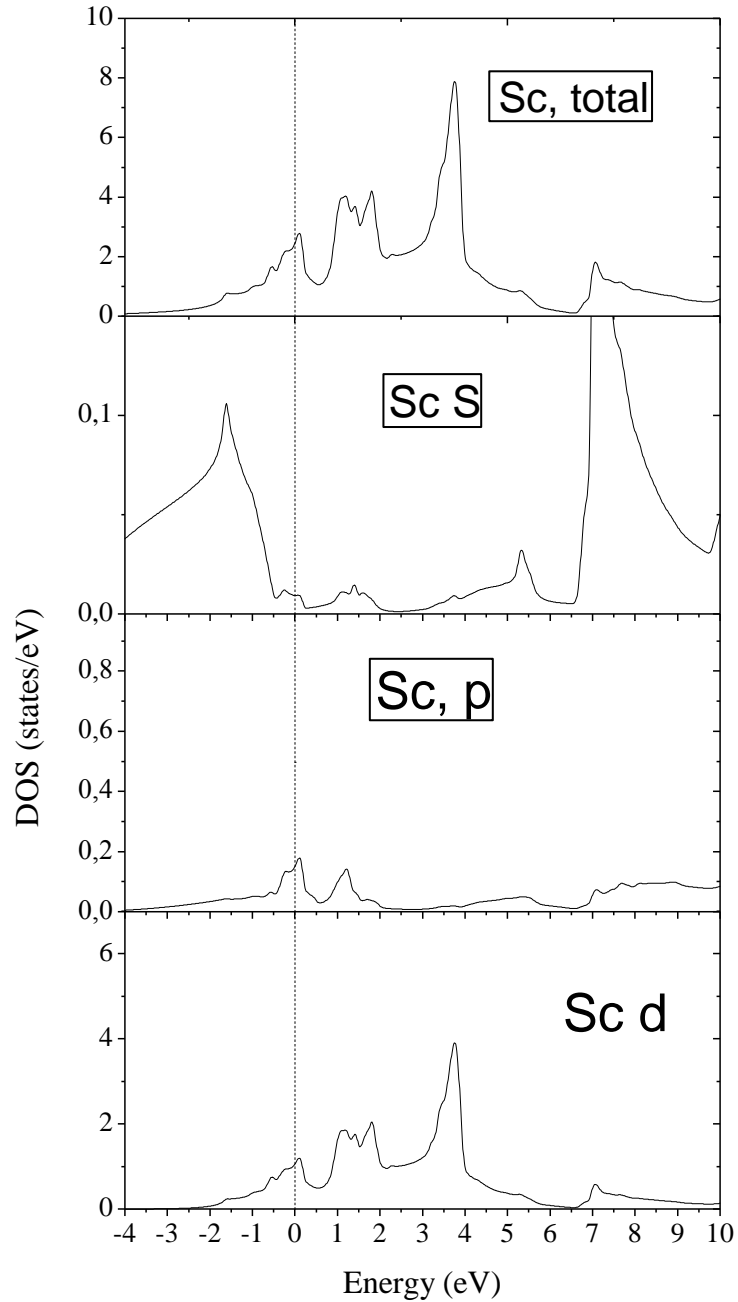
$$V(\mathbf{r}) = \begin{cases} \sum_{l,m} V_{l,m}(\mathbf{r}) Y_{l,m}(\bar{\mathbf{r}}) & (I) \\ \sum_K V(K) \exp(iK\bar{\mathbf{r}}) & (II) \end{cases}$$

Sin aproximaciones de forma para el potencial (“Full potential”)

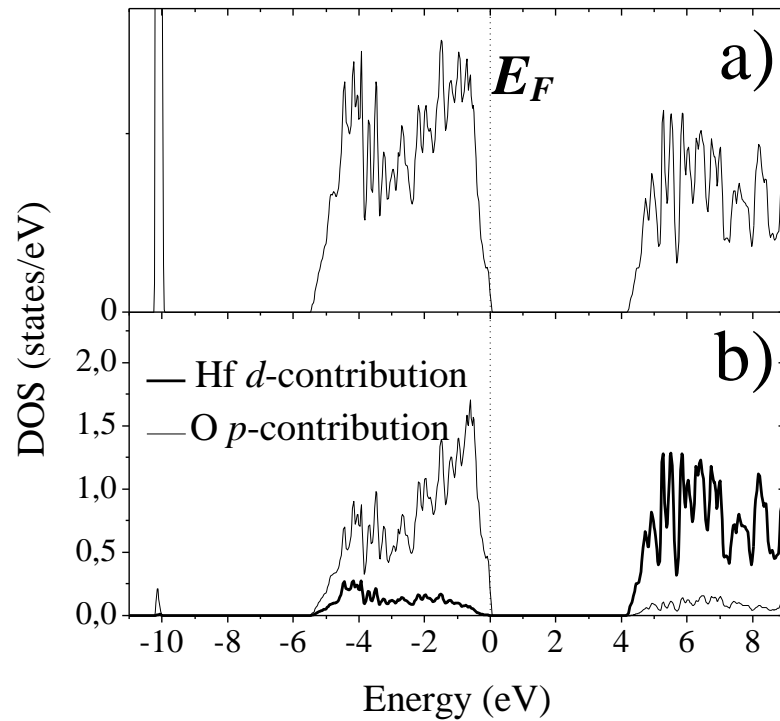
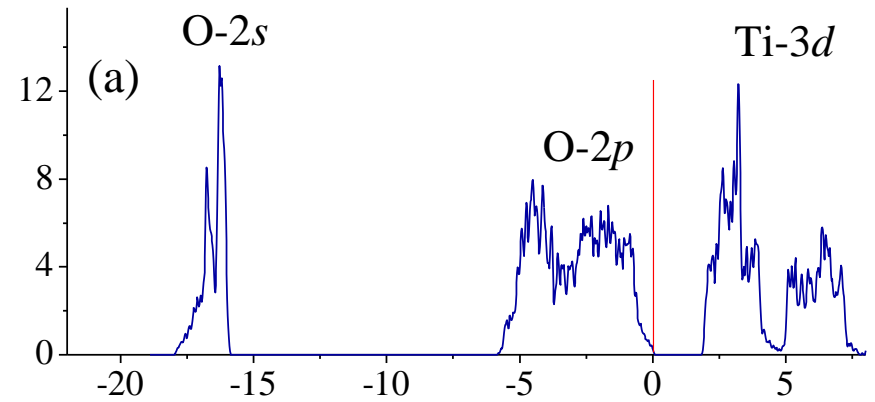
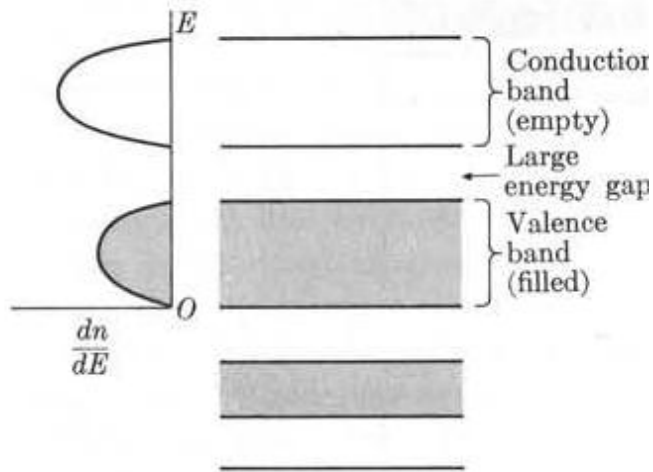
Hace unos ños, sólo $l = 0$, $m = 0$ y $k = 0$ (“muffin tin approximation”).



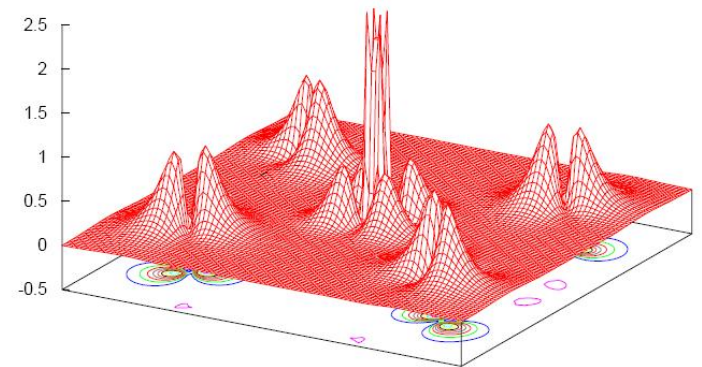
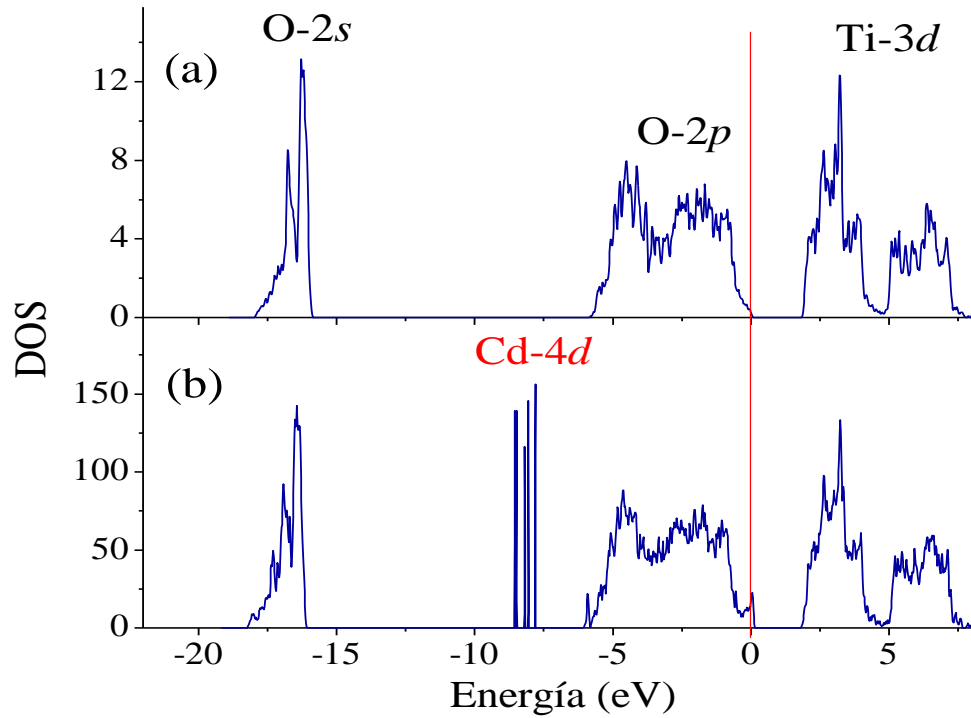
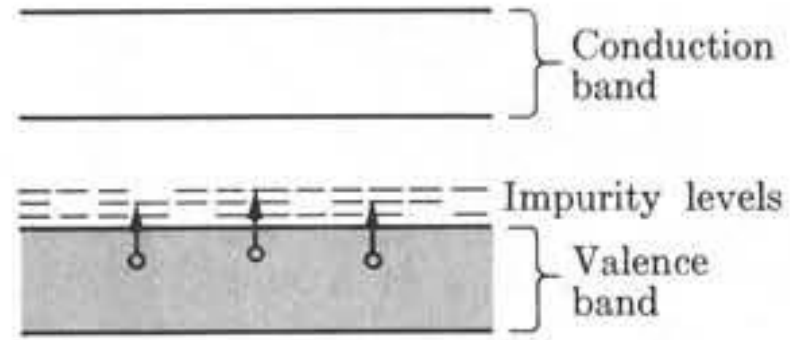
Ejemplo en metales. HCP Sc.



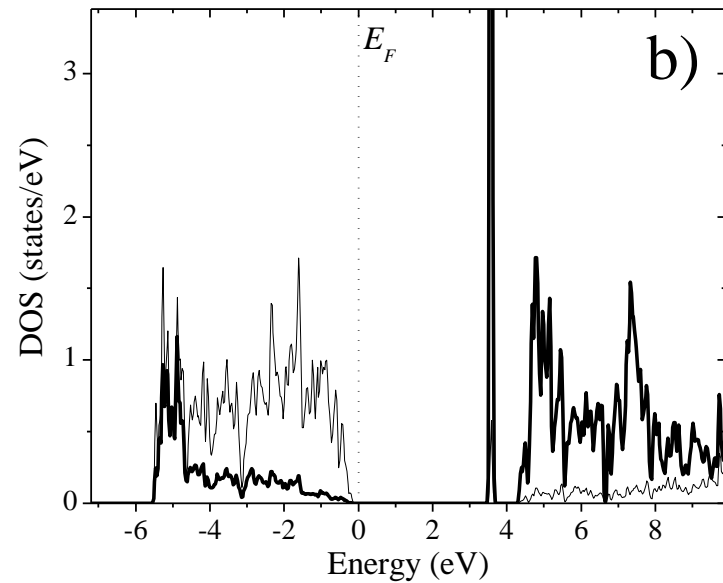
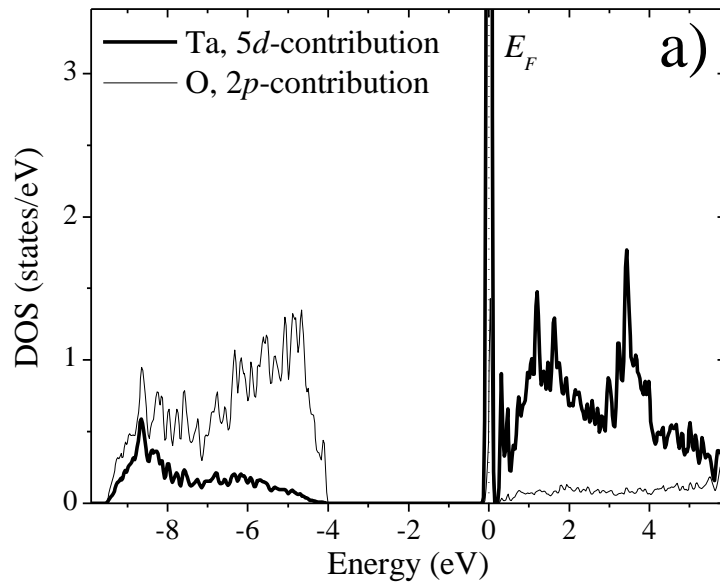
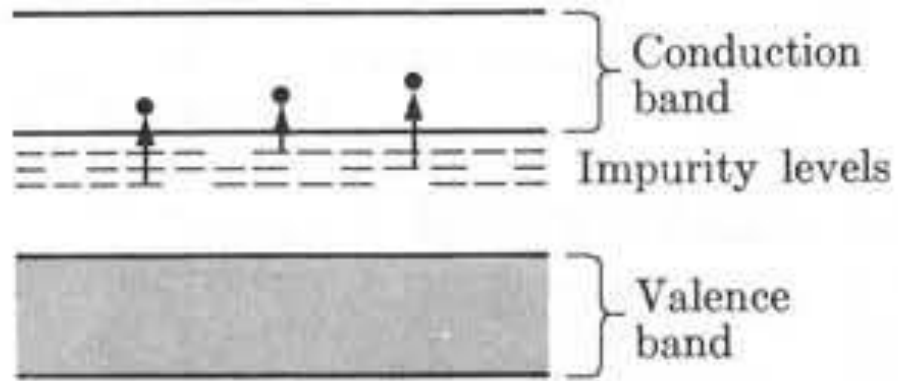
Semiconductores de ancho gap. TiO_2 y HfO_2



Impurezas aceptoras.

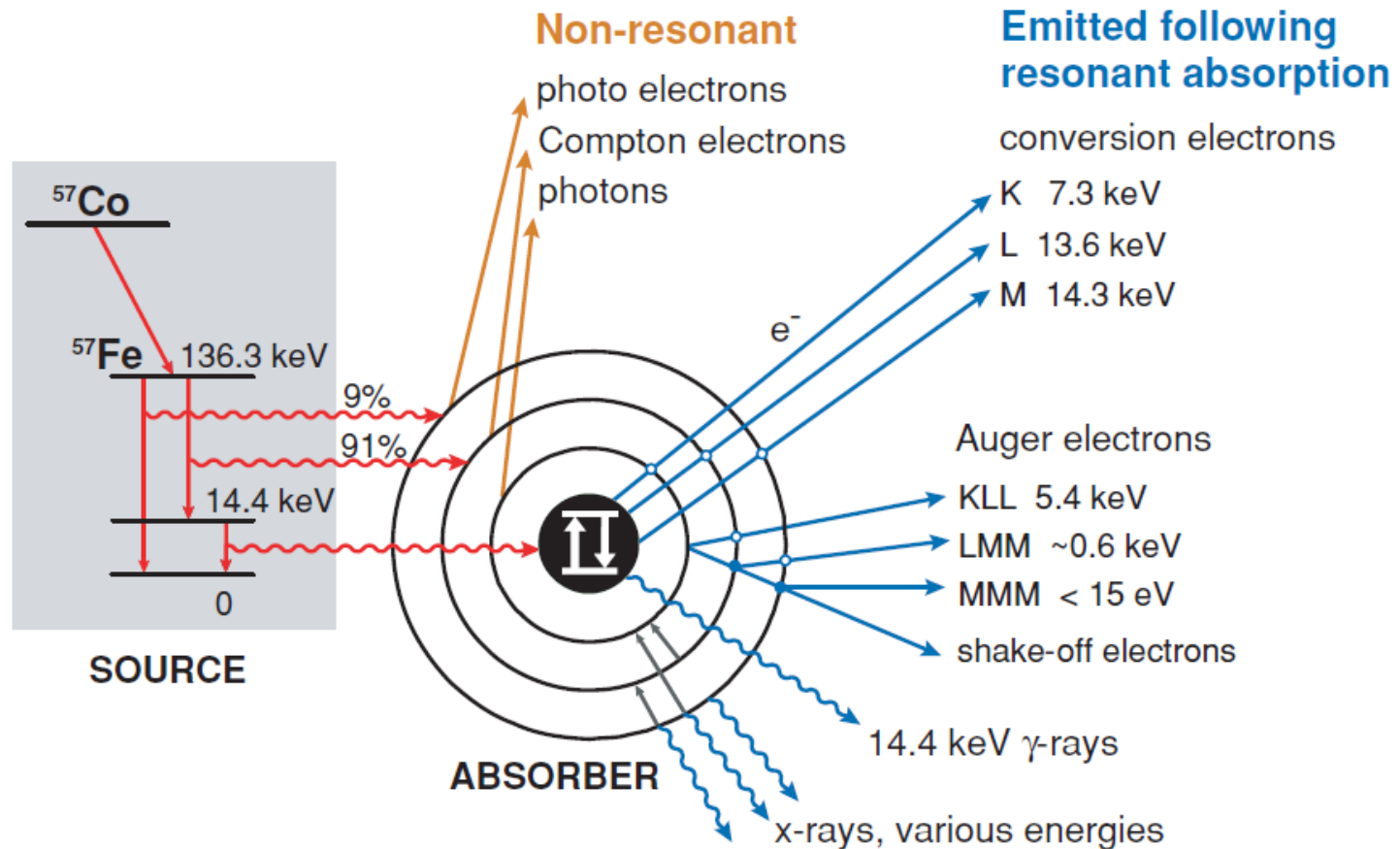


Impurezas donoras.

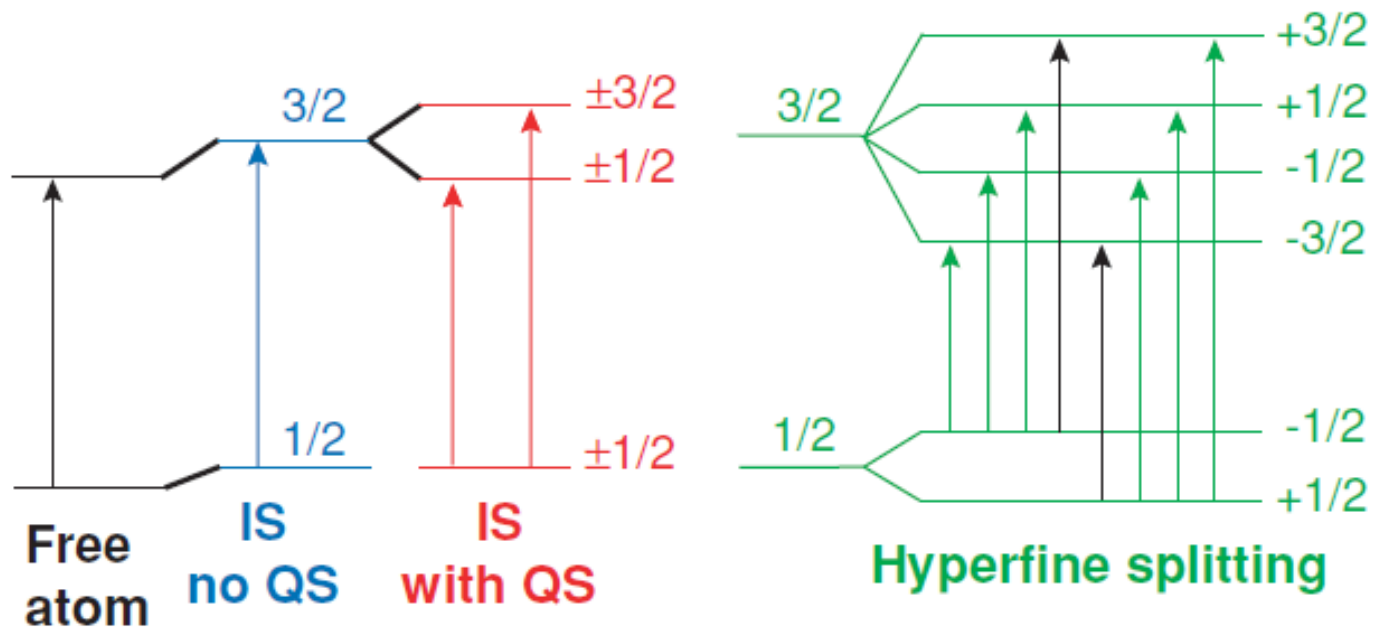
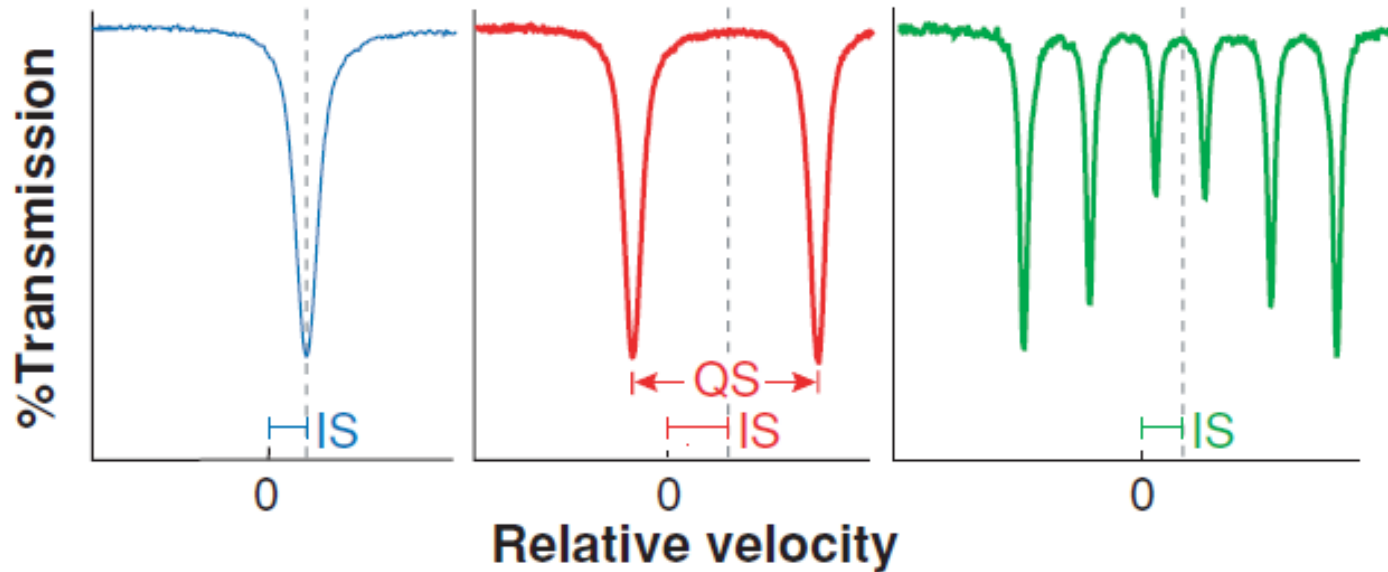


Espectroscopía Mössbauer. Propiedades hiperfinas.

Absorción resonante de radiación gamma emitida por un núcleo.

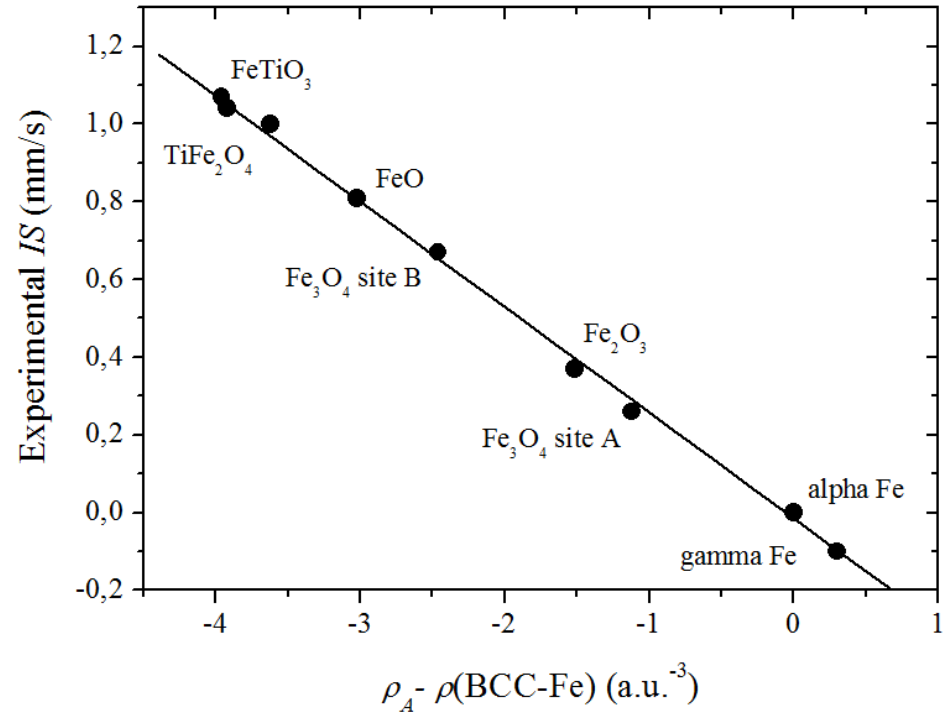
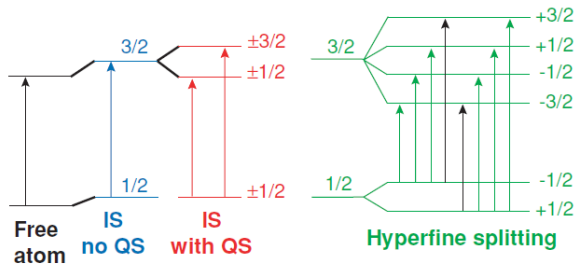
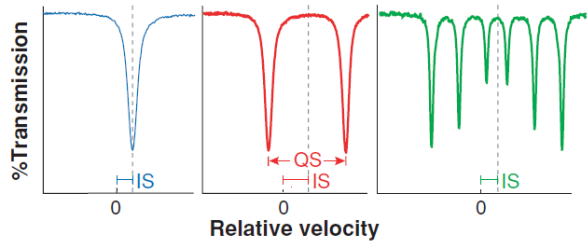


Espectroscopía Mössbauer. Propiedades hiperfinas.



Espectroscopía Mössbauer. Propiedades hiperfinas.

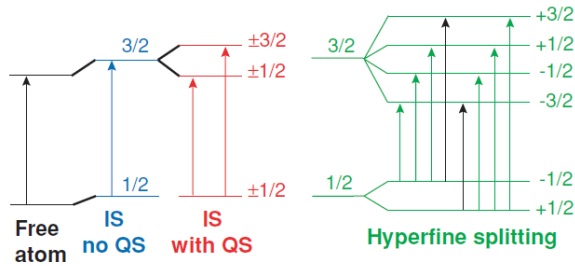
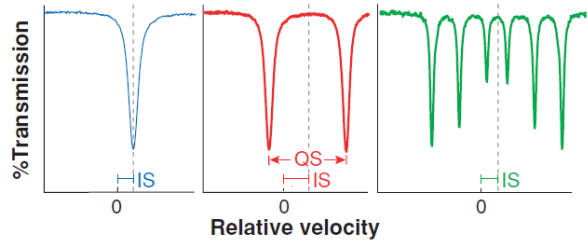
Corrimiento isomérico (IS).



$$IS = \alpha(\rho_A - \rho_R)$$

Espectroscopía Mössbauer. Propiedades hiperfinas.

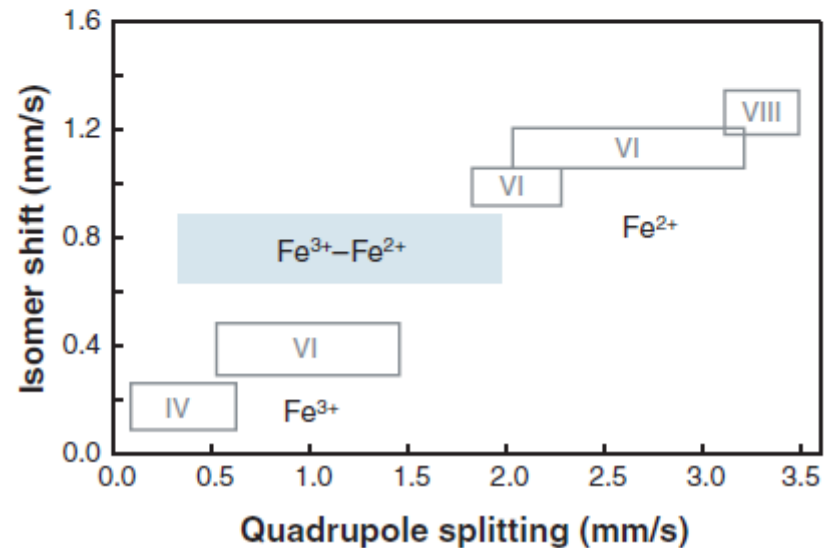
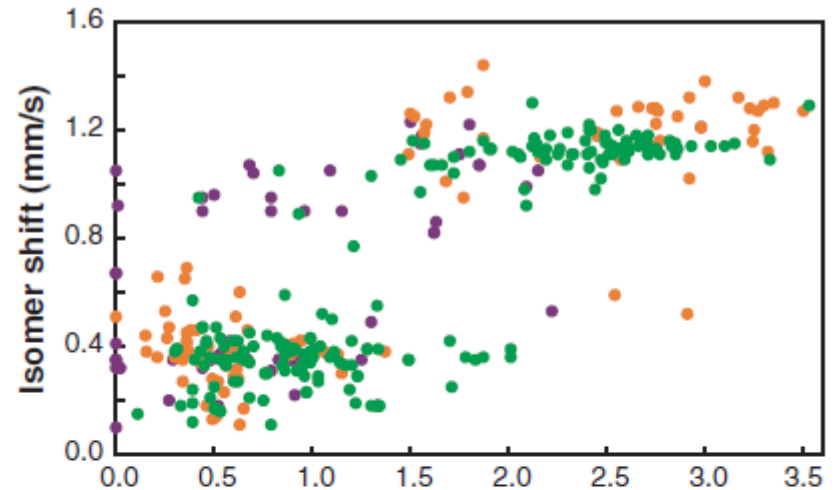
Desdoblamiento cuadrupolar.



$$\Delta E_Q = E_Q \left(\pm \frac{3}{2} \right) - E_Q \left(\pm \frac{1}{2} \right) = \frac{eQV_{ZZ}}{2} \left(1 + \frac{\eta^2}{3} \right)^{\frac{1}{2}}$$

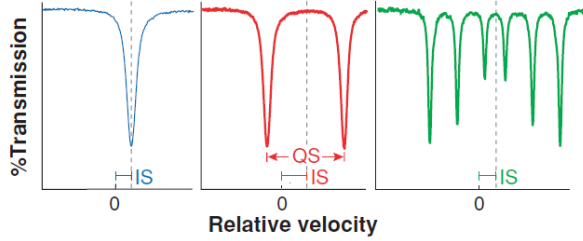
$$V_{ij} = \frac{\partial^2 V}{\partial^2 x_i x_j} = \frac{1}{4\pi\epsilon_0} \int_{Vol} \frac{\rho(\vec{r})(3x_i x_j - \delta_{ij} r^2)}{r^5} d\vec{r}$$

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

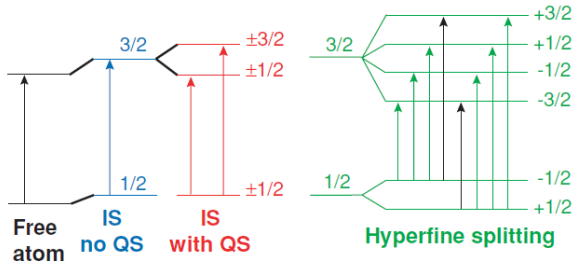


Espectroscopía Mössbauer. Propiedades hiperfinas.

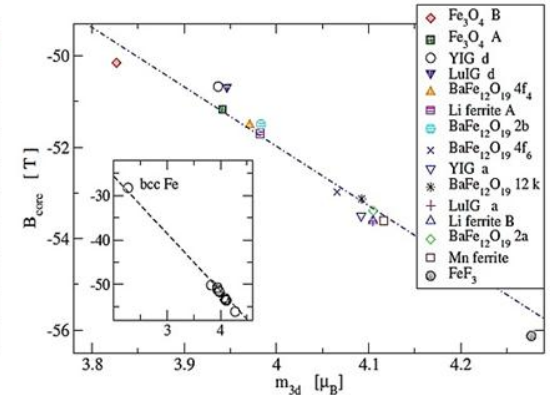
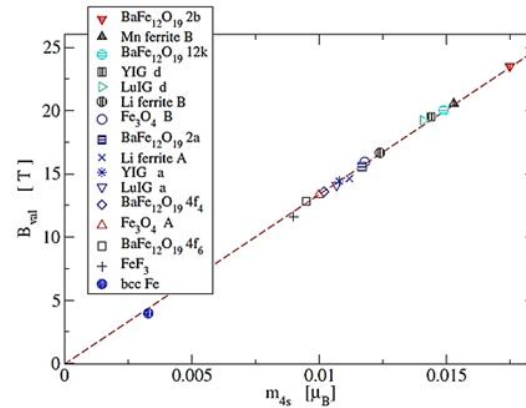
Campo hiperfino.



$$B_{HF} = B_C + B_{dip} + B_{orb}$$



$$B_{HF} \sim B_C$$



$$B_{hf} = a\mu_{3d} + b\mu_{4s}$$

Compound, site	$B_{\text{iso}}^{\text{exp}}$	$B_{\text{iso}}^{\text{calc}}$	$B_{\text{iso}}^{(1)\text{calc}}$	$B_{\text{iso}}^{\text{WIEN2k}}$
bcc Fe	-33.90	-37.99		-30.65
YIG a	55.25	53.86	54.52	38.41
YIG d	-47.35	-47.88	-47.15	-30.44
LuIG a	54.61	54.34	55.04	39.03
LuIG d	-46.74	-48.45	-47.82	-30.87
Li-ferrite B	-51.07	-52.48	-52.56	-36.19
Li-ferrite A	51.94	51.90	52.37	36.22
Mn-ferrite B	-51.07	-49.96	-49.10	-32.41
BaFe ₁₂ O ₁₉ $2a$	-54.68	-53.36	-53.72	-37.28
$2b$	-42.64	-45.63	-43.89	-27.25
$4f_4$	52.77	52.42	53.14	37.15
$4f_6$	55.40	54.79	55.85	39.58
$12k$	-50.83	-50.03	-49.29	-32.53
FeF ₃	-61.81	-58.88	-60.34	-44.22
Fe ₃ O ₄ A	50.77	51.94	52.70	33.46
B	-48.29	-47.90	-47.93	-32.04
bcc Fe	-33.90	-37.00		-30.65