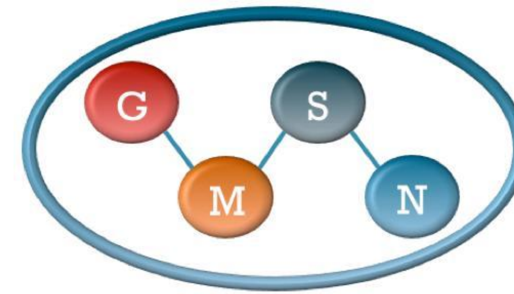
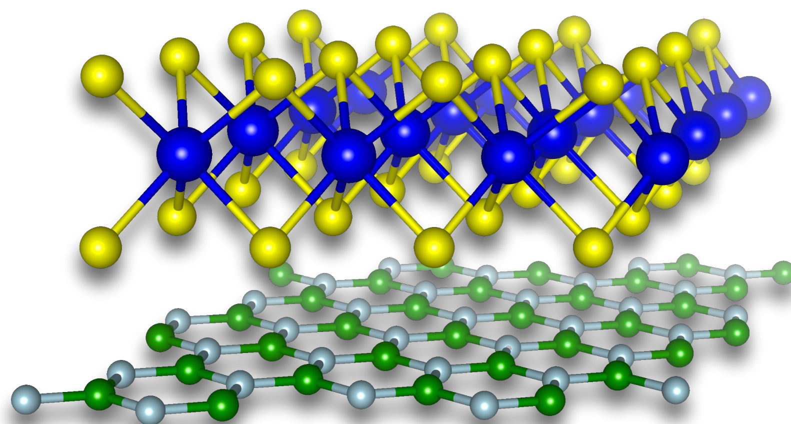


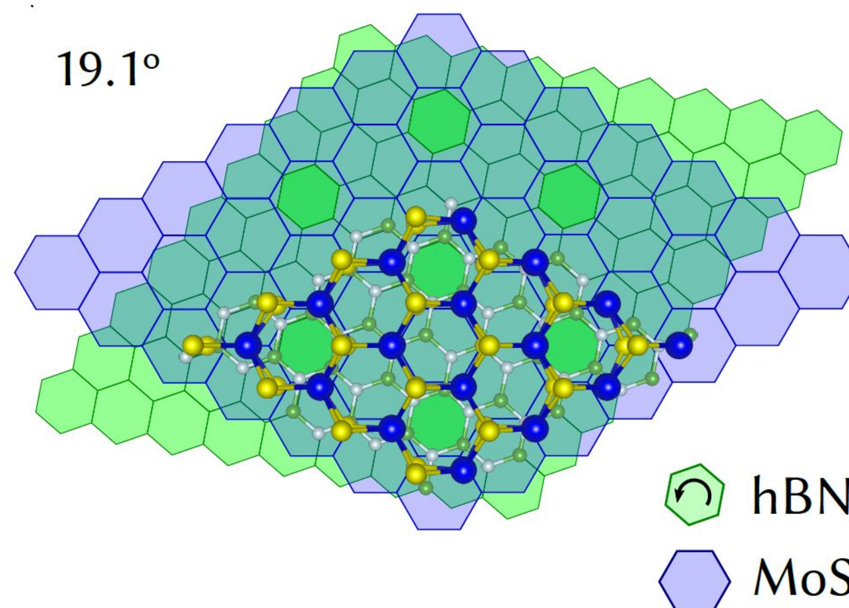
Método DFT-½: Fundamentos teóricos

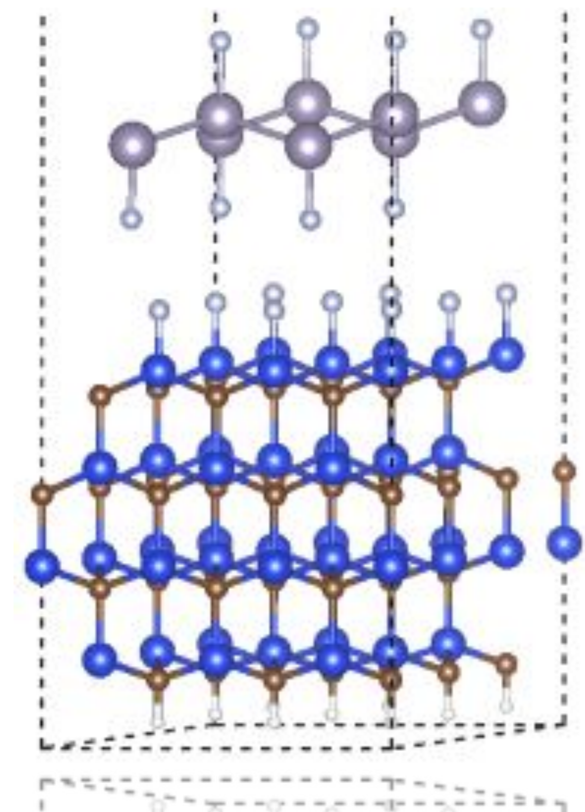
Prof. Dr. Ivan Guilhon

Grupo de Materiais Semicondutores e Nanotecnologia (GMSN)

Instituto Tecnológico de Aeronáutica







Roteiro

- Quem somos?
- Teoria do funcional da densidade (DFT)
  - Fundamentos teóricos
  - O ‘problema do gap’.
- Teorema de Janak
- O método DFT-½
  - Fundamentos teóricos
  - Desempenho em diferentes sistemas

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Linhas de pesquisa

Lara K. Teles

Marcelo Marques

Ivan Guilhon

André Chaves

Gabriela Nascimento

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Leticia Agra

C. Ataíde pos-doc

Gabriel de Paula

Vinícius Gomes

Felipe Martins

Bruno Lucatto

F. Matusalém pos-doc

D. Guedes pos-doc

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Ivan Guilhon

André Chaves

Perovskitas 2D

Ligas 3D

Propriedades Mecânicas @2D

óxidos

Ligas dumbbell

óxidos

Moléc.@2D

Qubit

Isolantes topológicos@2D

Perovskitas 3D

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Antônio M. da Silva Jr.

Adriano M dos Santos

Gil de Aquino Farias

Roteiro

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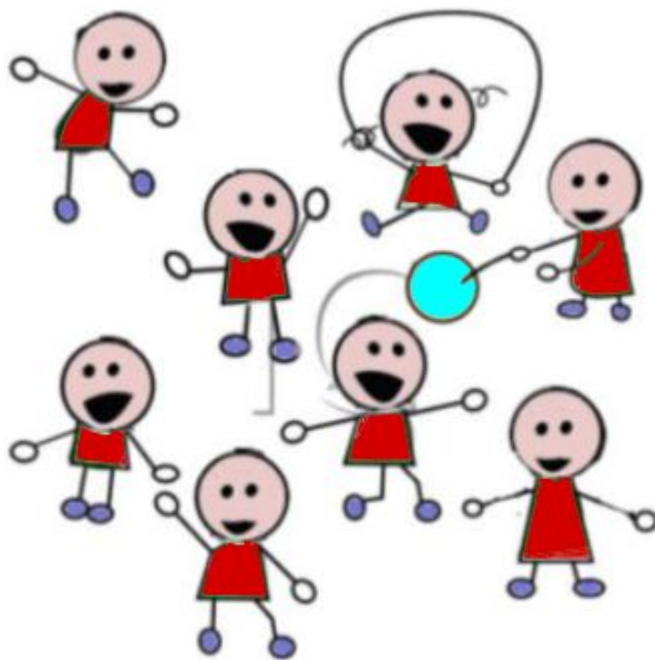
Teoria do funcional da densidade (DFT)

- The most common first-principles theoretical approach applied to study the electronic structure of solids is the **DFT (density functional theory).**

$$-\sum_{i=1}^{N+N_z}\frac{\hbar^2}{2m_i}\nabla_i^2\Psi(\vec{r_1},...,\vec{r}_{N+N_z})+\sum_{i=1}^{N+N_z}\sum_{j\neq i}\frac{q_iq_j}{4\pi\epsilon_0|\vec{r_i}-\vec{r_j}|}\Psi(\vec{r_1},...,\vec{r}_{N+N_z})=E\Psi(\vec{r_1},...,\vec{r}_{N+N_z})$$

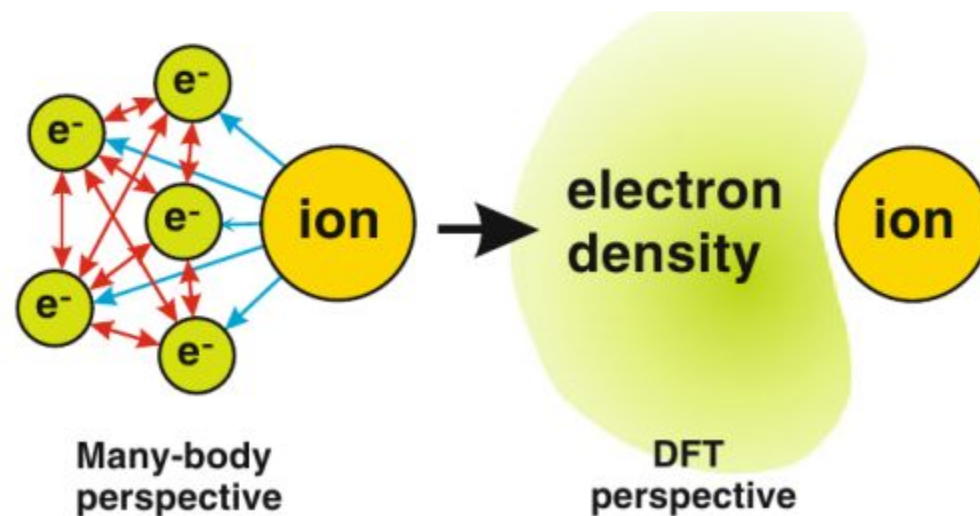


- Ψ as the main quantity.
- This is a very hard problem. Approximations are needed;
- System made by interacting particles with electronic density given by

$$n(\mathbf{r}) = N\int|\Psi(\mathbf{r},\mathbf{r}_2,\dots,\mathbf{r}_N)|^2 d^3r_2\dots d^3r_N$$

Teoria do funcional da densidade (DFT)

- A abordagem da teoria do funcional da densidade (DFT, sigla em inglês) é considerar a densidade eletrônica como quantidade fundamental do sistema.



F. Bechstedt. Many-Body Approach to Electronic Excitations: Concepts and Applications

- A teoria é baseada dois teoremas de Hohenberg-Kohn.

- Para calcular estados eletrônicos do sistema, costuma-se utilizar o formalismo de Kohn-Sham.

Teoria do funcional da densidade (DFT)

- Paper original da teoria do funcional da densidade (1964). (45540 citações)

PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†
École Normale Superieure, Paris, France

AND

W. KOHN‡
École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California

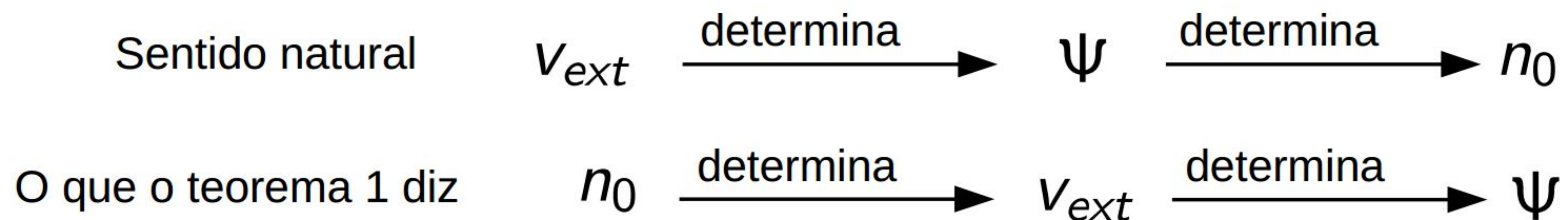
(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 << 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \to \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

1º Teorema de Hohenberg-Kohn

- Teorema #1: A densidade eletrônica do estado fundamental determina unicamente o potencial sentido pelos elétrons (a menos de uma constante aditiva) $v_{ext}(r)$.

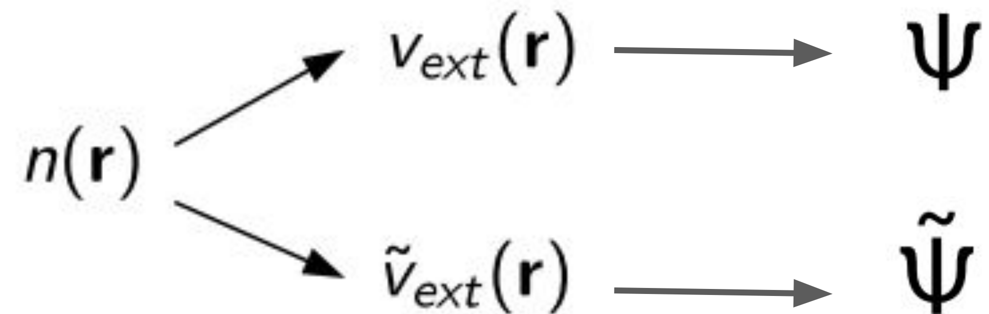
- O teorema 1 garante que a energia do estado fundamental é um funcional da densidade:



- Consequentemente, a energia total do sistema é um funcional da densidade eletrônica $n_0(r)$.

1º Teorema de Hohenberg-Kohn

- **Prova:** Provemos por contradição.



cada um dessas soluções é um estado fundamental associado a um operador hamiltoniano diferente

$$H\Psi = E\Psi \quad \Rightarrow \quad E = \langle\Psi|H|\Psi\rangle$$

$$\tilde{H}\tilde{\Psi} = \tilde{E}\tilde{\Psi} \quad \Rightarrow \quad \tilde{E} = \langle\tilde{\Psi}|\tilde{H}|\tilde{\Psi}\rangle$$

Como estamos tratando de estados fundamentais, temos que

$$E < \langle\tilde{\Psi}|H|\tilde{\Psi}\rangle \qquad \tilde{E} < \langle\Psi|\tilde{H}|\Psi\rangle$$

1º Teorema de Hohenberg-Kohn

Somando as desigualdades

$$E + \tilde{E} < \langle\tilde{\Psi}|H|\tilde{\Psi}\rangle + \langle\Psi|\tilde{H}|\Psi\rangle$$

e escrevendo

$$H = \tilde{H} + (H - \tilde{H})$$

$$\tilde{H} = H - (H - \tilde{H})$$

chegamos a expressão, que resulta em contradição (0<0).

$$E + \tilde{E} < \langle\tilde{\Psi}|\tilde{H}|\tilde{\Psi}\rangle + \langle\Psi|H|\Psi\rangle + \langle\tilde{\Psi}|H - \tilde{H}|\tilde{\Psi}\rangle - \langle\Psi|H - \tilde{H}|\Psi\rangle$$

$$E + \tilde{E} < E + \tilde{E} + \langle\tilde{\Psi}|H - \tilde{H}|\tilde{\Psi}\rangle - \langle\Psi|H - \tilde{H}|\Psi\rangle$$

$$\langle\Psi|H - \tilde{H}|\Psi\rangle = \int [v_{ext}(\mathbf{r}) - \tilde{v}_{ext}(\mathbf{r})] n(\mathbf{r}) d^3r$$

2º Teorema de Hohenberg-Kohn

- Teorema #2: A energia do estado fundamental pode ser obtida variacionalmente. A densidade que minimiza a energia total é a densidade exata do estado fundamental.

- O funcional da energia é dado pela expressão

$$E[n] = F[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) d^3 r$$

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

(Funcional universal F[n])

Varia de problema para problema

Formalismo de Kohn-Sham

- Até agora discutimos a existência do funcional E[n] e F[n], mas não sabemos como calculá-los.

- Isso foi proposto em um segundo trabalho em 1965. (51813 citações)

PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

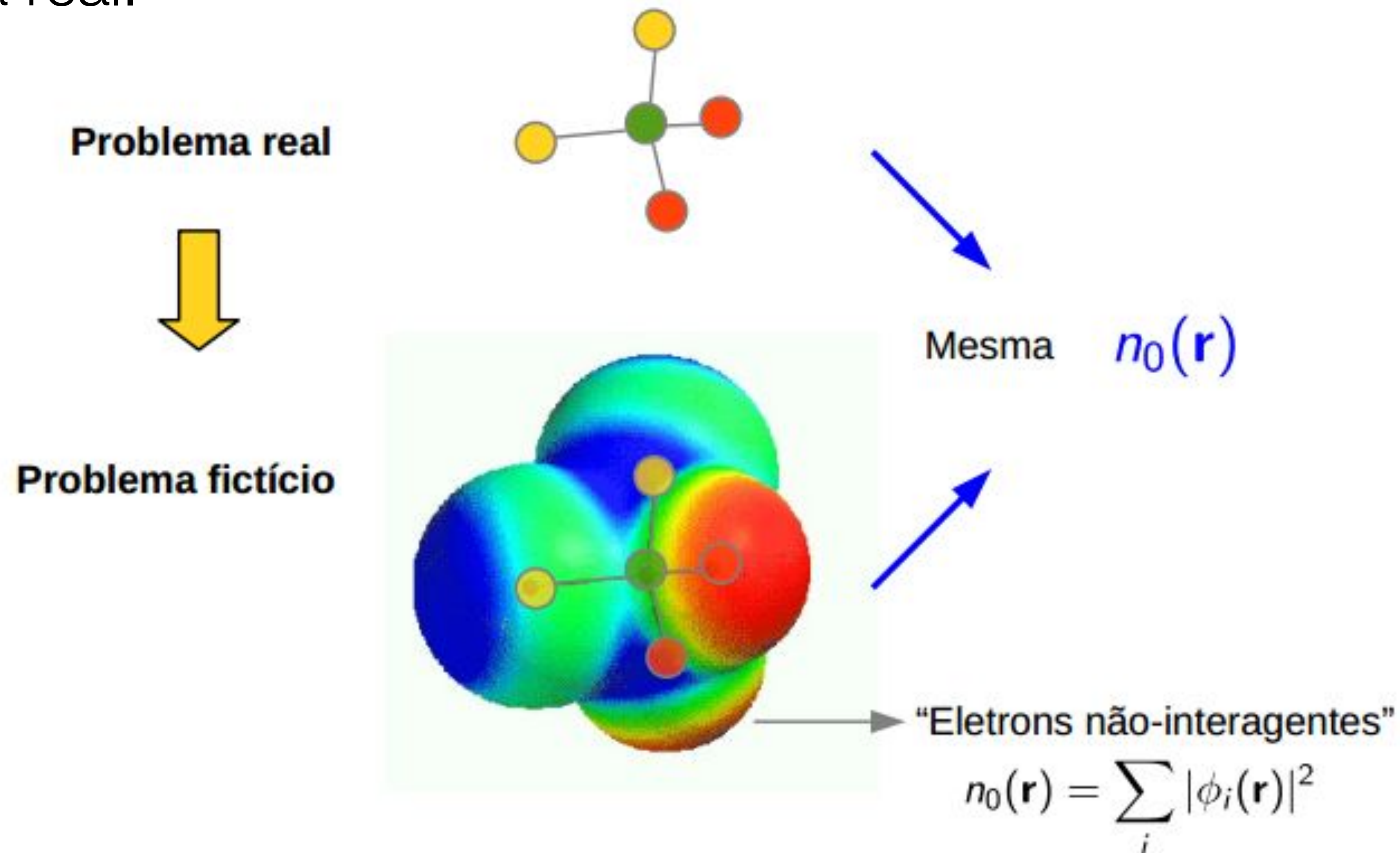
W. KOHN AND L. J. SHAM
University of California, San Diego, La Jolla, California

(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

Formalismo de Kohn-Sham

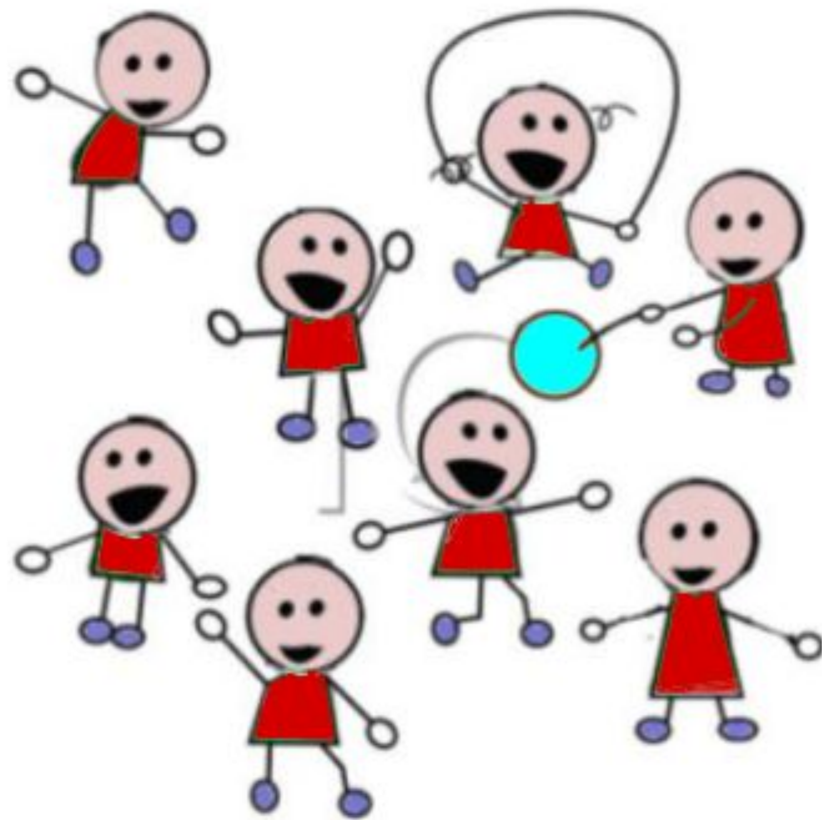
- Ideia fundamental: construir o potencial sentido pelo gás de elétrons fictício (não-interagentes) com mesma densidade de carga do sistema real.



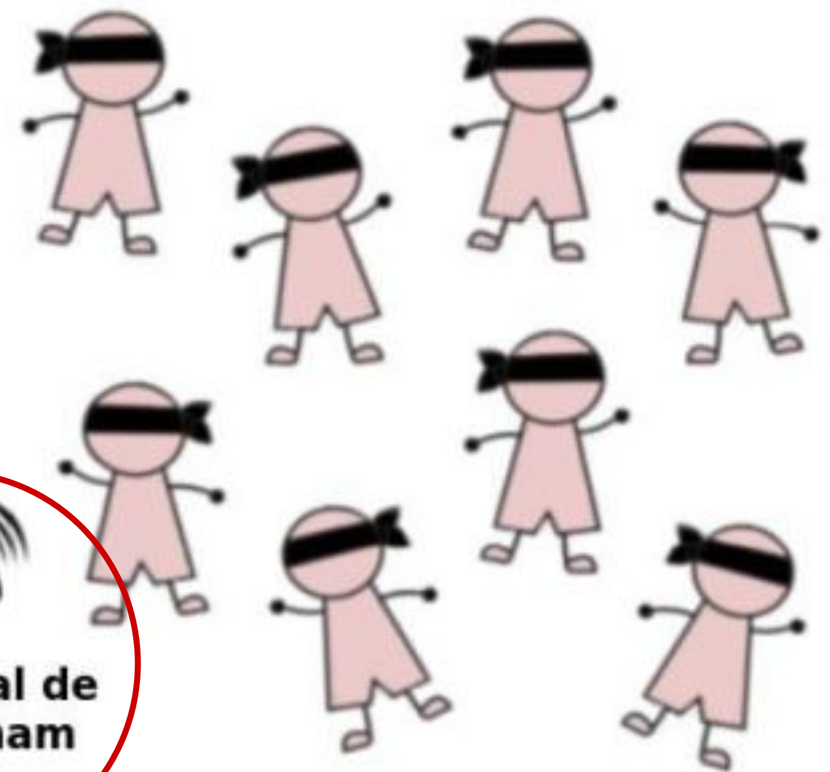
Formalismo de Kohn-Sham

- Como fazer isso?

  Calculando N problemas de 1 corpo sujeito a um potencial de Kohn-Sham V_{KS}.



Mesma densidade
n(x,y,z)



$E[n]=T[n]+V_{ee}[n]+V_{ext}[n]$

$E[n]=?$

Formalismo de Kohn-Sham

- Como o sistema de partículas não-interagentes é muito mais simples de resolver, escrevemos o funcional F[n] como

$$F[n] = U_0[n] + T_0[n] + E_{XC}[n]$$

Energia potencial de um gás de elétrons não interagentes

Energia cinética de um gás de elétrons não interagentes

$$U_0[n] = \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'$$

$$T_0[n] = -\frac{1}{2}\sum_{i=1}^{N}\int \phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r}) d^3r$$

em que

$$E_{XC}[n] = V_{ee}[n] - U_0[n] + T[n] - T_0[n]$$

(Energia de troca e correlação)

Formalismo de Kohn-Sham

- Para encontrar o estado fundamental do sistema, queremos minimizar o funcional

$$E[n] = U_0[n] + T_0[n] + E_{XC}[n] + \int v_{ext}(\mathbf{r})n(\mathbf{r})d^3r$$

respeitando a normalização dos estados

$$\int |\phi_i(\mathbf{r})|^2 d^3r = 1$$

- Utilizando a teoria dos multiplicadores de Lagrange

$$\frac{\delta E}{\delta \phi_i^*} - \epsilon_i \frac{\delta}{\delta \phi_i^*} \int |\phi_i(\mathbf{r})|^2 d^3r = 0$$

Formalismo de Kohn-Sham

- Após algum algebrismo, chegamos às equações de Kohn-Sham para os orbitais

$$\left[-\frac{1}{2}\nabla^2 + \underbrace{v_H(\mathbf{r}) + v_{XC}(\mathbf{r}) + v_{ext}(\mathbf{r})}_{v_{KS}(\mathbf{r})}\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

em que

$$v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$v_{XC}(\mathbf{r}) = \frac{\delta E_{XC}}{\delta n(\mathbf{r})}$$

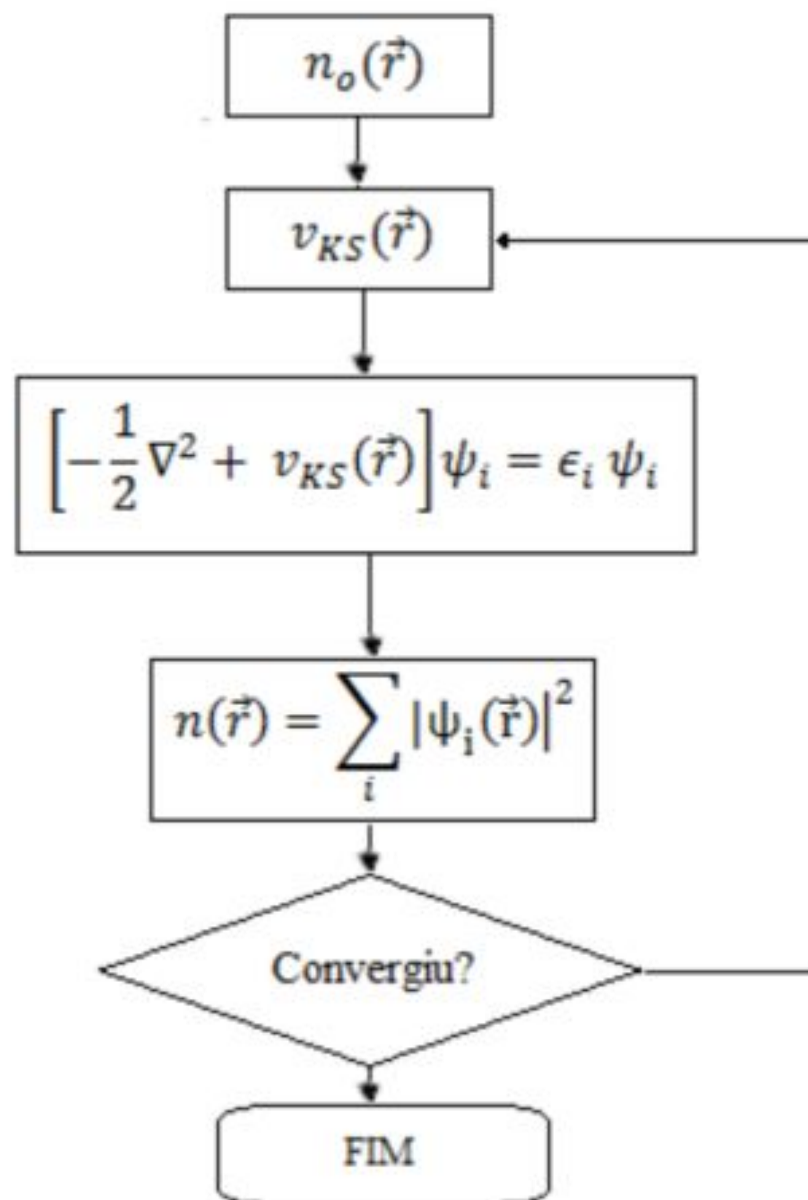
Termo a ser aproximado:
LDA, GGA, MGGA etc...

$$E_{\mathrm{XC}}^{\mathrm{LDA}}[n] = \int \varepsilon_{\mathrm{XC}}(n)n(\vec{r})\,\mathrm{d}^3r.$$

$$E_{\mathrm{XC}}^{\mathrm{GGA}}[n_\uparrow, n_\downarrow] = \int d^3r\, f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$$ [...]

Formalismo de Kohn-Sham

- Problema resolvido de maneira auto-consistente.



Implementação em pacotes de simulação:

[...]

entering main loop

	N	E	dE	d eps	ncg	rms	rms(c)
DAV:	1	0.285393328295E+02	0.28539E+02	-0.28913E+03	832	0.547E+02	
DAV:	2	-0.165075236582E+02	-0.45047E+02	-0.39158E+02	952	0.116E+02	
DAV:	3	-0.193802237964E+02	-0.28727E+01	-0.28727E+01	1048	0.386E+01	
DAV:	4	-0.193985248256E+02	-0.18301E-01	-0.18301E-01	1136	0.267E+00	
DAV:	5	-0.193985325832E+02	-0.77576E-05	-0.77585E-05	1056	0.597E-02	0.781E+00
RMM:	6	-0.178511407960E+02	0.15474E+01	-0.30496E+00	896	0.132E+01	0.382E+00
RMM:	7	-0.176621517668E+02	0.18899E+00	-0.26527E-01	940	0.386E+00	0.229E+00
RMM:	8	-0.175783521418E+02	0.83800E-01	-0.18932E-01	938	0.328E+00	0.309E-01
RMM:	9	-0.175743654443E+02	0.39867E-02	-0.70555E-03	962	0.655E-01	0.168E-01
RMM:	10	-0.175706438219E+02	0.37216E-02	-0.13366E-03	942	0.324E-01	0.708E-02
RMM:	11	-0.175710637622E+02	-0.41994E-03	-0.43836E-03	865	0.485E-01	0.152E-01
RMM:	12	-0.175699415587E+02	0.11222E-02	-0.19177E-03	821	0.293E-01	0.254E-02
RMM:	13	-0.175713646796E+02	-0.14231E-02	-0.71901E-04	780	0.195E-01	0.637E-02
RMM:	14	-0.175716948165E+02	-0.33014E-03	-0.33491E-04	805	0.136E-01	0.750E-03
RMM:	15	-0.175720054819E+02	-0.31067E-03	-0.44325E-05	631	0.473E-02	0.547E-03
RMM:	16	-0.175720604201E+02	**-0.54938E-04**	-0.19704E-05	689	0.295E-02	

1 F= -.17572060E+02 E0= -.17572074E+02 d E =0.402632E-04

writing wavefunctions

Teoria do funcional da densidade (DFT)

- A teoria do funcional da densidade é uma das abordagens mais populares na área de Física da Matéria Condensada com diversas aplicações como cálculos de :

1. geometria atômica
2. energias de ligação
3. coeficientes elásticos de materiais
4. estrutura eletrônica*
5. outros: supercondutividade, prop. magnéticas, prop. ópticas etc.

Roteiro

- Quem somos?
- Teoria do funcional da densidade (DFT)
  - Fundamentos teóricos
  - **O ‘problema do gap’.**
- Teorema de Janak
- O método DFT-½
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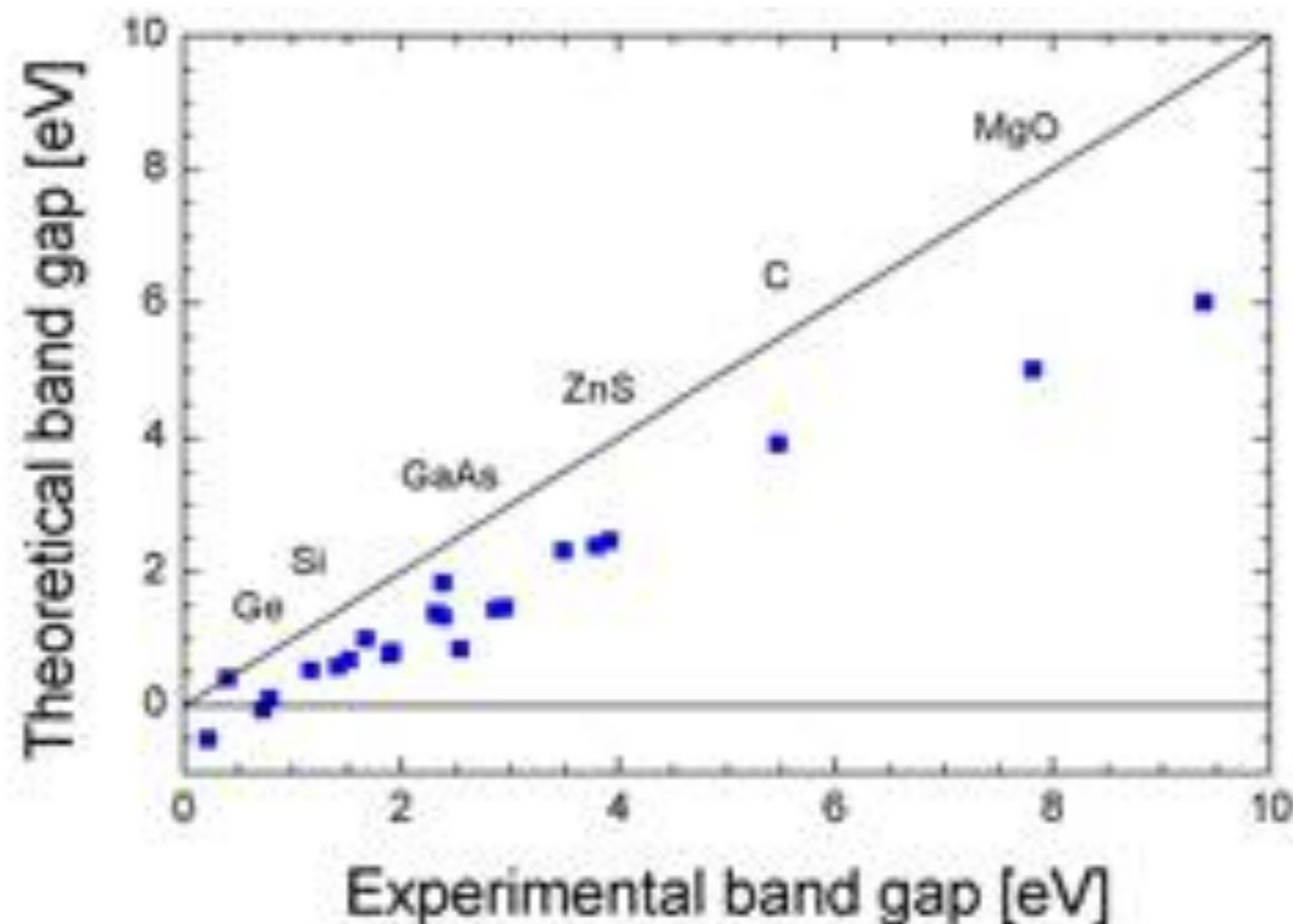
O problema do gap

- PROBLEMA: valores de bandgap previstos pela teoria são subestimados em 30-40% em relação aos valores experimentais.



O problema do gap

- Em alguns casos, o problema é ainda pior, e.g:
  - erro de 70% no ZnO (gap LDA = 0.8 eV, experimento = 3.4 eV)
  - predição de gaps negativos: InAs, InN, etc.

- A má descrição da estrutura de bandas de estados excitados tem consequências no estudo de defeitos, propriedades ópticas e interfaces (cálculo de *band offsets*).

Métodos de correção de gap

Além da DFT-padrão, diferentes abordagens teóricas podem ser encontradas na literatura para cálculo do bandgap. *

GW
Days

Hybrid (HSE)
Hours

LDA
seconds
minutes

*Altos custo computacionais inclusos.

Métodos de correção de gap

- Diversas abordagens foram desenvolvidas para superar o problema do gap, e.g. LDA+U, HSE, GW...

- A maioria dos cálculos é muito elaborada e computacionalmente cara ou simples, mas não isenta de parâmetros externos.

- A modelagem de sistemas complexos como interfaces, ligas, defeitos, superfícies e nanoestruturas requer muitas vezes centenas de átomos.

DFT na prática

Atividade Prática #1:

Cálculos DFT utilizando o VASP

Roteiro

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Teorema de Janak

- Vamos discutir um sentido físico (ou matemático) para os autovalores de KS;

- O nosso principal problema no DFT é minimizar o valor do funcional

$$E[n] = U_0[n] + T_0[n] + E_{XC}[n] + \int v_{ext}(\mathbf{r})n(\mathbf{r})d^3r$$

obedecendo a condição de normalização de cada orbital

$$\int |\phi_i(\mathbf{r})|^2 d^3r = 1$$

Teorema de Janak

- A minimização condicionada pode ser realizada através do formalismo de multiplicadores de Lagrange, chegando a equação de KS

$$\left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) + v_{XC}(\mathbf{r}) + v_{ext}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

os autovalores de energia surgem a partir dos multiplicadores de Lagrange.

- Permita agora que as ocupações de cada orbital possam assumir valores fracionário f_i. Dessa maneira, podemos escrever

$$n(\mathbf{r}) = \sum_{i=1}^{N} f_i|\phi_i(\mathbf{r})|^2 \quad \text{ou} \quad \int |\phi_i(\mathbf{r})|^2 d^3r = f_i$$

Teorema de Janak

- Para prosseguir com a demonstração, usaremos um resultado obtido a partir da teoria de multiplicadores de Lagrange.

- Defina a função f(x,y,z) a ser minimizada respeitando as condições de contorno g(x,y,z)=α e h(x,y,z)=β. O que nos leva à função

$$L(x,y,z) = f(x,y,z) - \lambda\,[g(x,y,z) - \alpha] - \theta\,[h(x,y,z) - \beta]$$

- A mudança do valor minimizado da função f com respeito a uma variação da condição de contorno é dada por

$$\frac{\partial f}{\partial \alpha} = \lambda \qquad\qquad \frac{\partial f}{\partial \beta} = \theta$$

Teorema de Janak

- Essa propriedade dos multiplicadores de Lagrange ainda vale para minimização de funcionais.

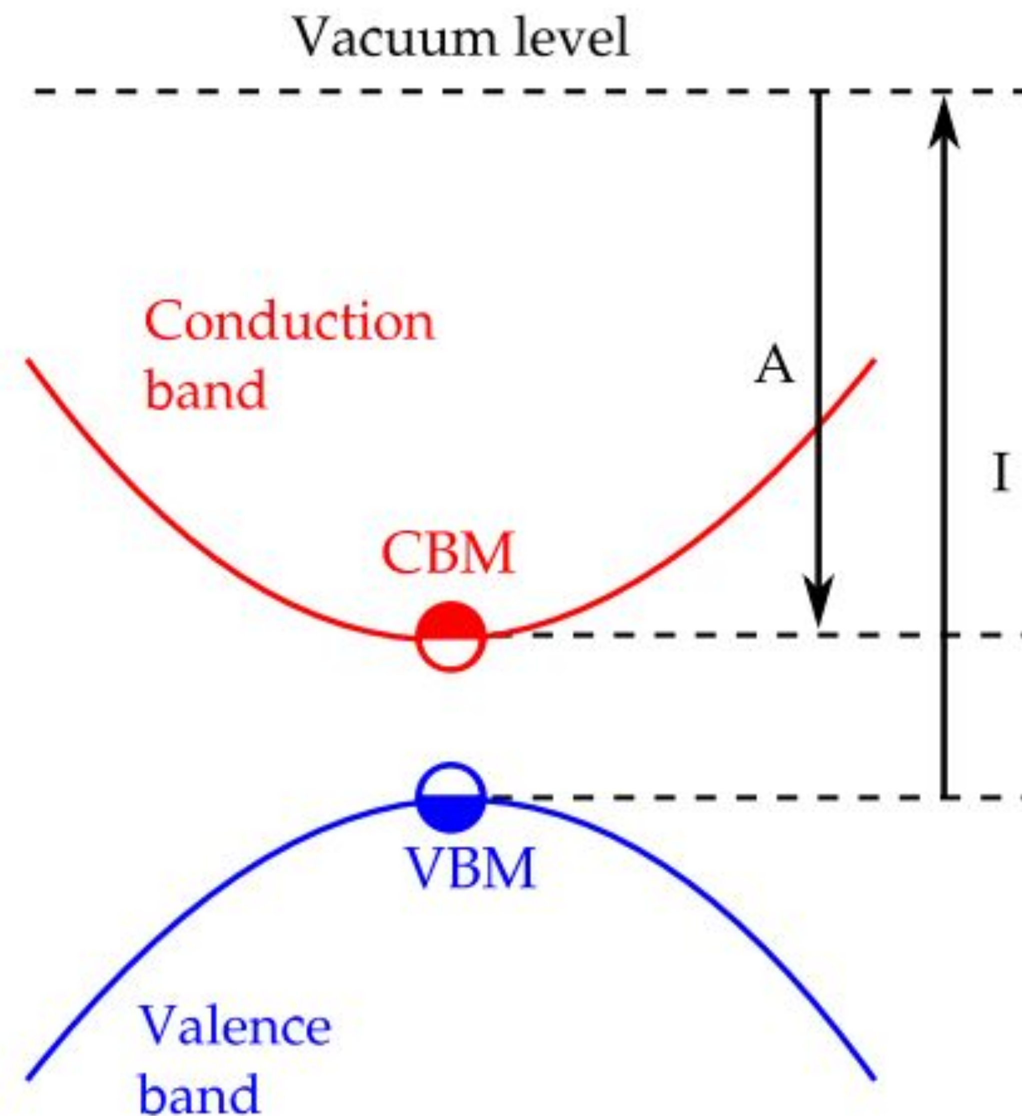
- Dessa maneira os autovalores de energia podem ser identificados por

$$\frac{\partial E}{\partial f_i} = \epsilon_i$$

- As auto energias do sistema podem ser identificadas como a variação da energia do sistema com a variação do parâmetro de ocupação f_i.

Teorema de Janak

- Cálculo de energia de ionização/ afinidade eletrônica:



Teorema de Janak

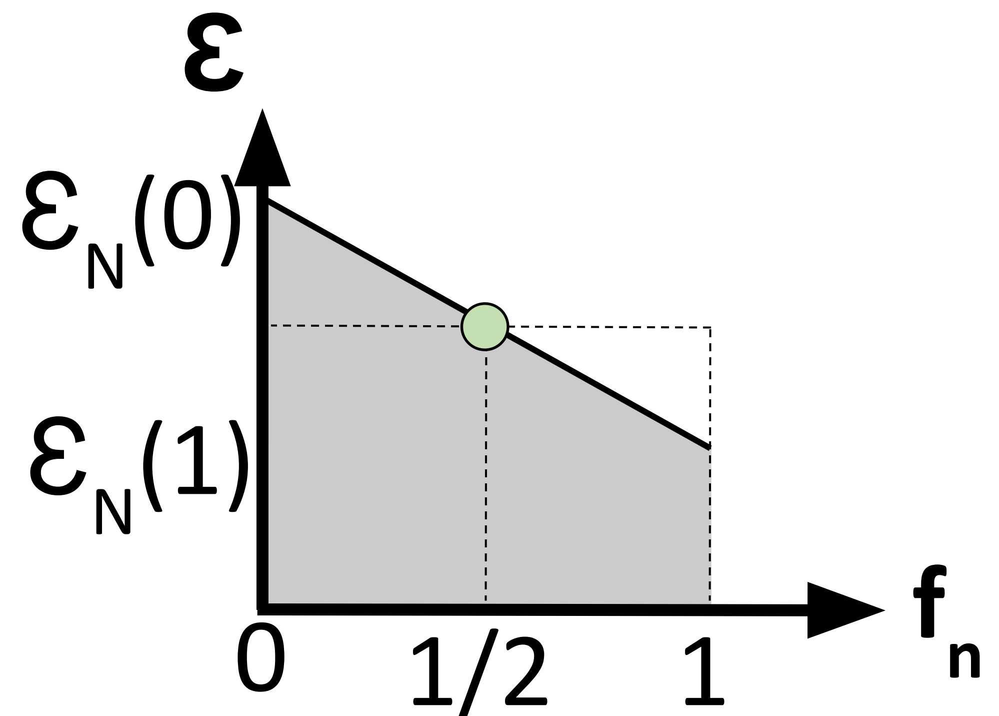
- Uma aplicação imediata do teorema de Janak é para calcular a energia de ionização

$$I(N) = E(N-1) - E(N) = -\int_0^1 \frac{\partial E}{\partial f_N} df_N$$

$$I(N) = -\int_0^1 \epsilon_N df_N$$

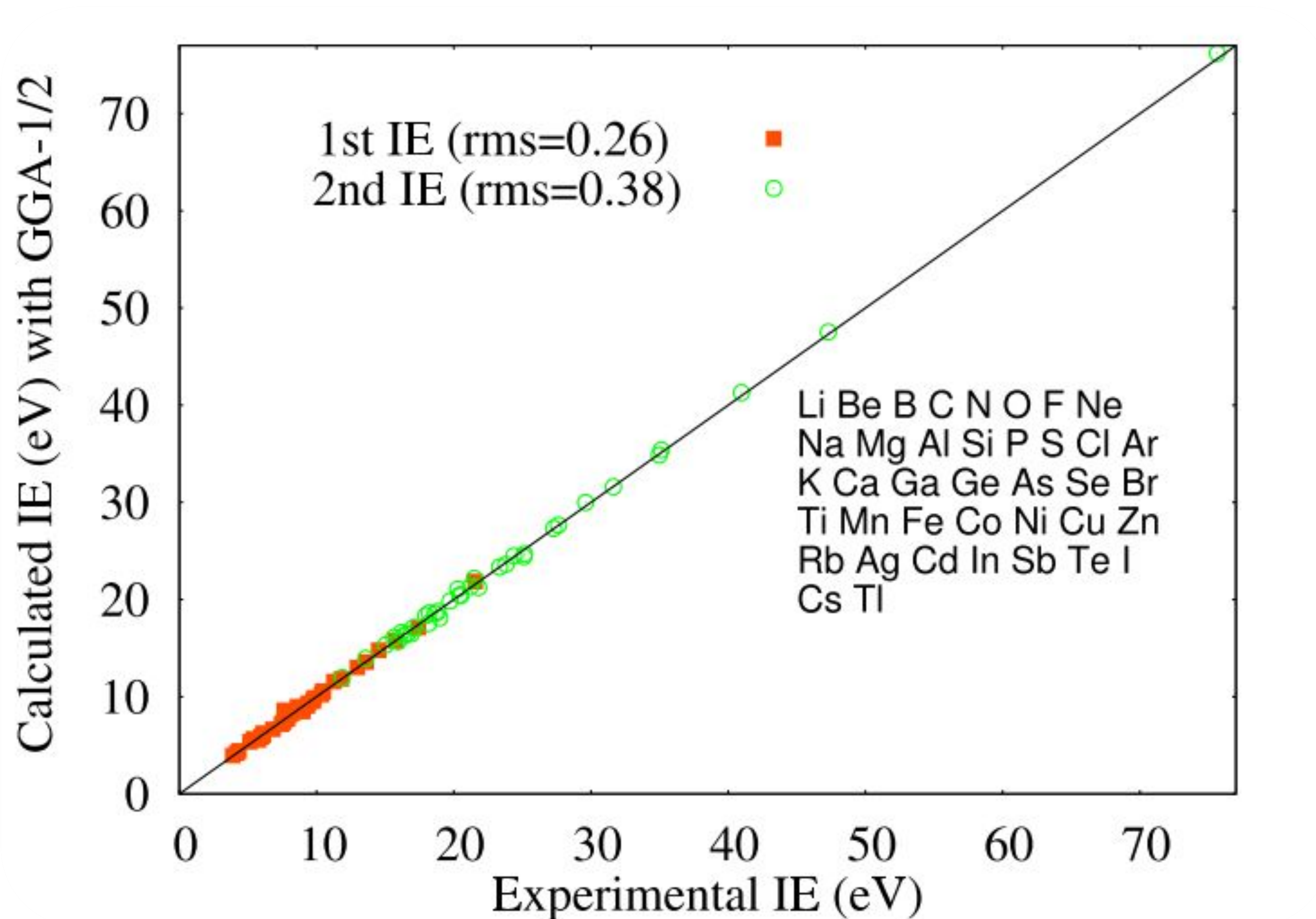
- Se o autovalor varia linearmente com a ocupação, podemos escrever

$$I(N) = -\epsilon_N(1/2)$$



Teorema de Janak

Results for calculation of Ionization Energies (IE)



Teorema de Janak

- Analogamente, para a afinidade eletrônica A,

$$A(N) = -\epsilon_{N+1}(1/2)$$

- Portanto, o gap de partícula de um material, pode ser escrito por

$$E_g(N) = \epsilon_{N+1}(1/2) - \epsilon_N(1/2)$$

Programa atômico

- Para calcular os autovalores de sistemas atômicos por DFT, usaremos o programa ATOM , escrito por Sverre Froyen (1982) e mantido por José Luis Martins (1990+).

- Estaremos interessados no cálculo de (i) energias totais dos sistemas e em (ii) seus autovalores DFT.

- O programa também gera arquivos de pseudopotenciais que serão utilizados no método DFT-½.

Teorema de Janak

Atividade Prática #2:
Cálculo de energias de ionização com técnicas de semiocupação

Roteiro

- Quem somos?
- Teoria do funcional da densidade (DFT)
  - Fundamentos teóricos
  - O ‘problema do gap’.
- Teorema de Janak
- **O método DFT-½**
  - Fundamentos teóricos
  - Desempenho em diferentes sistemas

O Método DFT-½

Idea: based on

Slater transition-state method
(also called half-occupation technique)

- ➔ good scheme for obtaining ionization potential of atoms and molecules
- ➔ excitation energies are obtained from the theory by performing calculations at intermediate values (1/2) of the orbital occupation numbers
- ➔ Used at seventies without the modern exchange-correlation approximations (LDA, GGA, etc).

Of course, removing 1/2 electron from an infinite system is no perturbation

A special handling of the half-occupation technique is required: DFT-1/2

O Método DFT-½

PHYSICAL REVIEW B **78**, 125116 (2008)

Approximation to density functional theory for the calculation of band gaps of semiconductors

Luiz G. Ferreira*
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Marcelo Marques† and Lara K. Teles‡
Instituto Tecnológico de Aeronáutica, 12228-900 São José dos Campos, São Paulo, Brazil

AIP ADVANCES **1**, 032119 (2011)

Slater half-occupation technique revisited: the LDA-1/2 and GGA-1/2 approaches for atomic ionization energies and band gaps in semiconductors

Luiz G. Ferreira,[1,2,a] Marcelo Marques,[2] and Lara K. Teles[2]
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O Método DFT-½

Janak Theorem

(1978 in DFT context)

$$\frac{\partial E}{\partial f_\alpha} = e_\alpha(f_\alpha)$$

linear variation of $e_\alpha(f_\alpha)$

Slater Scheme

$$E(0) - E(-1) = e_\alpha\left(f_\alpha = -1/2\right)$$

-IP = half-occupied eigenvalue of alpha level

DFT theory + Hellman-Feynman:

$$\frac{\partial e_\alpha}{\partial f_\alpha} = 2S_\alpha$$

$$e_\alpha\left(-1/2\right) = e_\alpha(0) - \frac{1}{2}\frac{\partial e_\alpha}{\partial f_\alpha} = e_\alpha(0) - S_\alpha$$

O Método DFT-½

$$E(0) - E(-1) = e_\alpha(0) - S_\alpha$$

$$S_\alpha = \int d^3 r\, n_\alpha(\vec{r}) V_S(\vec{r})$$

$$V_S(\vec{r}) = \frac{1}{2}\int d^3r\,' \frac{n_\alpha(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \frac{1}{2}\int d^3r\,' \frac{\delta^2 E_{xc}}{\delta n(\vec{r})\delta n(\vec{r}\,')} n_\alpha(\vec{r}\,')$$

$$+ \frac{1}{2}\int d^3r\,' \frac{\sum_\beta f_\beta \frac{\partial n_\beta(\vec{r}\,')}{\partial f_\alpha}}{|\vec{r}-\vec{r}\,'|} + \frac{1}{2}\int d^3r\,' \frac{\delta^2 E_{xc}}{\delta n(\vec{r})\delta n(\vec{r}\,')} \sum_\beta f_\beta \frac{\partial n_\beta(\vec{r}\,')}{\partial f_\alpha}$$

Propomos uma aproximação atômica para $V_s(r)$:

$$V(0, r) - V(-1/2, r) = V_S(r)$$

KS potential of atom

KS potential of half ion

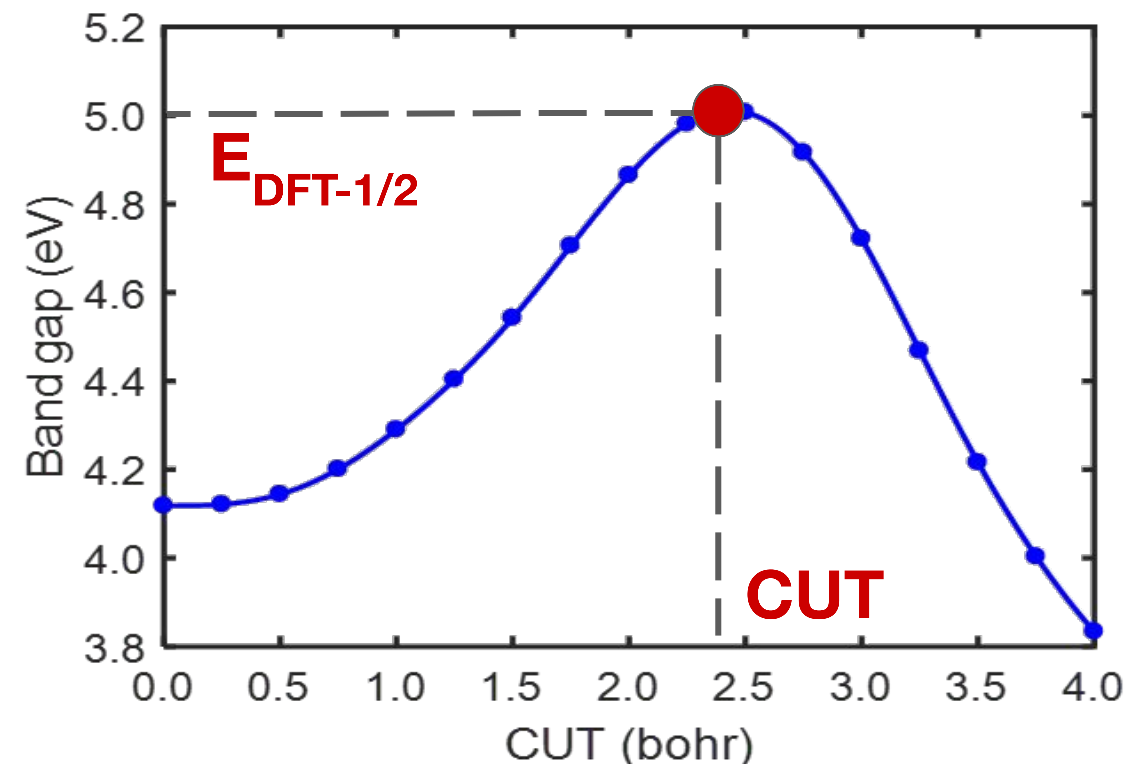
$$\Theta(r) = \begin{cases} \left[1 - \left(\frac{r}{CUT}\right)^m\right]^3 & r \leq CUT \\ 0 & r > CUT \end{cases}$$

O Método DFT-½

- Devido a interação de longa distância ~e/2r, existe uma interpenetração de potenciais de auto-energia $V_s(r)$;

- Fazemos uso de uma função de corte $\boldsymbol{\Theta}$, o parâmetro de corte CUT é maximizando o bandgap;

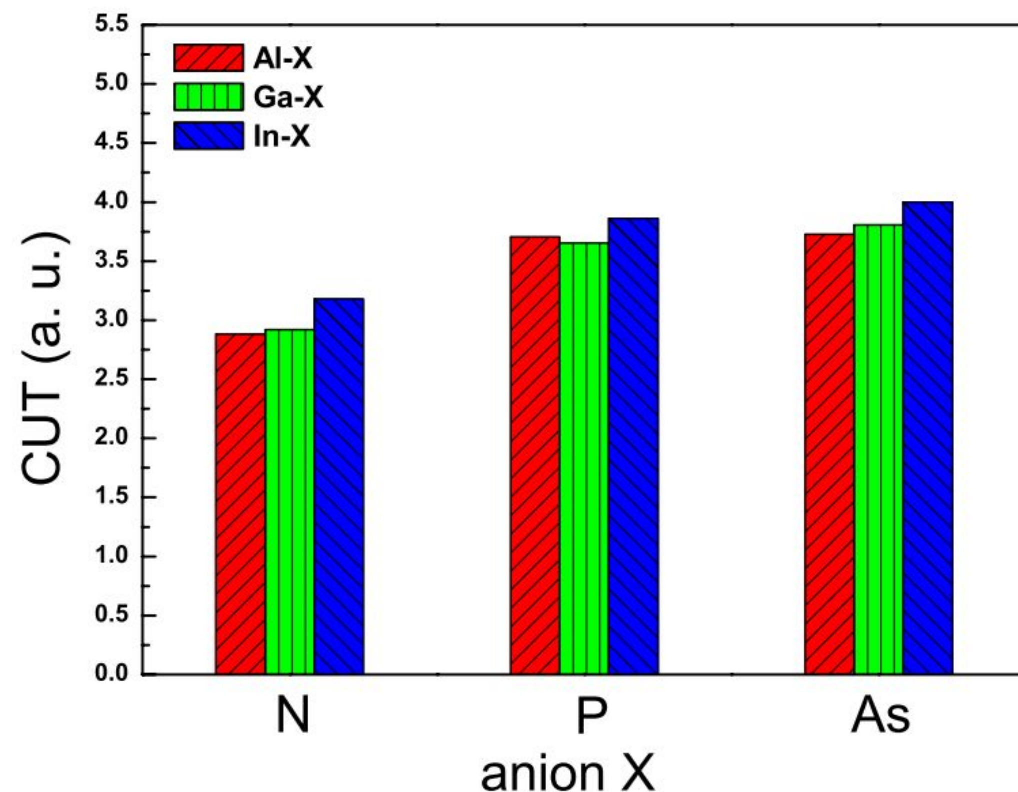
$$\Theta(r) = \begin{cases} \left[1 - \left(\dfrac{r}{CUT}\right)^n\right]^3, & r \leq CUT \\ 0, & r > CUT. \end{cases}$$



O Método DFT-½

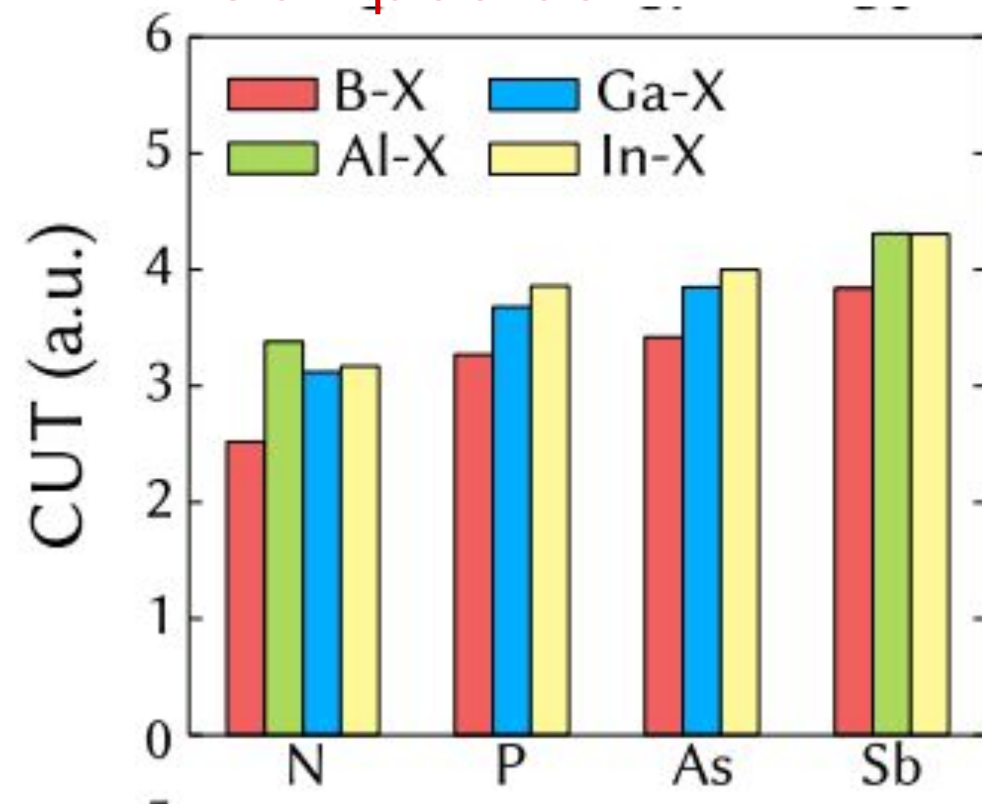
- Há boa transferibilidade dos potenciais corrigidos de um mesmo elemento para diferentes sistemas químicos.

Compostos III-V 3D



Luiz G. Ferreira, Marcelo Marques, and Lara K. Teles, Phys. Rev. B 78, 125116 – Published 30 September 2008

Compostos III-V 2D



I. Guilhon et al., Phys. Rev. B 97, 045426 – Published 24 January 2018

O Método DFT-½

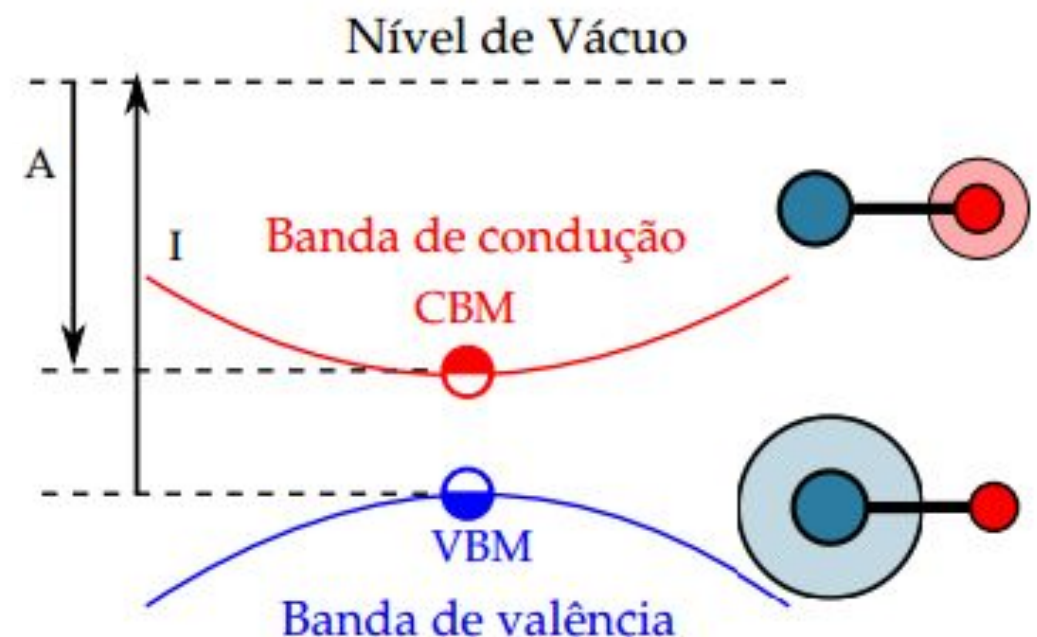
- Aplicando a correção de quasipartícula na banda de valência e condução, temos

$$E_{gap} = \text{I-A}$$

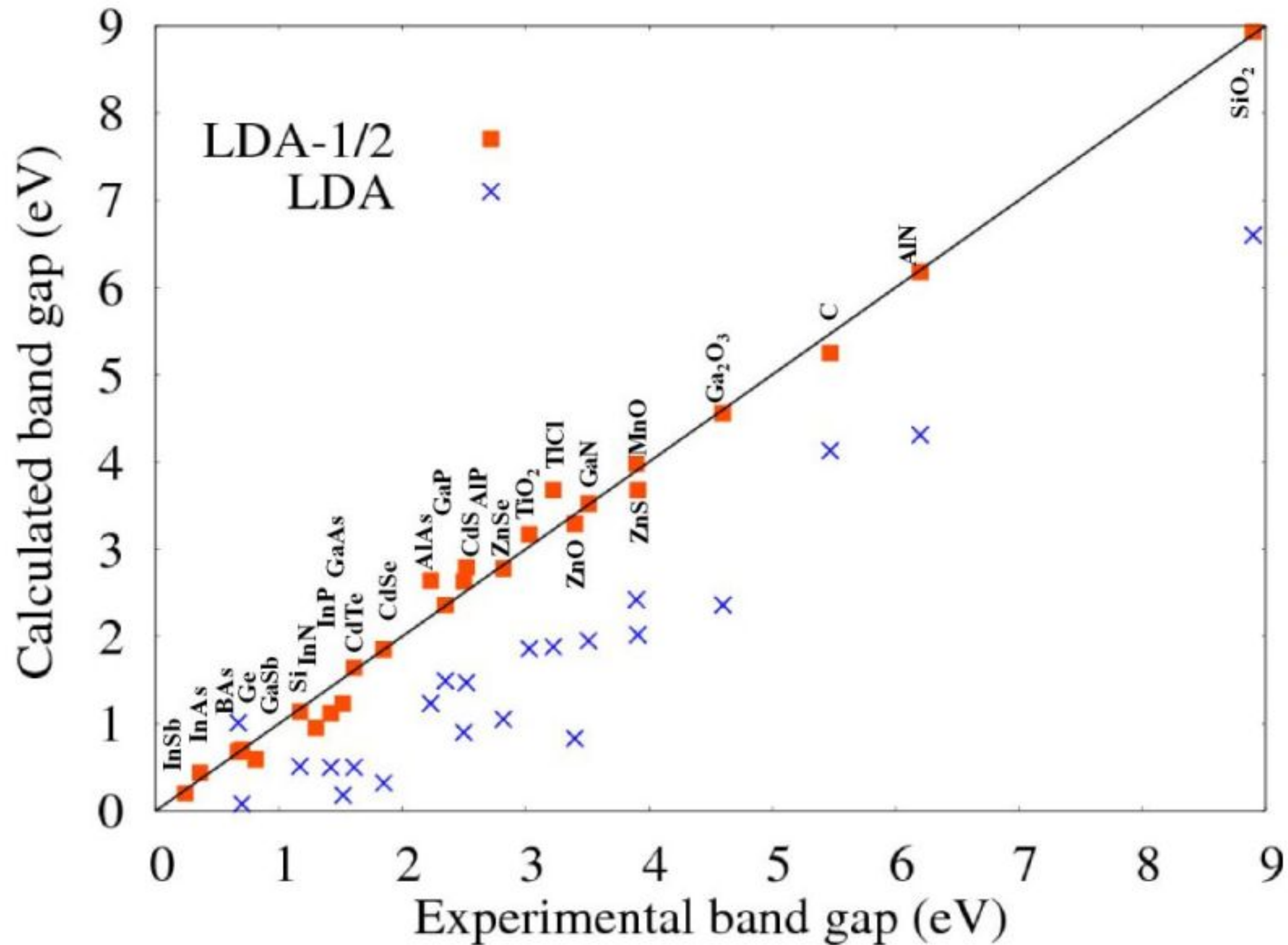
$$E_{gap} = \varepsilon_{cond}(1/2) - \varepsilon_{val}(1/2)$$

$$\text{True Band Gap} = e_c(0) - e_v(0) - S_c + S_v$$

$$E_{gap}^{LDA-1/2} = E_{gap}^{LDA} + S_{valence} - S_{conduction}$$



Performance do DFT-½ em compostos 3D



DFT-½: acurácia comparável, custo computacional reduzido

The same for MEMORY

GW
Days

Hybrid (HSE)
Hours

LDA
seconds
minutes

LDA-1/2
seconds
minutes

SAME ACCURACY !

O Método DFT-½

The DFT-½ is a

- ➢ simple to implement,
- ➢ accurate;
- ➢ parameter-free; and
- ➢ computationally efficient;

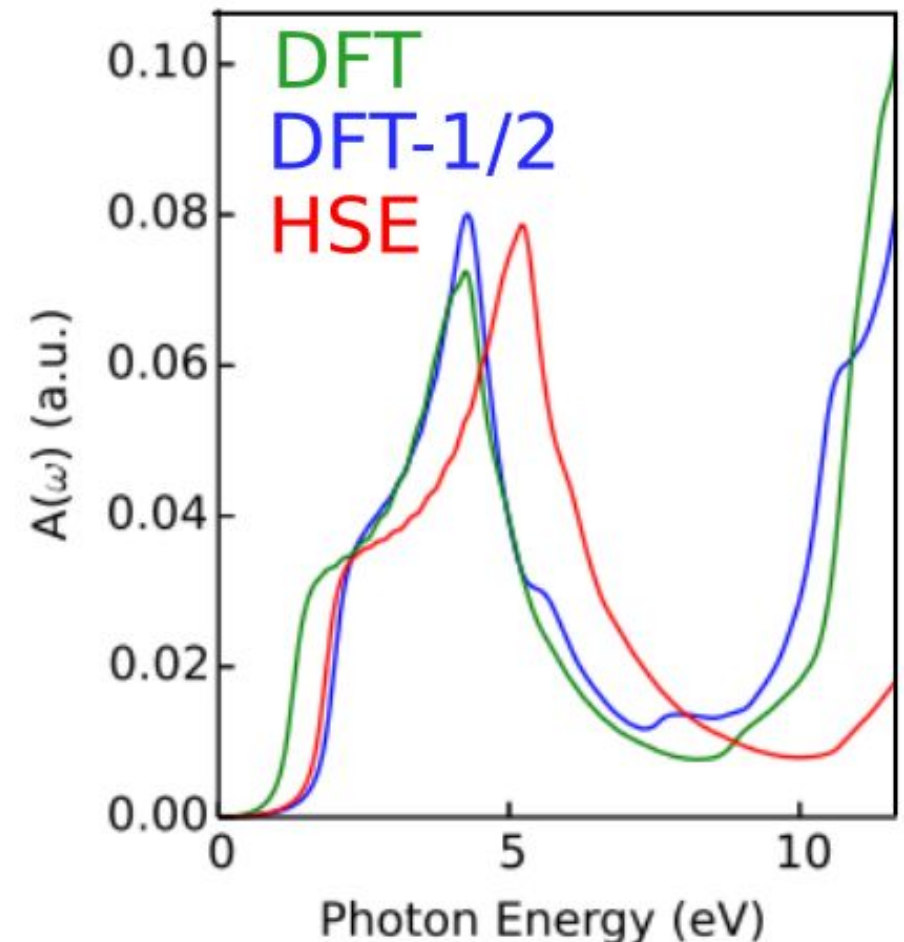
DFT-based method to calculate excitations of many-electron systems.

Notas sobre o método DFT-½

- Uma vez que o potencial de ½ elétron da camada de valência ajusta os níveis de energia dos autovalores na região de energia próxima do gap;

- Estados com energia distante da região de gap não apresentam correção significativa;

- O método **não** calcula energia total do sistema. *(DFT já faz isso bem)*



Espectro óptico de absorção para um sistema BCN bidimensional.

Implementações do DFT-½

O método DFT-½ já está implementado nos códigos:

- WIEN2k
  - http://susi.theochem.tuwien.ac.at/
- Exciting!
  - http://exciting-code.org/boron10-dft05
- VASP
  - http://www.gmsn.ita.br/?q=en/node/16
- SIESTA
  - http://www.eedevice.com/siesta-half.aspx

DFT-1/2 na prática

Atividade Prática #3:

Cálculos DFT-1/2 utilizando o VASP

Roteiro

- Quem somos?
- Teoria do funcional da densidade (DFT)
  - Fundamentos teóricos
  - O ‘problema do gap’.
- Teorema de Janak
- O método DFT-½
  - Fundamentos teóricos
  - **Desempenho em diferentes sistemas**

Desempenho do método DFT-½

- **Cálculo de band offset**
- Estados de defeitos
- Estados hibridizados
- DFT+A-½
- Ligas semicondutoras
- Materiais 2D
- Casos patológicos

Cálculo de band offset: Si/SiO_2

➢ O DFT-½ é capaz de contornar os altos custos associados ao GW em simulações de interface.

PHYSICAL REVIEW B **79**, 241312(R) (2009)

Accurate prediction of the Si/SiO_2 interface band offset using the self-consistent *ab initio* DFT/LDA-1/2 method

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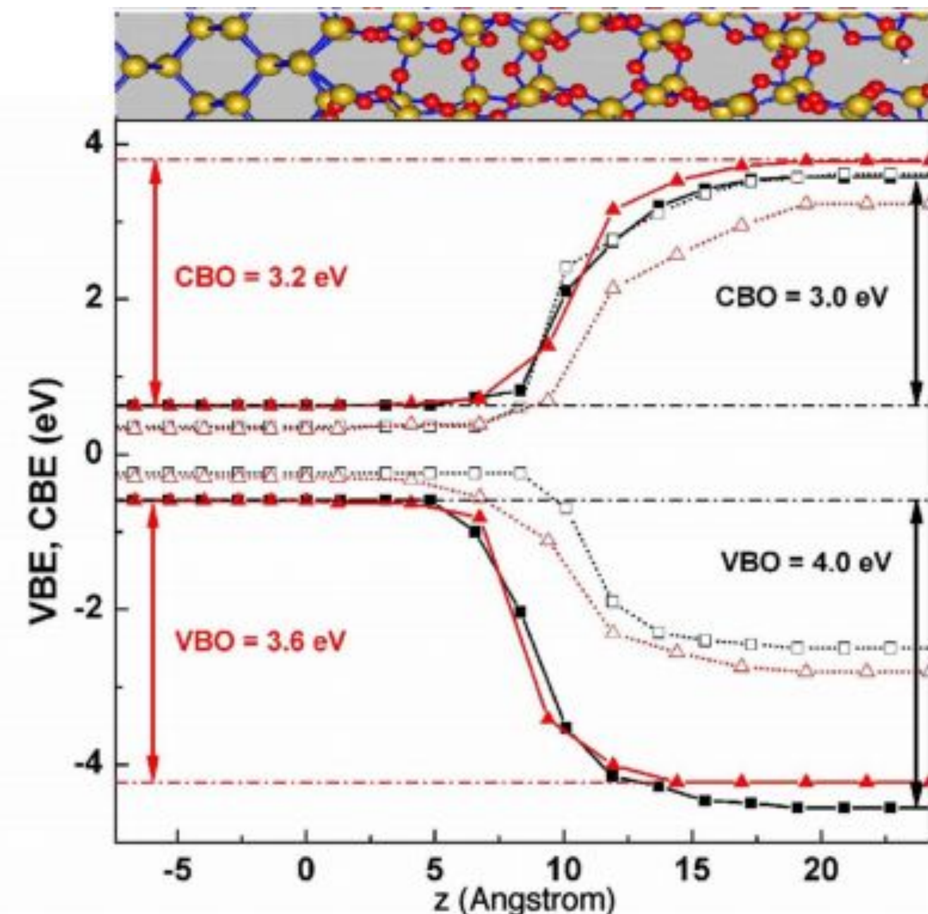
(Received 31 March 2009; published 23 June 2009)

We use the density functional theory/local-density approximation (DFT/LDA)-1/2 method [L. G. Ferreira *et al.*, Phys. Rev. B **78**, 125116 (2008)], which attempts to fix the electron self-energy deficiency of DFT/LDA by half-ionizing the whole Bloch band of the crystal, to calculate the band offsets of two Si/SiO_2 interface models. Our results are similar to those obtained with a "state-of-the-art" *GW* approach [R. Shaltaf *et al.*, Phys. Rev. Lett. **100**, 186401 (2008)], with the advantage of being as computationally inexpensive as the usual DFT/LDA. Our band gap and band offset predictions are in excellent agreement with experiments.

DOI: 10.1103/PhysRevB.79.241312 PACS number(s): 73.20.At, 71.15.Mb, 71.15.Qe, 71.20.Nr



Cálculo de band offset: Si/SiO_2

Correção do gap

TABLE II. Bulk and stack Si and SiO_2 band gaps.

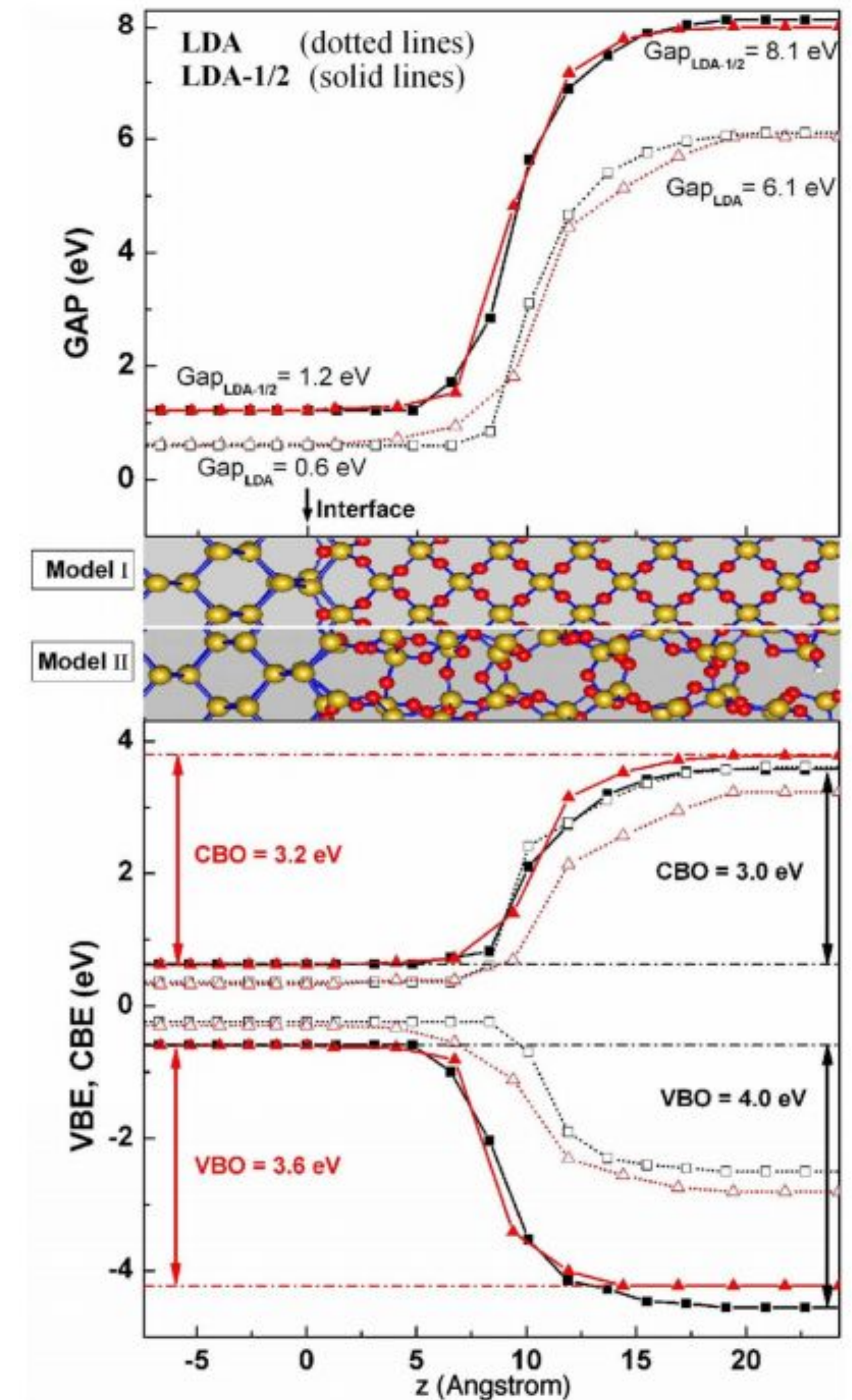
Gap gap (eV)	LDA	LDA-1/2	*GW*	Exp.[a]
Bulk Si	0.5	1.2	1.3	1.2
Bulk βc-SiO_2	6.6	8.6	8.8	8.9

Alinhamento de bandas

TABLE III: Valence and conduction band offsets for Models I and II calculated with LDA, LDA-1/2, GW, and from experimental data.

	LDA	LDA-1/2	GW [a]	Exp. [b]
VBO (I)	2.2	4.0	4.1	4.5
VBO (II)	2.4	3.6		
CBO (I)	3.3	3.0	2.9	3.3
CBO (II)	3.0	3.2		

[a]Ref. [4]
[b]Ref. [14] measured for amorphous SiO_2 on Si



Cálculo de band offset: AlN/GaN

➢ Resultados com precisão equivalente ao GW para outro sistema, agora com semicondutores III-V.

JOURNAL OF APPLIED PHYSICS **114**, 033709 (2013)

All-out band structure and band offset *ab initio* predictions for AlN/GaN and AlP/GaP interfaces

O. P. Silva Filho,[1,2] M. Ribeiro, Jr.,[1] R. R. Pelá,[1,a)] L. K. Teles,[1,a)] L. G. Ferreira,[1,3] and M. Marques[1,a)]
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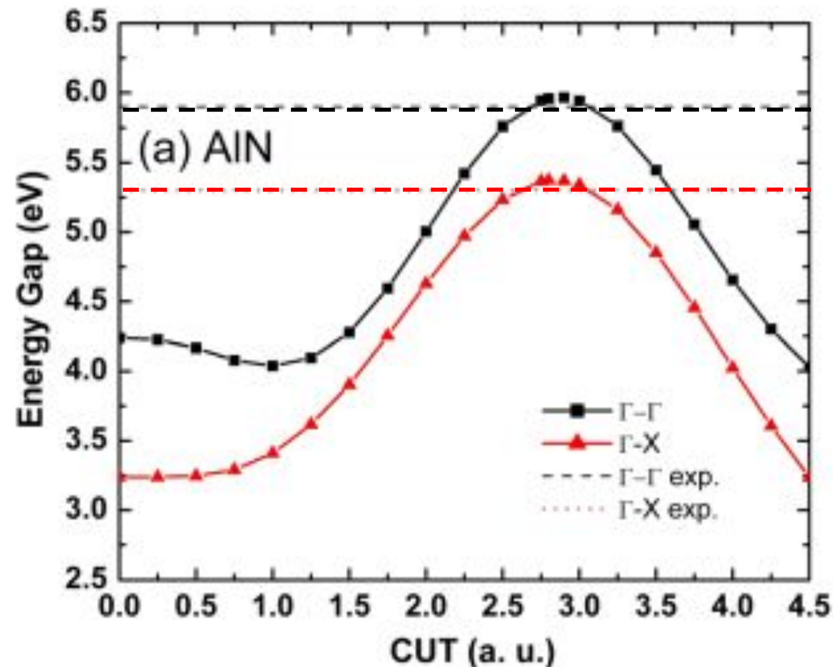
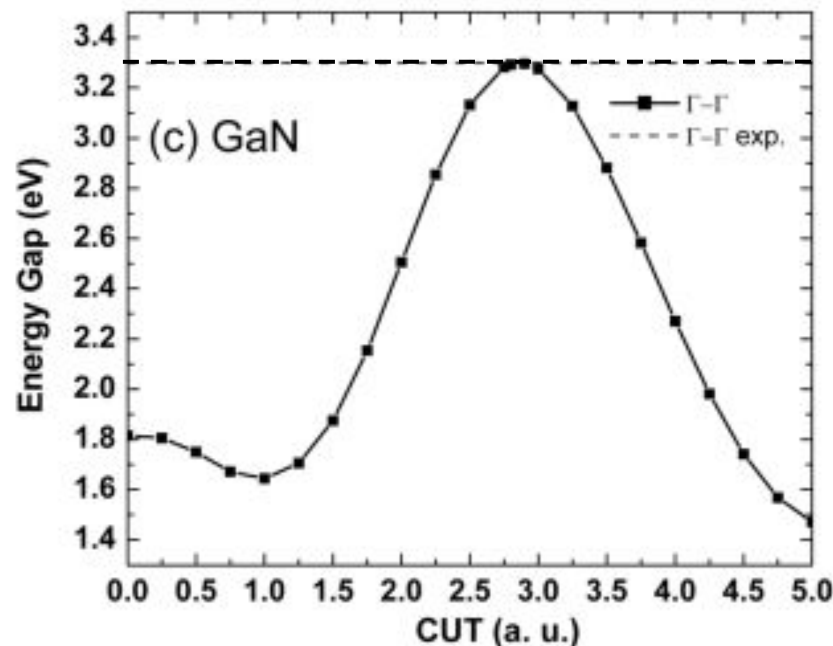
(Received 22 May 2013; accepted 12 June 2013; published online 18 July 2013)

We studied the electronic properties of the AlP/GaP and AlN/GaN interfaces and their cubic constituents. The work is developed using approximate quasiparticle approach LDA-1/2 method. First, we provide a detailed calculation of bulk AlN, AlP, GaN, and GaP. In addition to accurate results for fundamental band gap, we also obtained accurate electronic transition levels along valence and conduction bands profiles, compared to experiments and theoretical results using GW and hybrid functionals methods. For the conduction (valence) band offset we obtained 0.27 eV (0.43 eV) for AlP/GaP and 1.47 eV (0.36 eV) for AlN/GaN interfaces, in good agreement with experimental results. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4812493]

Cálculo de band offset: AlN/GaN

Correção do gap





Alinhamento de bandas

TABLE IV. Conduction and valence band offsets calculated in this work according to the functional used (LDA or LDA-1/2). Ratios (CBO:VBO) are calculated, as well as experimental values are shown for comparison.

		CBO	VBO	Ratio
AlN/GaN	LDA	0.44	1.08	29:71
	LDA-1/2	1.49	0.47	76:24
	[a] G_0W_0	0.98–1.32	0.54–0.91	70:30
	[a] Exp.	1.41	0.50	74:26
AlP/GaP	LDA	0.53	0.51	51:49
	LDA-1/2	0.27	0.46	37:63
	[b] Exp.	0.24	0.43	36:64

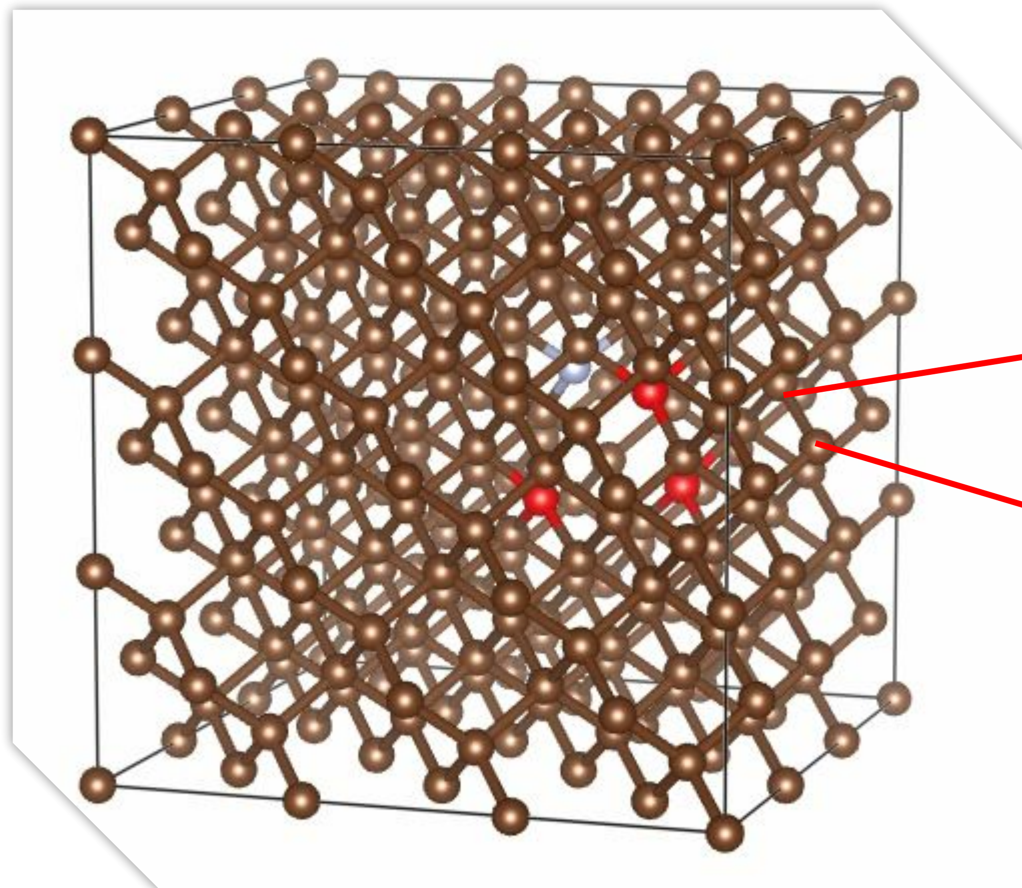
[a] Ref.[23]; [b] Ref.[64].

Aplicações do método DFT-½

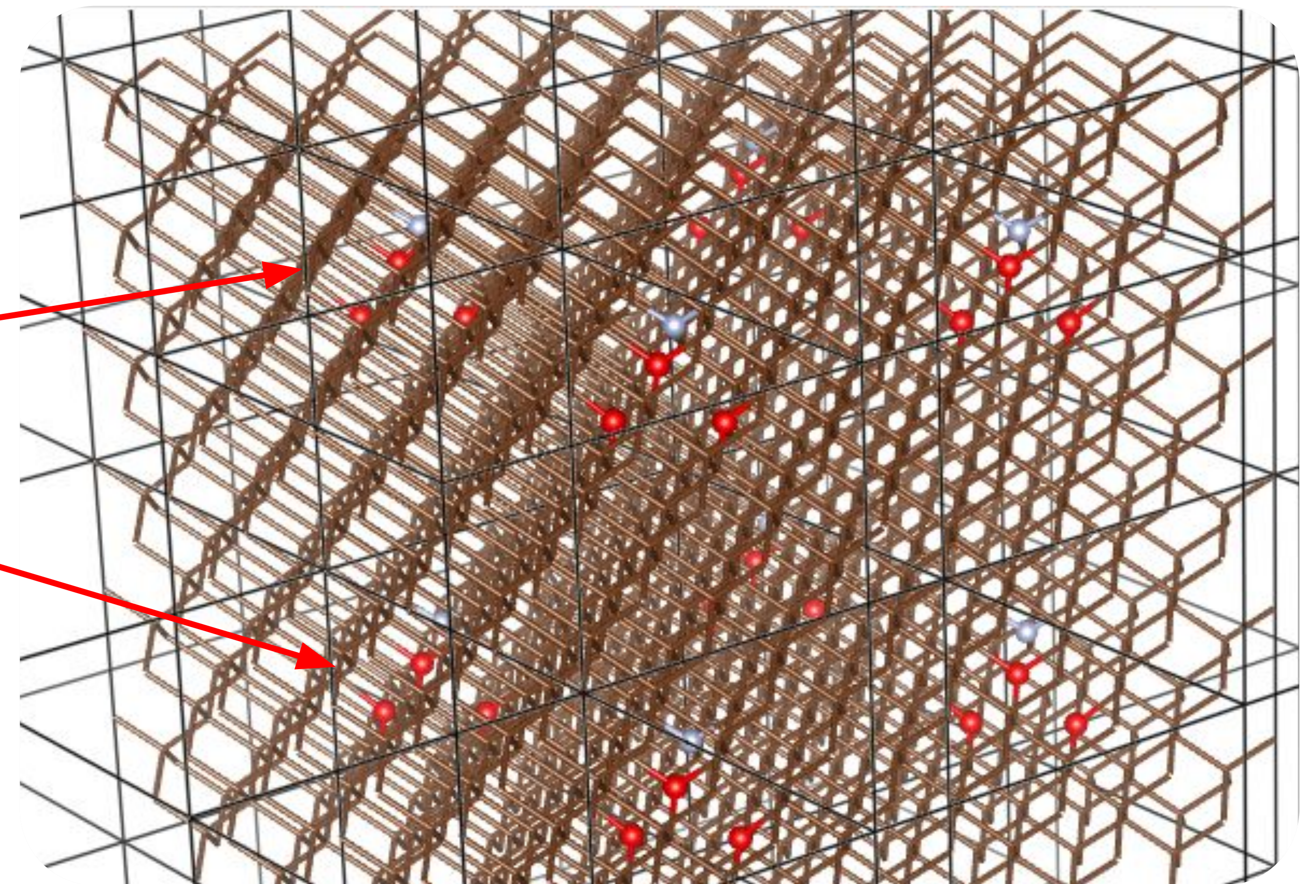
- Cálculo de band offset
- **Estados de defeitos**
- Estados hibridizados
- DFT+A-½
- Ligas semicondutoras
- Materiais 2D
- Casos patológicos

Aplicações do método DFT-½

Devido às condições periódicas de contorno, **grandes supercélulas são necessárias** para o estudo de defeitos.



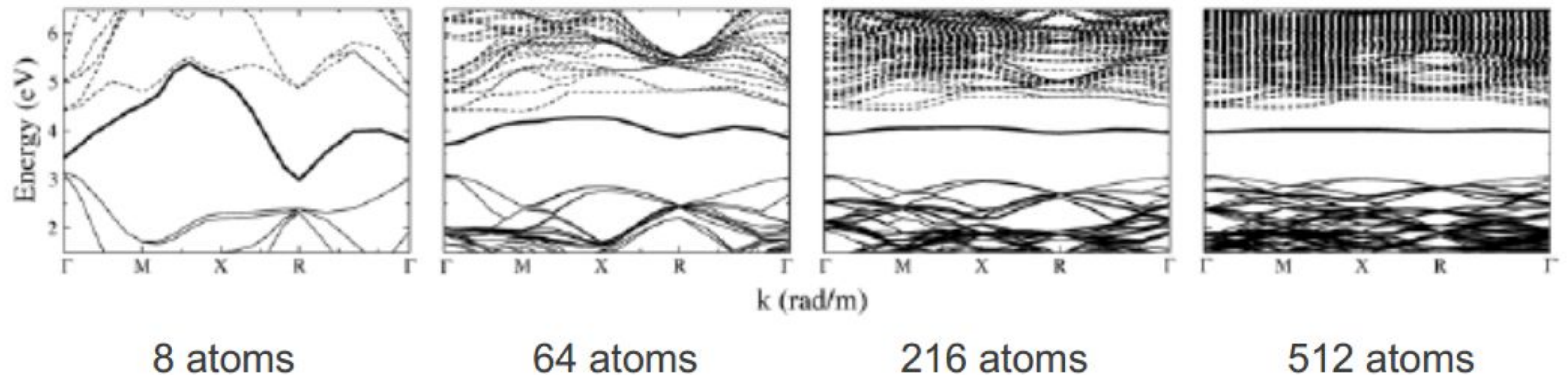
Célula unitária



Sistema simulado

Estados de defeito

➢ Necessidade de grandes supercélulas para evitar interações não-físicas decorrentes das condições de contorno periódicas.



C W M Castleton et al., Modelling Simul. Mater. Sci. Eng. 17 (2009) 084003

➢ A DFT acessa bem as propriedades estruturais, mas não consegue descrever bem propriedades eletrônicas, como as posições dos níveis.

Estados de defeito

- Dois exemplos de aplicação do DFT-½:

Defeitos de Si em Si

PHYSICAL REVIEW B **88**, 224102 (2013)

Combined LDA and LDA-1/2 method to obtain defect formation energies in large silicon supercells

Filipe Matusalem,[1,*] Mauro Ribeiro, Jr.,[1] Marcelo Marques,[1] Ronaldo R. Pelá,[1] Luiz G. Ferreira,[2,1] and Lara K. Teles[1]
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[2]*Departamento de Física dos Materiais e Mecânica, Instituto de Fís*
(Received 23 September 2013; revised manuscript re

A source of uncertainty in the state of the art calculati
energies. Several approaches were developed to surpa
remains: the small number of clustered atoms impo
LDA-1/2 method is explored in an attempt to overco
considered the self-interstitial defects in silicon as a be
levels of point defects in semiconductors. We found r
4.65, 4.49, and 4.87 eV, for hexagonal, split ⟨110⟩ and
most experimental results.

Defeitos de Mn em Si

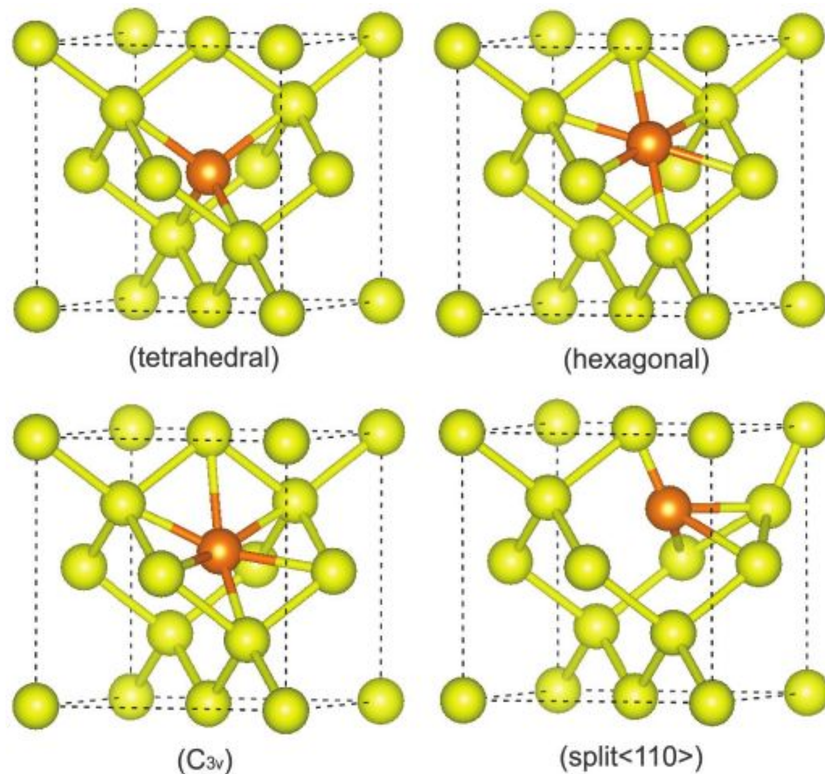
PHYSICAL REVIEW B **90**, 224102 (2014)

Charge transition levels of Mn-doped Si calculated with the GGA-1/2 method

Filipe Matusalem,* Ronaldo R. Pelá, Marcelo Marques, and Lara K. Teles
Group of Semiconductor Materials and Nanotechnology (GMSN), Technological Institute of Aeronautics (ITA), 12228-900 São José dos Campos/SP, Brazil
(Received 24 September 2014; revised manuscript received 21 November 2014; published 3 December 2014)

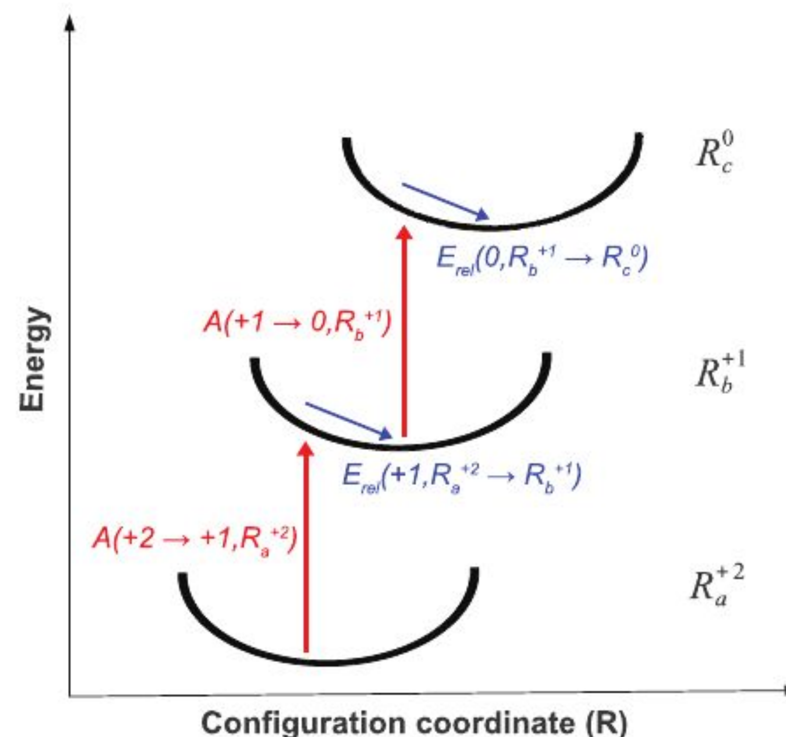
Although Mn impurities are promising to bring Si, the most widespread semiconductor employed in electronic devices, into the spintronics realm, few theoretical works exist that calculate the charge transition levels of Mn in Si. Among these works, none of them makes use of gap correction methods. To fill this void, we performed first principles calculations for Mn-doped Si, using the GGA-1/2 method, which approximately includes quasiparticle corrections at a small computational price. Our results improve the theoretical description of these charge transition levels, achieving good agreement with experimental results for interstitial and substitutional sites. Furthermore, the GGA-1/2 method allowed us to use reasonably large supercells, up to 217 atoms.

Impureza auto-intersticial em silício



silicon self-interstitial defect

- Cálculo de energias de formação.
- Lembre-se que o DFT-½ não calcula energias totais.
- Ideia: Decompor a energia de formação em diferentes contribuições.

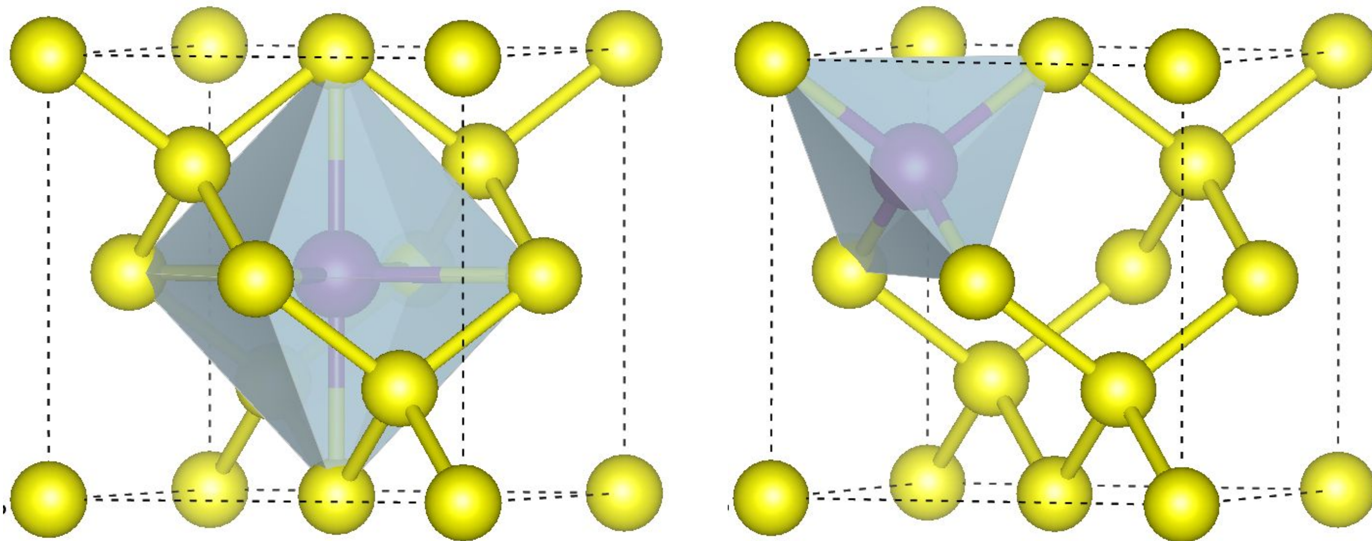


Matusalem et. al, PHYSICAL REVIEW B 88, 224102 (2013)

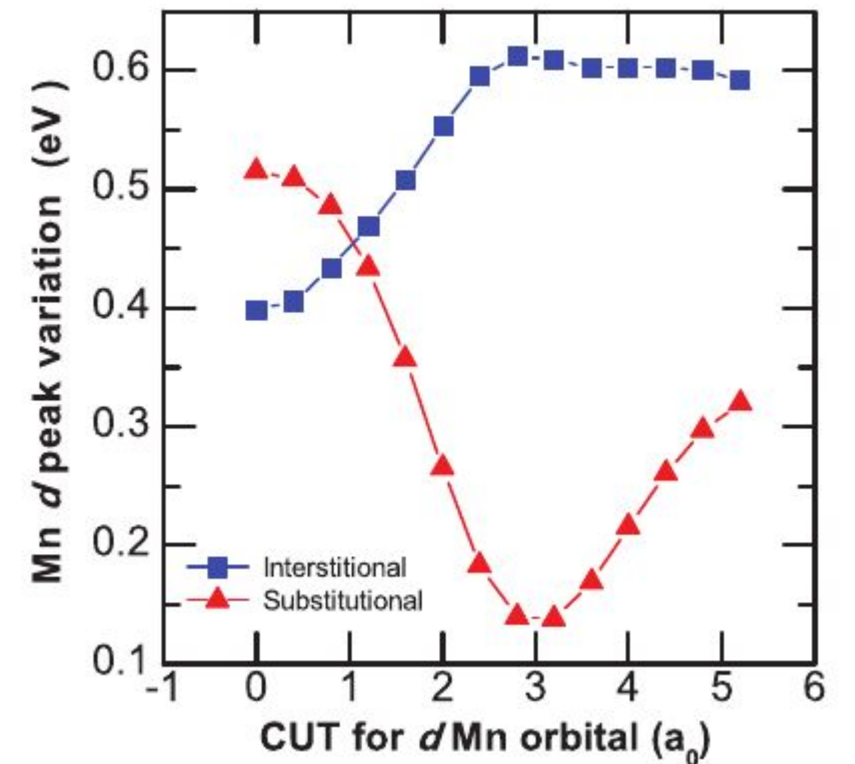
Termodinamic charge transition levels (eV)

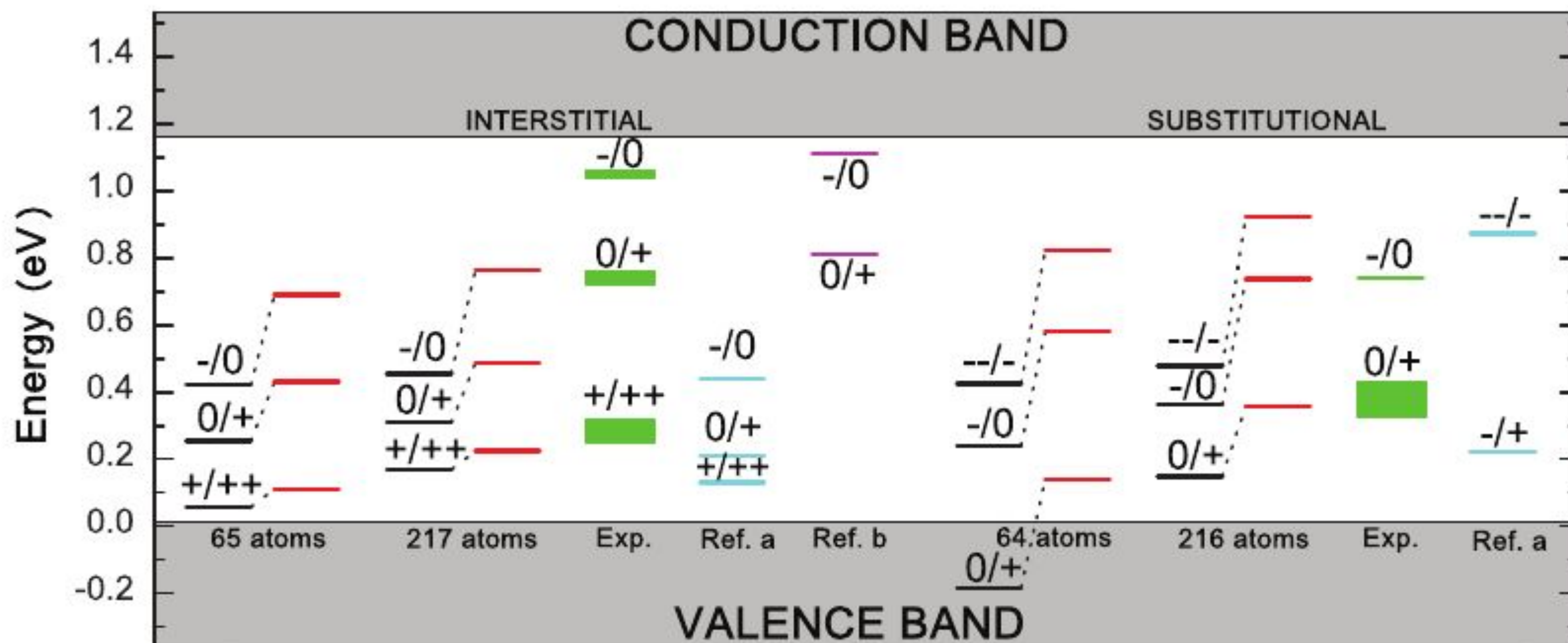
Geometry	C_{3v}			hex			split			
Atoms per cell	65	217	$65(G_0W_0)$	65	217	$65(G_0W_0)$	65	217	$65(G_0W_0)$	Exp.
$+/2+$	0.96	1.02	1.24	0.25	0.55	0.58	0.20	0.48	0.50	0.4
$0/+$	0.93	0.95	0.62	0.08	0.15	0.09	−0.11	−0.08	0.05	0.1–0.2
$-/0$	1.44	1.29	...	1.29	1.26	...	1.00	0.99	...	...

Impureza de Maganês em silício



Interstitial site　　　　Substitutional site





Matusalem et. al, PHYSICAL REVIEW B 90, 224102 (2014)

Aplicações do método DFT-½

- Cálculo de band offset
- Estados de defeitos
- **Estados hibridizados**
- DFT-½+A
- Ligas semicondutoras
- Materiais 2D
- Casos patológicos

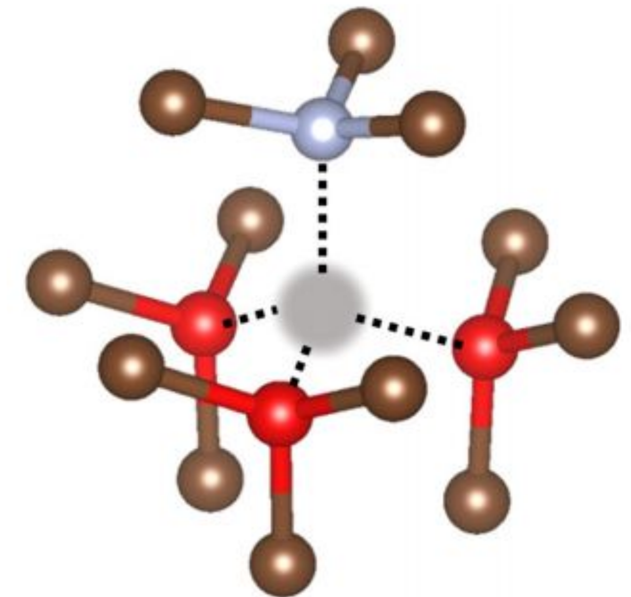
Defeitos NV$^-$ center em silício para qubits

PHYSICAL REVIEW B **96**, 075145 (2017)

General procedure for the calculation of accurate defect excitation energies from DFT-1/2 band structures: The case of the NV$^-$ center in diamond

Bruno Lucatto,[1,*] Lucy V. C. Assali,[2] Ronaldo Rodrigues Pela,[1] Marcelo Marques,[1] and Lara K. Teles[1]
[1]*Grupo de Materiais Semicondutores e Nanotecnologia (GMSN), Technological Institute of Aeronautics (ITA), 12228-900 São José dos Campos, SP, Brazil*
[2]*Institute of Physics, University de São Paulo (USP), 05315-970 São Paulo, SP, Brazil*
(Received 29 May 2017; published 23 August 2017)

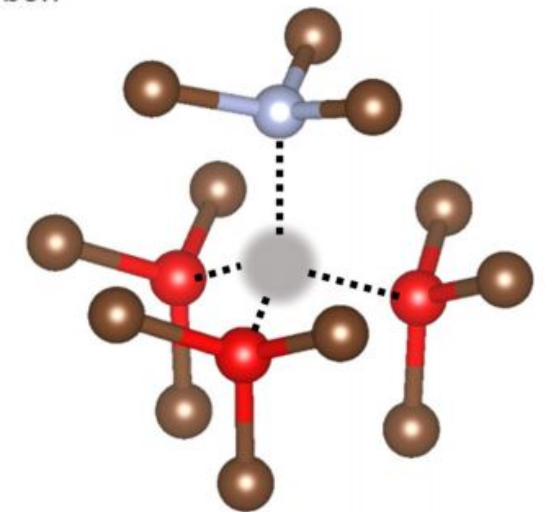
A major challenge in creating a quantum computer is to find a quantum system that can be used to implement the qubits. For this purpose, deep centers are prominent candidates, and *ab initio* calculations are one of the most important tools to theoretically study their properties. However, these calculations are highly involved, due to the large supercell needed, and the computational cost can be even larger when one goes beyond the Kohn-Sham scheme to correct the band gap problem and achieve good accuracy. In this work, we present a method that overcomes these problems and provides the optical transition energies as a difference of Kohn-Sham eigenvalues; even more, provides a complete and accurate band structure of the defects in a semiconductor. Despite the original motivations, the presented methodology is a general procedure, which can be used to systematically study the optical transitions between localized levels within the band gap of any system. The method is an extension of the low-cost and parameter-free DFT-1/2 approximate quasiparticle correction, and allows it to be applied in the study of complex defects. As a benchmark, we apply the method to the NV$^-$ center in diamond. The agreement with experiments is remarkable, with an accuracy of 0.1 eV. The band structure agrees with the expected qualitative features of this system, and thus provides a good intuitive physical picture by itself.



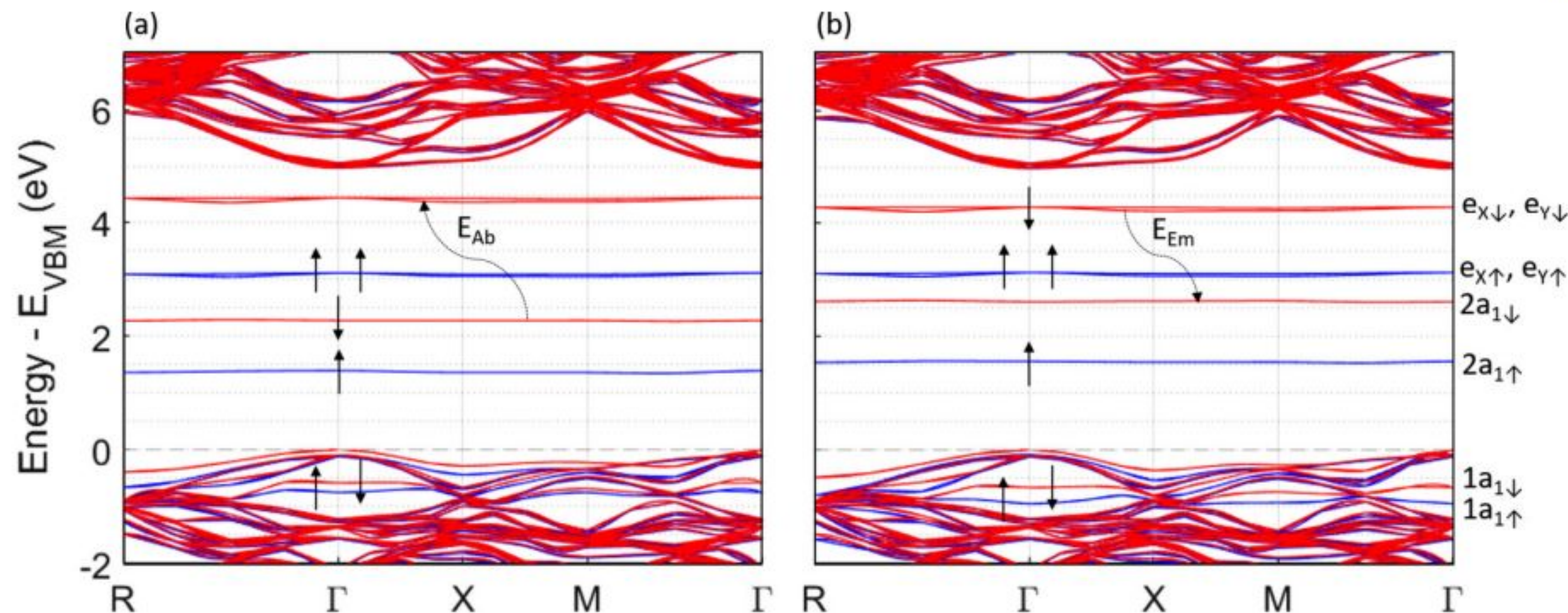
Defeitos NV⁻ center em silício para qubits

TABLE I. Orbital character of the defect levels and fractions of electron to be removed from and added to each potential (denoted by ξ and ζ, respectively).

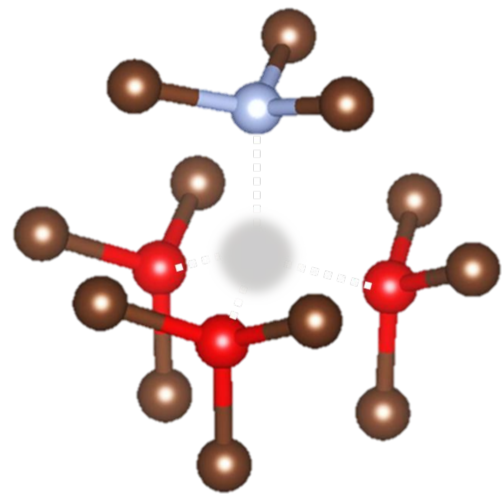
	Ground state				Excited state			
$X\phi$	$2a_{1\downarrow}$	$\xi_{X\phi}$	$e_{x\downarrow}+e_{y\downarrow}$	$\zeta_{X\phi}$	$2a_{1\downarrow}$	$\xi_{X\phi}$	$e_{x\downarrow}+e_{y\downarrow}$	$\zeta_{X\phi}$
C_{2s}	0.6%	0.00	3.1%	0.02	0.6%	0.00	2.2%	0.01
C_{2p}	17.7%	0.09	30.2%	0.15	21.7%	0.11	31.1%	0.16
N_{2s}	4.6%	0.02	0.0%	0.00	4.9%	0.02	0.0%	0.00
N_{2p}	40.7%	0.20	0.3%	0.00	28.1%	0.14	0.3%	0.00



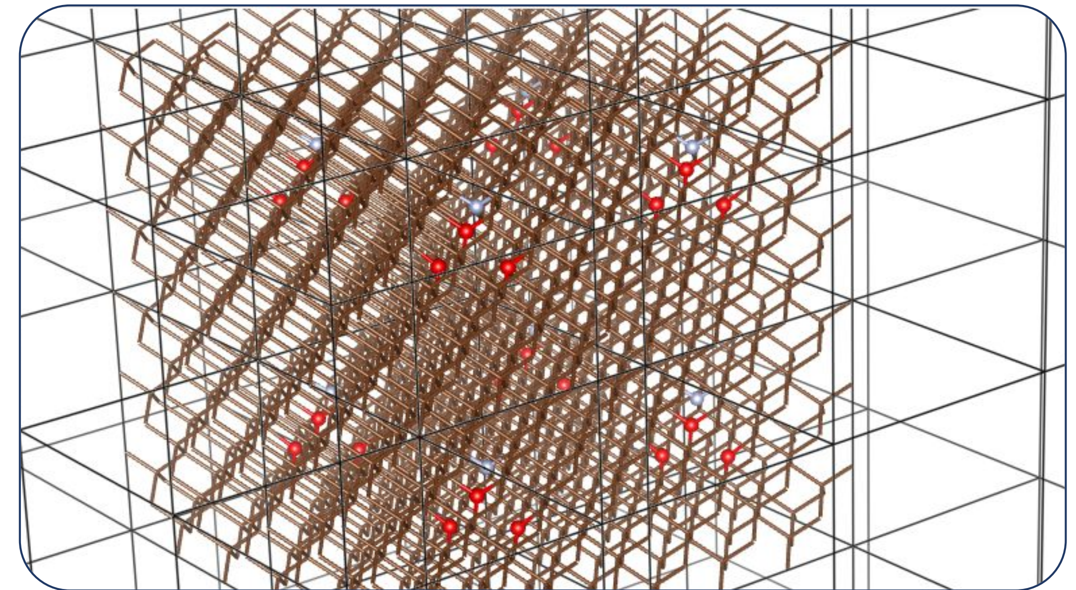
$$\xi_{X\phi} = \mathrm{char}_{X\phi}[\psi_\alpha(\Gamma)] \times \frac{1}{2}$$

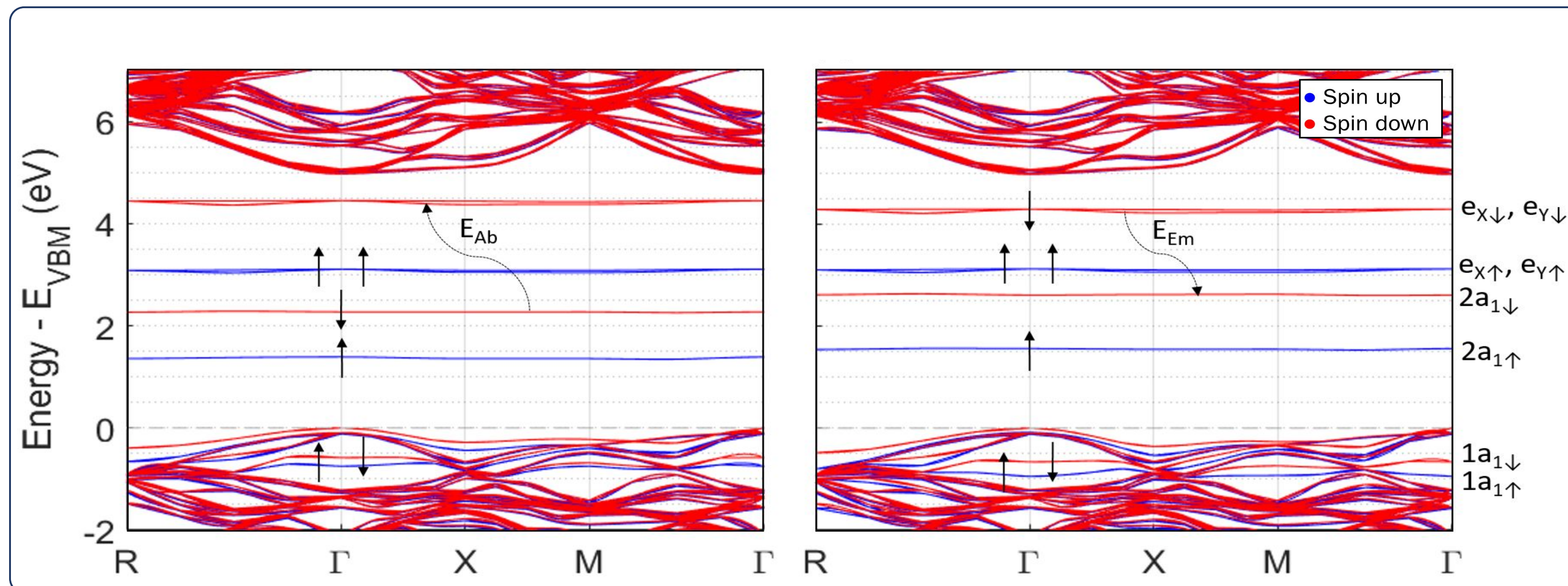


Defeitos NV$^-$ center em silício para qubits



Periodic boundary conditions





	E_{Ab} (eV)	E_{Em} (eV)
GGA	1.89	1.54
HSE06*	2.21	1.74
DFT-1/2	2.18	1.68
Exp**	2.18	1.76

* A. Gali *et al.* PRL 103, 186404 (2009)

** G. Davies *et al.* Proc. Roy. Soc. Lond. A 348, 285 (1976)

Aplicações do método DFT-½

- Cálculo de band offset
- Estados de defeitos
- Estados hibridizados
- **DFT+A-½**
- Ligas semicondutoras
- Materiais 2D
- Casos patológicos

Abordagem DFT+A-½

PHYSICAL REVIEW B **95**, 045126 (2017)

Fast and accurate approximate quasiparticle band structure calculations of ZnO, CdO, and MgO polymorphs

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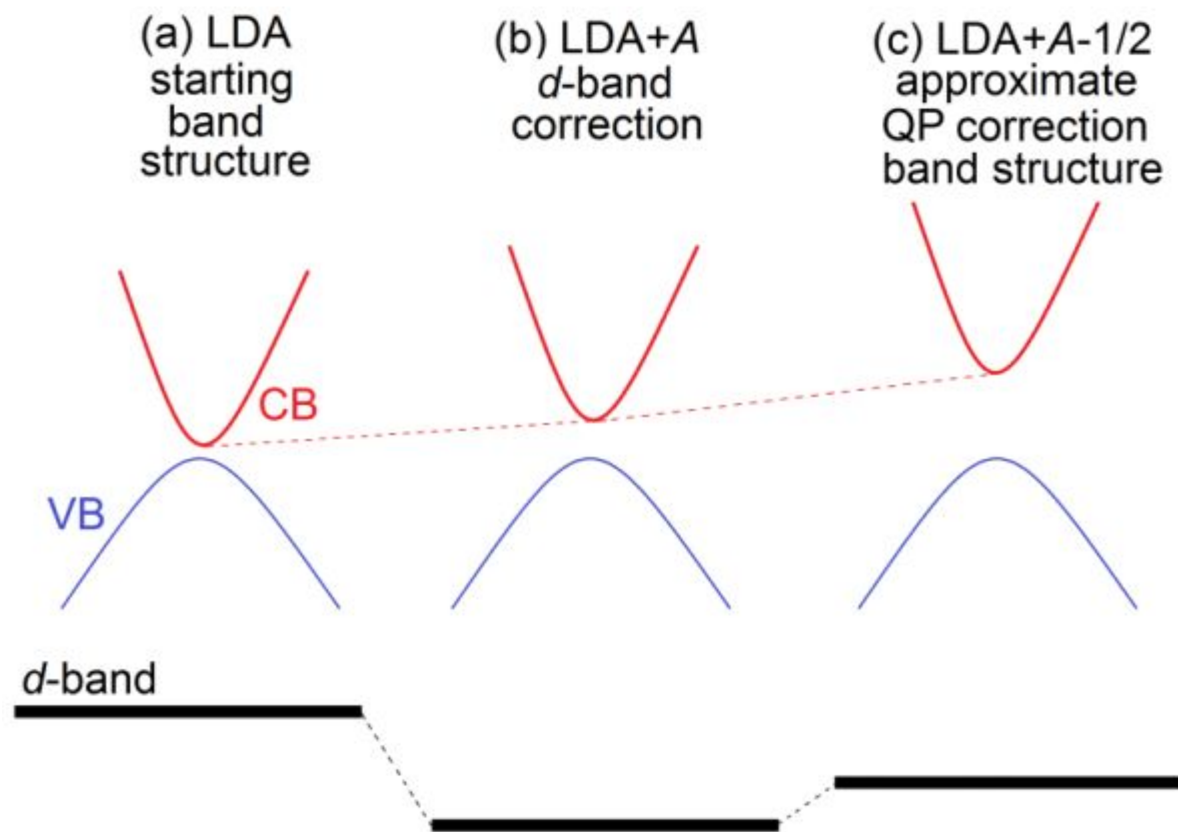
(Received 26 October 2016; published 17 January 2017)

We investigate ZnO, CdO, and MgO oxides crystallizing in rocksalt, wurtzite, and zincblende structures. Whereas in MgO calculations, the conventional LDA-1/2 method is employed through a self-energy potential (V_S), the shallow d bands in ZnO and CdO are treated through an increased amplitude (A) of V_S to modulate the self-energy of the d states to place them in the quasiparticle position. The LDA+A-1/2 scheme is applied to calculate band structures and electronic density of states of ZnO and CdO. We compare the results with those of more sophisticated quasiparticle calculations and experiments. We demonstrate that this new LDA+A-1/2 method reaches accuracy comparable to state-of-the-art methods, opening a door to study more complex systems containing shallow core electrons to the prize of LDA studies.

DOI: 10.1103/PhysRevB.95.045126

Abordagem DFT+A-½

- Ajuste dos níveis d para evitar hibridação espúria de estados, melhorando a qualidade da correção de gap do sistema.



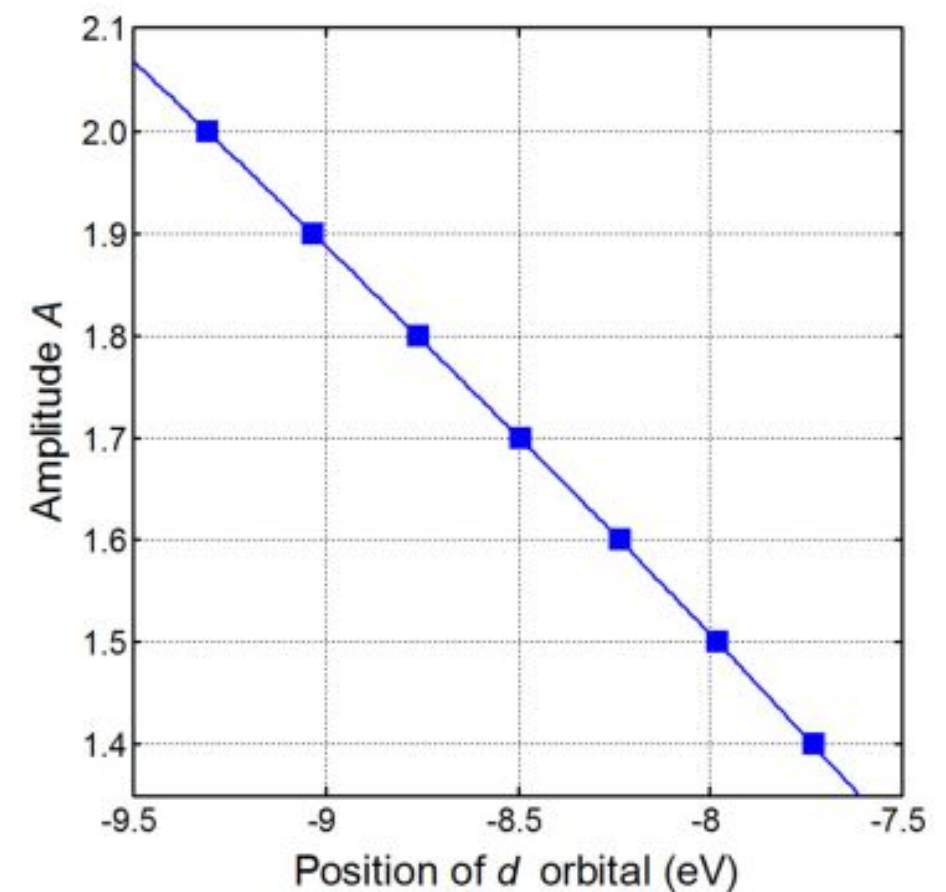


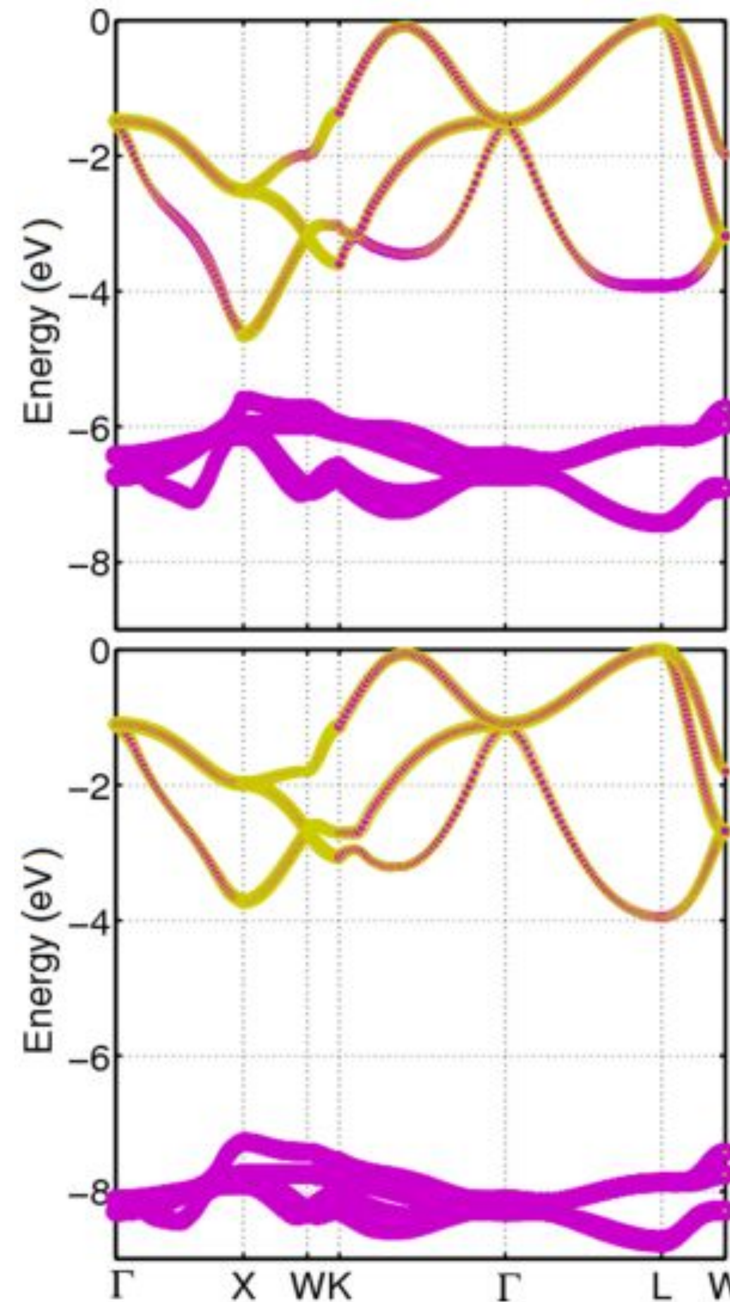
FIG. 1. Plot of the amplitude A vs the d state position below VBM. This plot refers to WZ ZnO.

Abordagem DFT+A-½

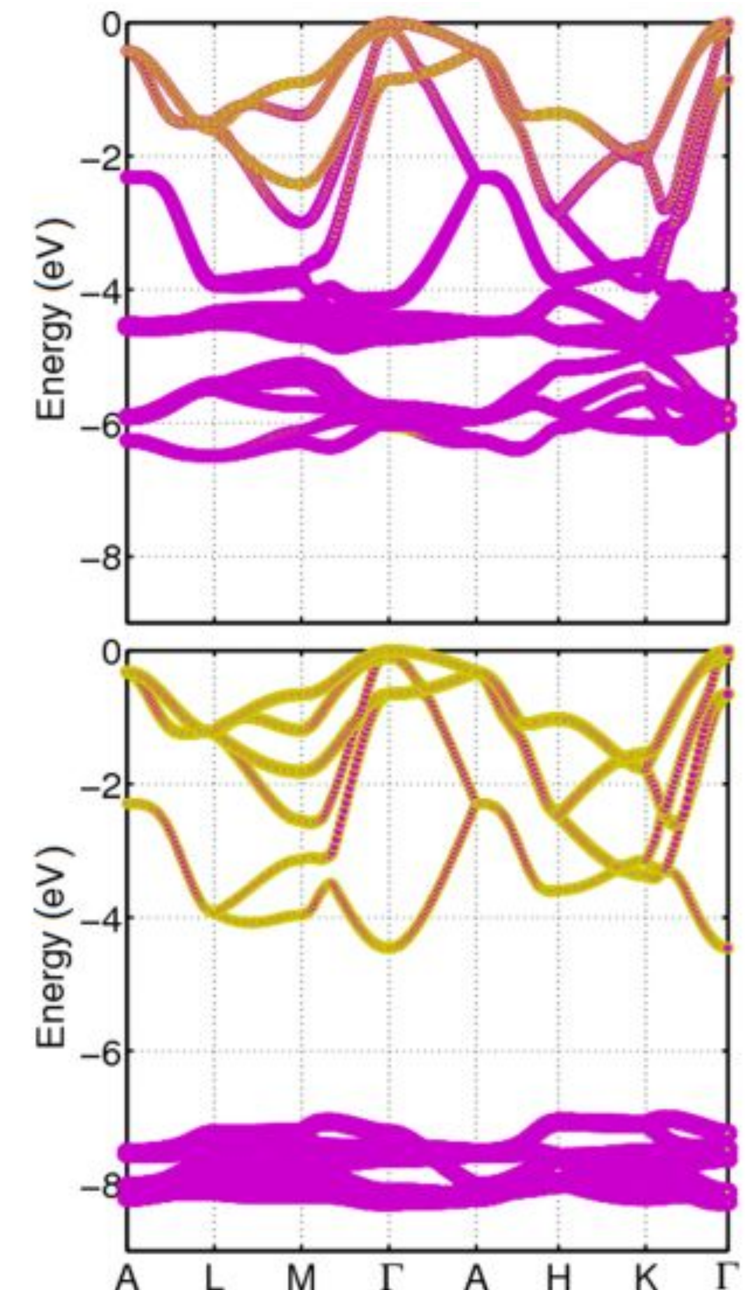
TABLE I. VBM character analysis using LDA and the LDA+A correction for ZnO, CdO, and MgO in WZ, RS, and ZB phases. All values are expressed in percentage.

Struct.	Method	Orbital	Zn	O	Cd	O	Mg	O
RS	LDA	p	0.0	66.5	0.0	76.2	2.5	97.6
		d	33.5	0.0	23.8	0.0	0.0	0.0
	LDA+A	p	0.0	84.5	0.0	85.6		
		d	15.5	0.0	14.4	0.0		
ZB	LDA	p	2.4	63.5	1.8	74.9	1.2	94.5
		d	34.1	0.0	23.3	0.0	4.3	0.0
	LDA+A	p	2.6	84.5	2.1	83.5		
		d	16.8	0.0	14.4	0.0		
WZ	LDA	p	2.5	63.5	2.1	73.6	0.8	96.1
		d	34.7	0.0	24.3	0.0	3.2	0.0
	LDA+A	p	2.6	80.8	2.5	82.8		
		d	16.7	0.0	14.8	0.0		

CdO (RS)



ZnO (WZ)



Abordagem DFT+A-½

TABLE III. The direct band gap $E_g(\Gamma_C - \Gamma_V)$. The width of the uppermost p-like valence band W_p and the average d band position below VBM E_d. All results are for WZ phase and the values are in eV. The theoretical results are divided into hybrid + GW (square brackets), others recipes of GW (brace), hybrid DFT (parentheses), and other DFT results.

Oxide	$E_g(\Gamma - \Gamma)$	W_p	E_d	Reference
	3.49	**4.35**	**7.45**	This Work
ZnO	0.73[a], (2.1[c]), {2.99[f]}, [3.2[b]] [3.2[c]], [3.21[d]], [3.37[f]], [3.6[e]]	3.99[g], 5.2[g], {4.9[e]}	5.0[a], [7.1[c]], [6.96[b]] [6.9[h]], [6.9[i]], [6.8[e]]	Theo.
	3.30[n], 3.37[m], 3.435[k] 3.436[j], 3.437[p], 3.438[o] 3.445[l], 3.53[q], 3.555[r]	5.3[g]	8.81[w], 8.5[v], 7.6[s], 7.5[t] 7.5[u], 7.4[c], 7.3[h], 6.95[x]	Exp.
CdO	**1.30**	**3.67**	**7.67**	This Work
	−0.34[ab], 0.9[aa], [0.96[x]], [1.06[z]]			Theo.
MgO	**6.06**	**2.75**		This Work
	3.78[ac], [6.19[y]], [6.52[z]]			Theo.

[a]Ref. [11]; [b]Ref. [41]; [c]Ref. [20]; [d]Ref. [36]; [e]Ref. [31]; [f]Ref. [32]; [g]Ref. [55]; [h]Ref. [21]; [i]Ref. [67]; [j]Ref. [68]; [k]Ref. [69]; [l]Ref. [70]; [m]Ref. [71]; [n]Ref. [72]; [o]Ref. [73]; [p]Ref. [74]; [q]Ref. [75]; [r]Ref. [76]; [s]Ref. [14]; [t]Ref. [15]; [u]Ref. [16]; [v]Ref. [17]; [w]Ref. [18]; [x]Ref. [19]; [y]Ref. [10]; [z]Ref. [56]; [aa]Ref. [77]; [ab]Ref. [62]; [ac]Ref. [78].

Aplicações do método DFT-½

- Cálculo de band offset
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- **Ligas semicondutoras**
- Materiais 2D
- Casos patológicos

DFT-½ em ligas semicondutoras

- Combinação de expansão de cluster (GQCA) + DFT-½:

Comparing LDA-1/2, HSE03, HSE06 and G_0W_0 approaches for band gap calculations of alloys

R R Pela[1,2], M Marques[1] and L K Teles[1]

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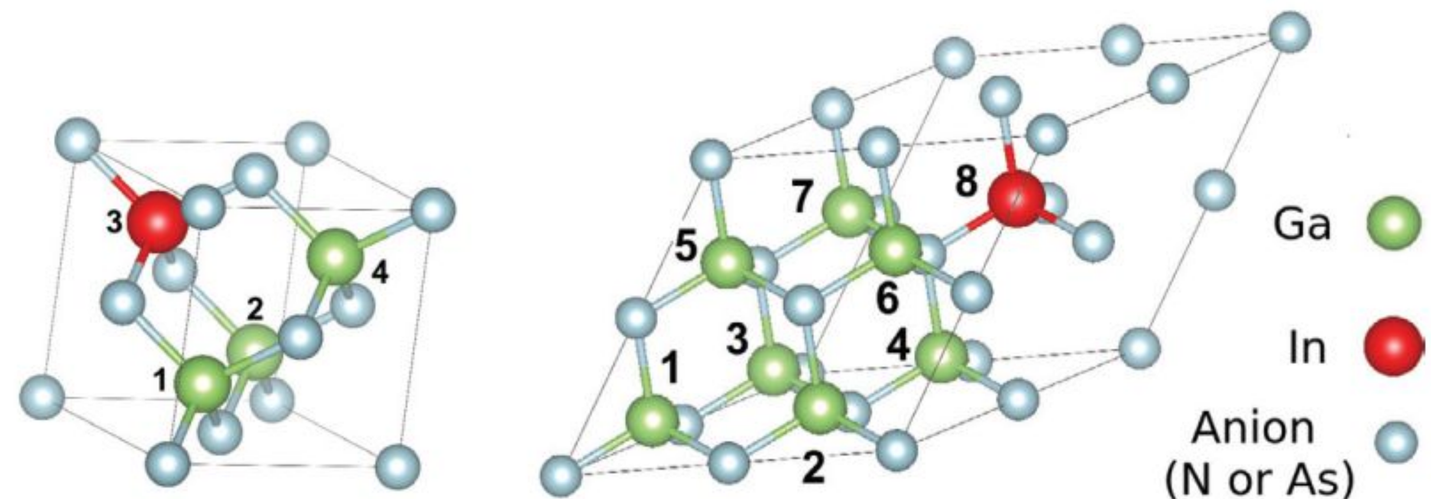
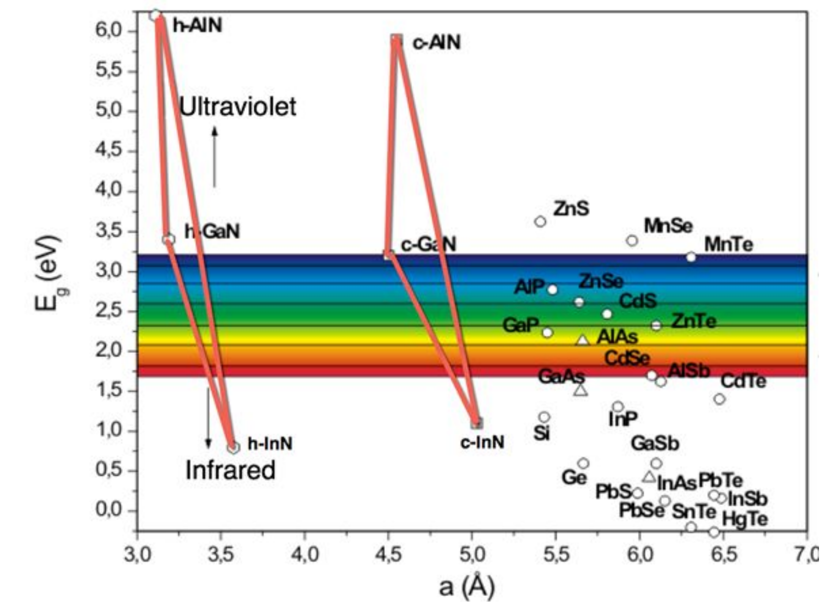


Table 4. Required computational resources and accuracy (measured by the root mean square error, ER, in eV) of each approach.

	InGaAs					InGaN					
	LDA-1/2		HSE03	HSE06	G_0W_0	LDA-1/2		HSE03	HSE06	G_0W_0	$G_0W_0(2)$
	8 atoms	16 atoms	8atoms			8 atoms	16 atoms	8 atoms			
T	0.005	0.03	4.7	3.0	18.0	0.01	0.02	4.6	3.7	13.5	15.8
M	0.7	0.8	1.4	1.4	32.0	1.1	2.3	1.2	1.2	30.2	30.2
ER	0.10	0.09	0.19	0.06	0.09	0.39	0.35	0.40	0.25	0.52	0.28

Note: The computational time (*T*, given in hours) and the memory (*M*, given in GB) were averaged among all the clusters employed in GQCA.

DFT-½ em ligas semicondutoras



APPLIED PHYSICS LETTERS **98**, 151907 (2011)

Accurate band gaps of AlGaN, InGaN, and AlInN alloys calculations based on LDA-1/2 approach

R. R. Pelá,[1,a)] C. Caetano,[2] M. Marques,[1] L. G. Ferreira,[1,3] J. Furthmüller,[4] and L. K. Teles[1,b)]

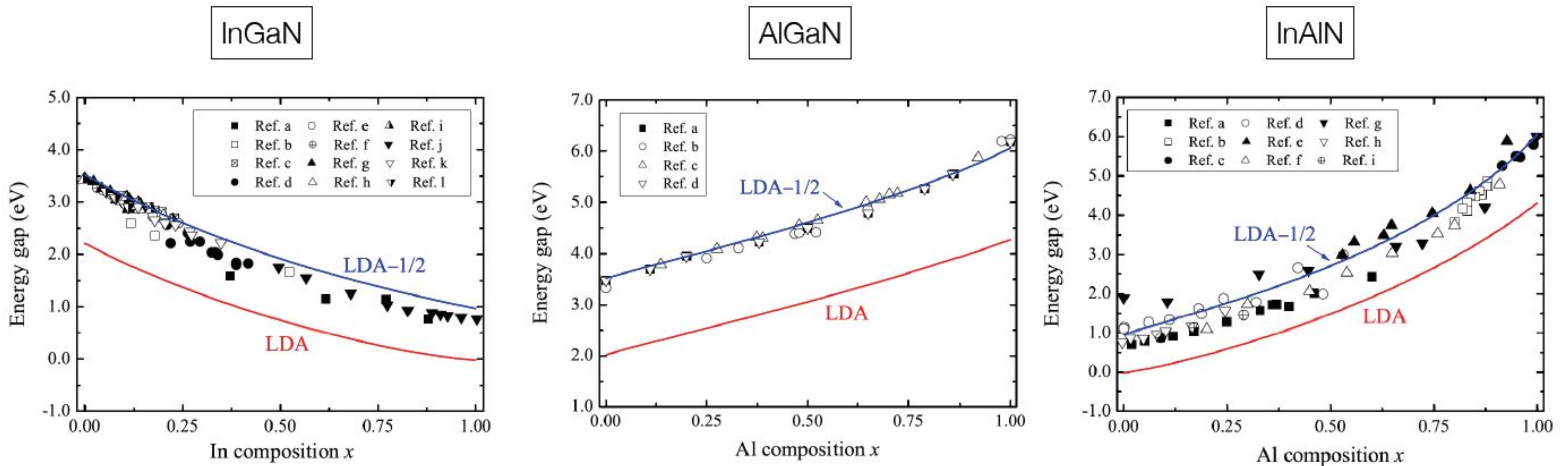
[1]*Instituto Tecnológico de Aeronáutica, 12228-900 São José dos Campos, SP, Brazil*
[2]*Universidade Federal da Fronteira Sul, 85770-000 Realeza, PR, Brazil*
[3]*Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil*
[4]*Institut für Festkörpertheorie und optik, Friedrich-Schiller-Universität, 07743 Jena, Germany*

(Received 31 January 2011; accepted 22 March 2011; published online 14 April 2011)

We present parameter-free calculations of electronic properties of InGaN, InAlN, and AlGaN alloys. The calculations are based on a generalized quasichemical approach, to account for disorder and composition effects, and first-principles calculations within the density functional theory with the LDA-1/2 approach, to accurately determine the band gaps. We provide precise results for AlGaN, InGaN, and AlInN band gaps for the entire range of compositions, and their respective bowing parameters. © *2011 American Institute of Physics*. [doi:10.1063/1.3576570]

DFT-½ em ligas semicondutoras

- Curvas de gap de energia *versus* composição:



- Resultados acurados e custo computacional equivalente ao DFT padrão!

Aplicações do método DFT-½

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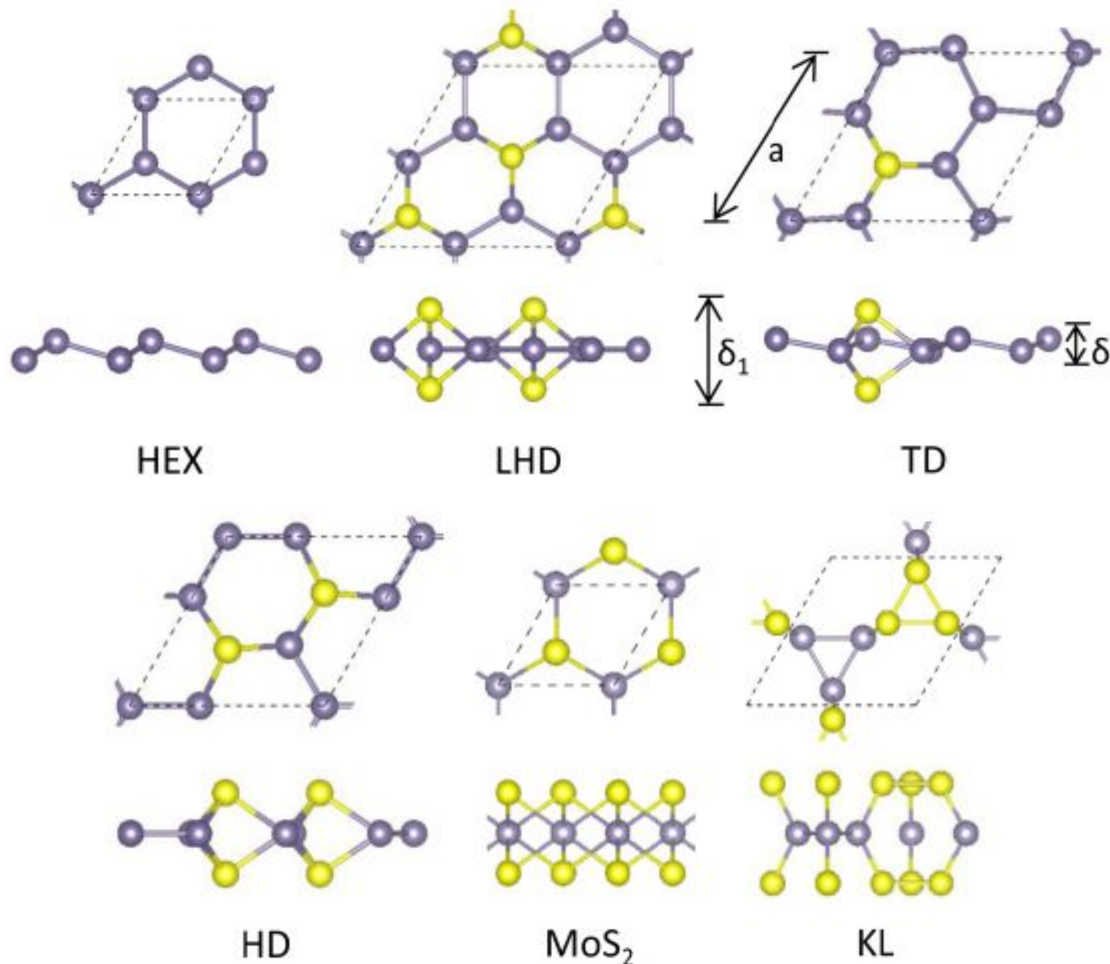
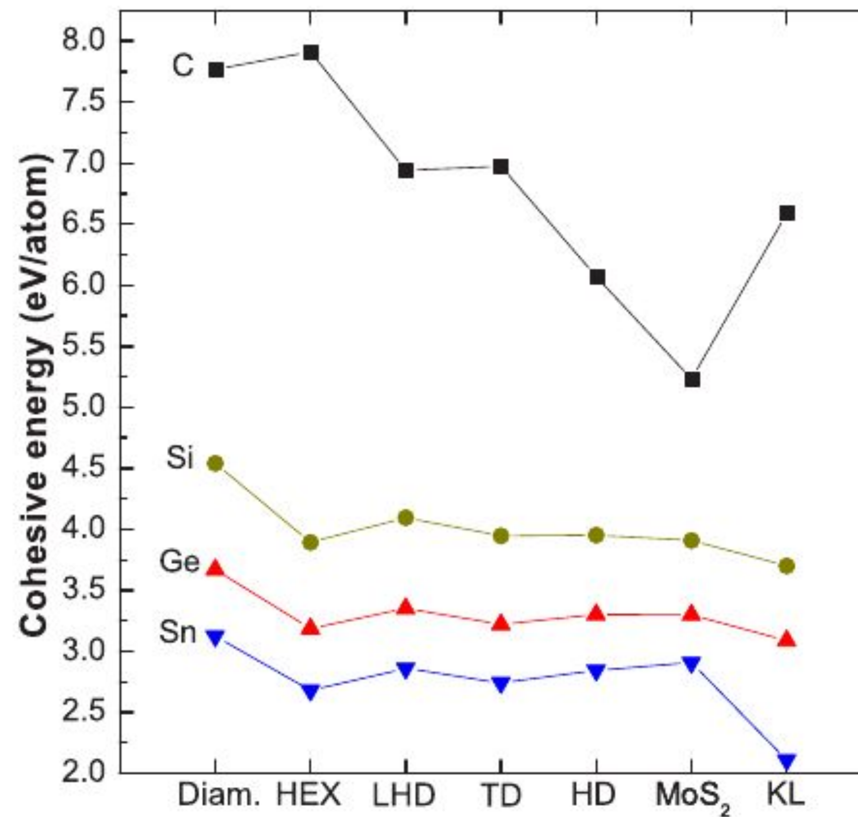
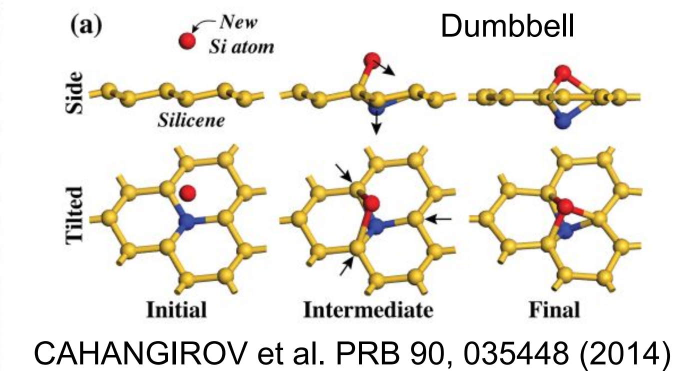
Group-IV graphene-like compounds

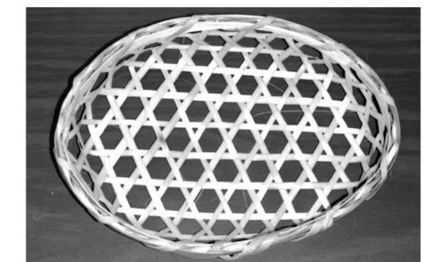






CAHANGIROV et al. PRB 90, 035448 (2014)

Japanese bamboo basket



KL = kagome

Matusalem, et. al. PHYSICAL REVIEW B 92, 045436 (2015)

Band gap (eV)

	Diamond				LHD			HD		
	GGA	GGA-1/2(CUT)	HSE	EXP	GGA	GGA-1/2(CUT)	HSE	GGA	GGA-1/2(CUT)	HSE
C	4.09	4.93(2.36)	5.29[5.76[c]] [60]	5.4 [46]	1.70	2.21(2.68)	2.71	Metal	Metal	Metal
Si	0.62	1.30(3.68)	1.22[1.23[c]] [60]	1.17 [46]	0.25	0.54(4.08)	0.73	0.15	0.32(3.49)	0.43
Ge	0.00	0.41[a][0.86[b]]	0.12[0.74[d]] [59]	0.74 [46]	0.00	0.26[f]	0.36	0.50	0.72[g]	0.79
Sn	0.00	0.00(4.70)	0.00[0.00[e]] [61]	0.00 [46]	0.02	0.23(4.84)	0.32	0.31	0.40(4.29)	0.63

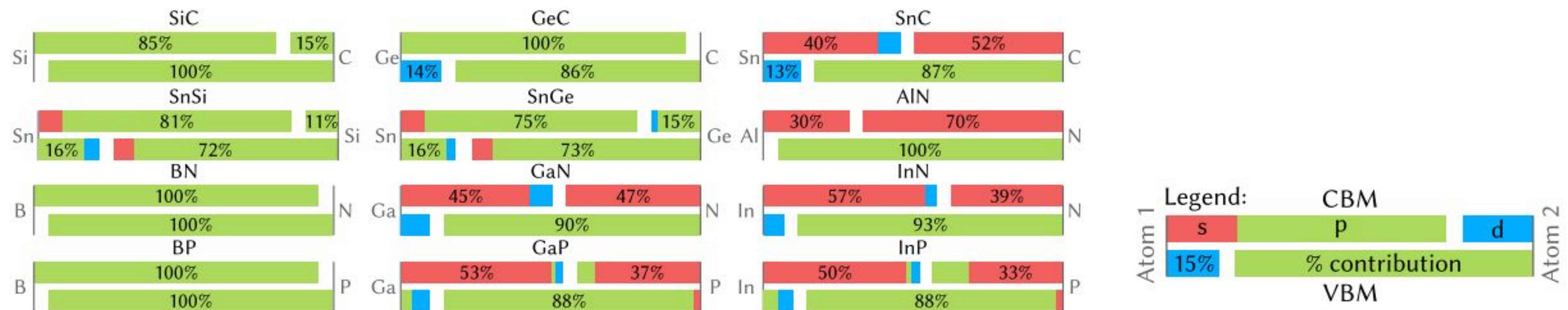
DFT-½ Method on 2D Materials

PHYSICAL REVIEW B **97**, 045426 (2018)

Approximate quasiparticle correction for calculations of the energy gap in two-dimensional materials

I. Guilhon,[1,*] D. S. Koda,[1,†] L. G. Ferreira,[2] M. Marques,[1,‡] and L. K. Teles[1,§]
[1]*Grupo de Materiais Semicondutores e Nanotecnologia, Instituto Tecnológico de Aeronáutica, DCTA, 12228-900 São José dos Campos, Brazil*
[2]*Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil*

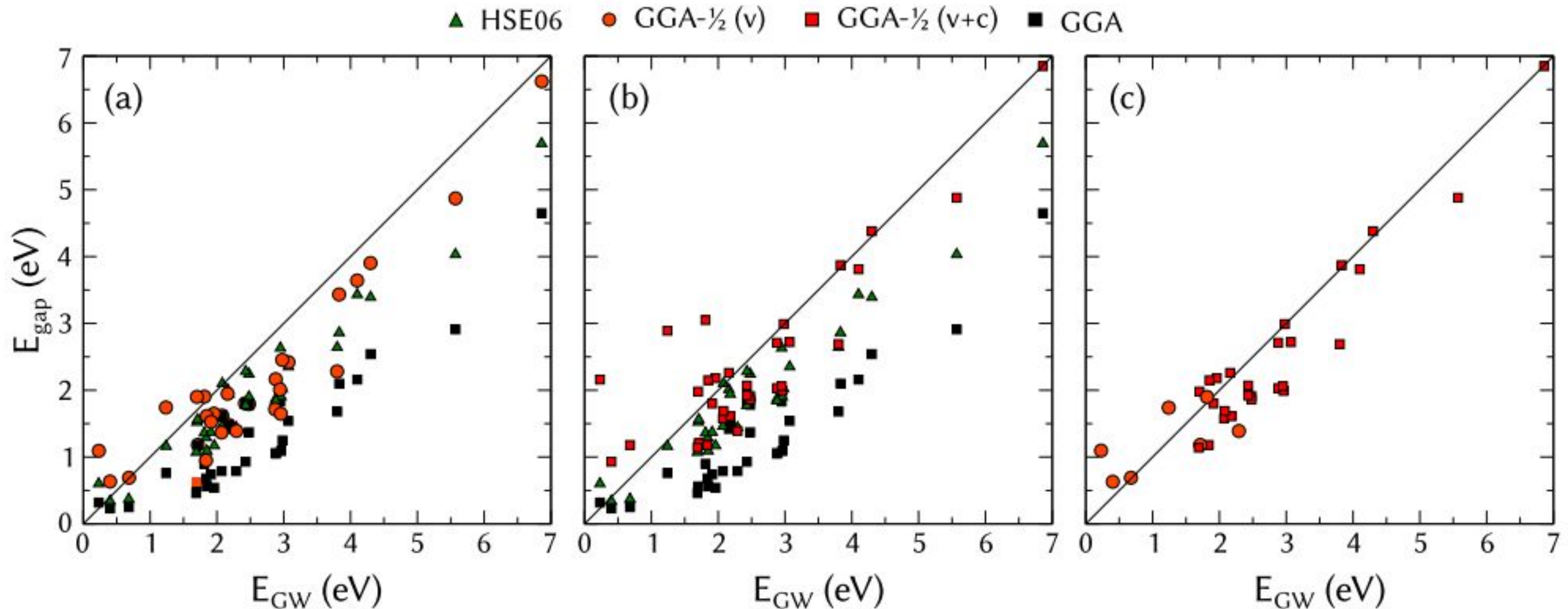
(Received 29 November 2017; published 24 January 2018)



+22 other materials

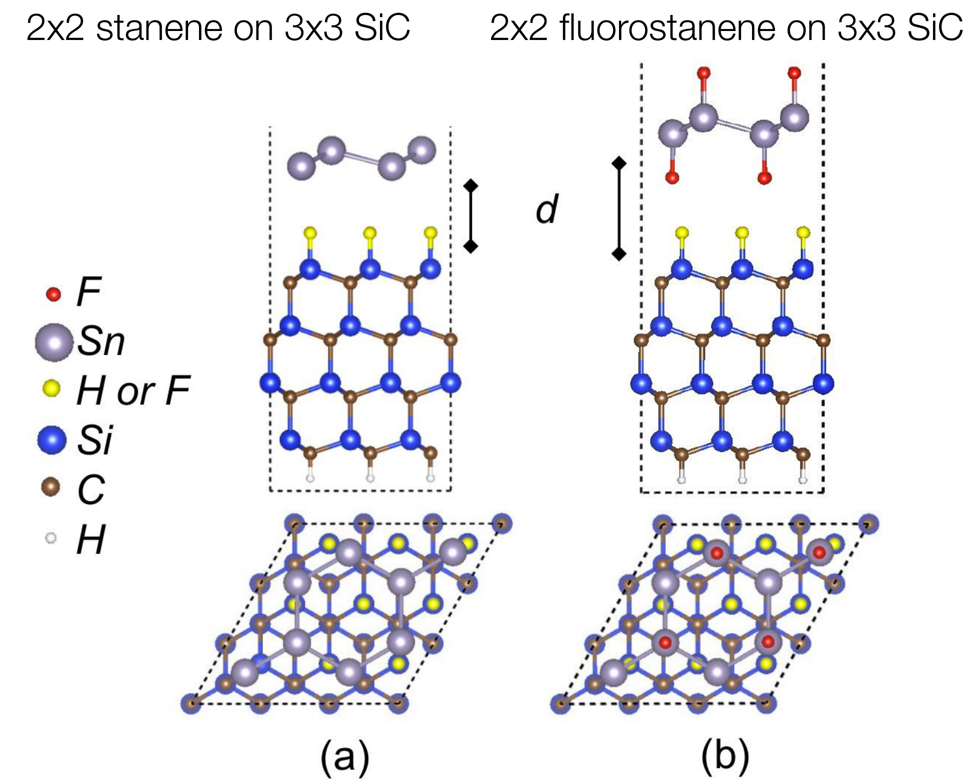
DFT-½ Method on 2D Materials

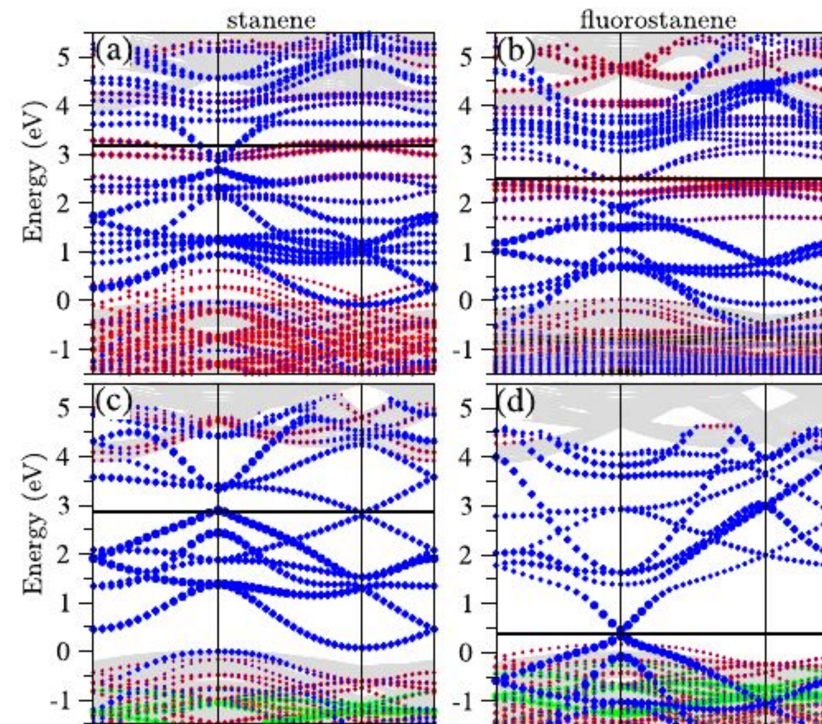
I. Guilhon et al., Rhys Rev B 97, 045426 (2018).

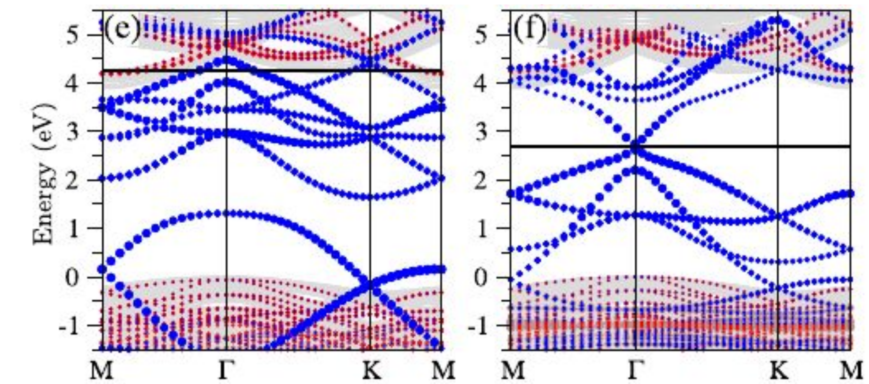


- The DFT-½ methods achives energy gaps comparable with HSE06 and GW approaches for most of materials in the test set.

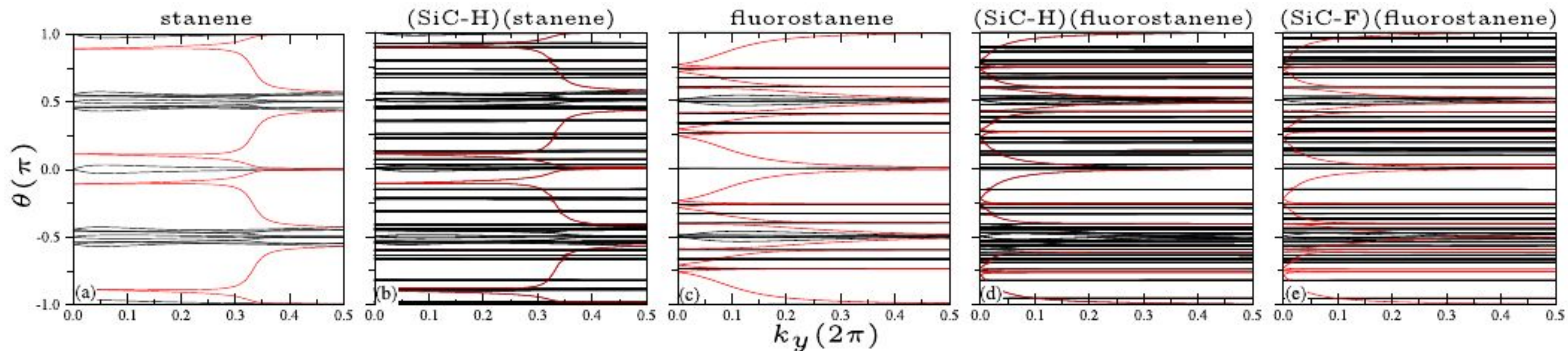
Deposition of (F-) stanene on 4H-SiC(0001) passivated or not with H- or F-







F. Matusalem et al., PHYSICAL REVIEW B 94, 241403(R) (2016)



Aplicações do método DFT-½

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Casos patológicos

Nestes artigos são reportados alguns casos patológicos do método:

Approximate quasiparticle correction for calculations of the energy gap in two-dimensional materials

I. Guilhon,[1,*] D. S. Koda,[1,†] L. G. Ferreira,[2] M. Marques,[1,‡] and L. K. Teles[1,§]
[1]*Grupo de Materiais Semicondutores e Nanotecnologia, Instituto Tecnológico de Aeronáutica, DCTA, 12228-900 São José dos Campos, Brazil*
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(Received 29 November 2017; published 24 January 2018)

At the same time that two-dimensional (2D) systems open possibilities for new physics and applications, they present a higher challenge for electronic structure calculations, especially concerning excitations. The achievement of a fast and accurate practical model that incorporates approximate quasiparticle corrections can further open an avenue for more reliable band structure calculations of complex systems such as interactions of 2D materials with substrates or molecules, as well as the formation of van der Waals heterostructures. In this work, we demonstrate that the performance of the fast and parameter-free DFT-1/2 method is comparable with state-of-the-art *GW* and superior to the HSE06 hybrid functional in the majority set of the 34 different 2D materials studied. Moreover, based on the knowledge of the method and chemical information of the material, we can predict the small number of cases in which the method is not so effective and also provide the best recipe for an optimized DFT-1/2 method based on the electronegativity difference of the bonding atoms.

Limitations of the DFT–1/2 method for covalent semiconductors and transition-metal oxides

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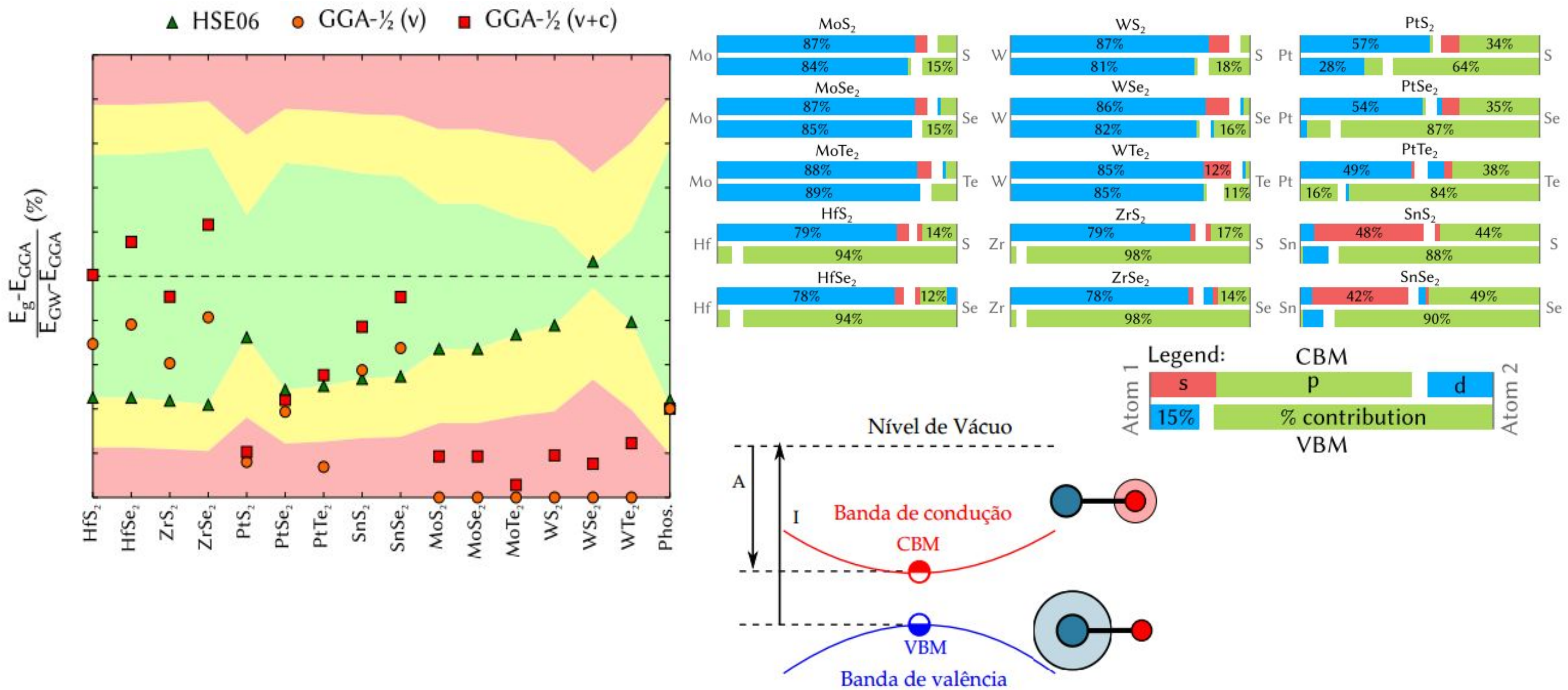
(Dated: January 16, 2019)

The DFT–1/2 method in density functional theory [L. G. Ferreira *et al.*, Phys. Rev. B **78**, 125116 (2008)] aims to provide accurate band gaps at the computational cost of semilocal calculations. The method has shown promise in a large number of cases, however some of its limitations or ambiguities on how to apply it to covalent semiconductors have been pointed out recently [K.-H. Xue *et al.*, Comput. Mater. Science **153**, 493 (2018)]. In this work, we investigate in detail some of the problems of the DFT–1/2 method with a focus on two classes of materials: covalently bonded semiconductors and transition-metal oxides. We argue for caution in the application of DFT–1/2 to these materials, and the condition to get an improved band gap is a spatial separation of the orbitals at the valence band maximum and conduction band minimum.

Limitações do método DFT-½

- A aproximação atômica do potencial de autoenergia $V_s(r)$ depende da correção independente dos estados de valência e condução.



Obrigado!

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Teorema de Koopmans

- Relaciona a energia de ionização de um sistema

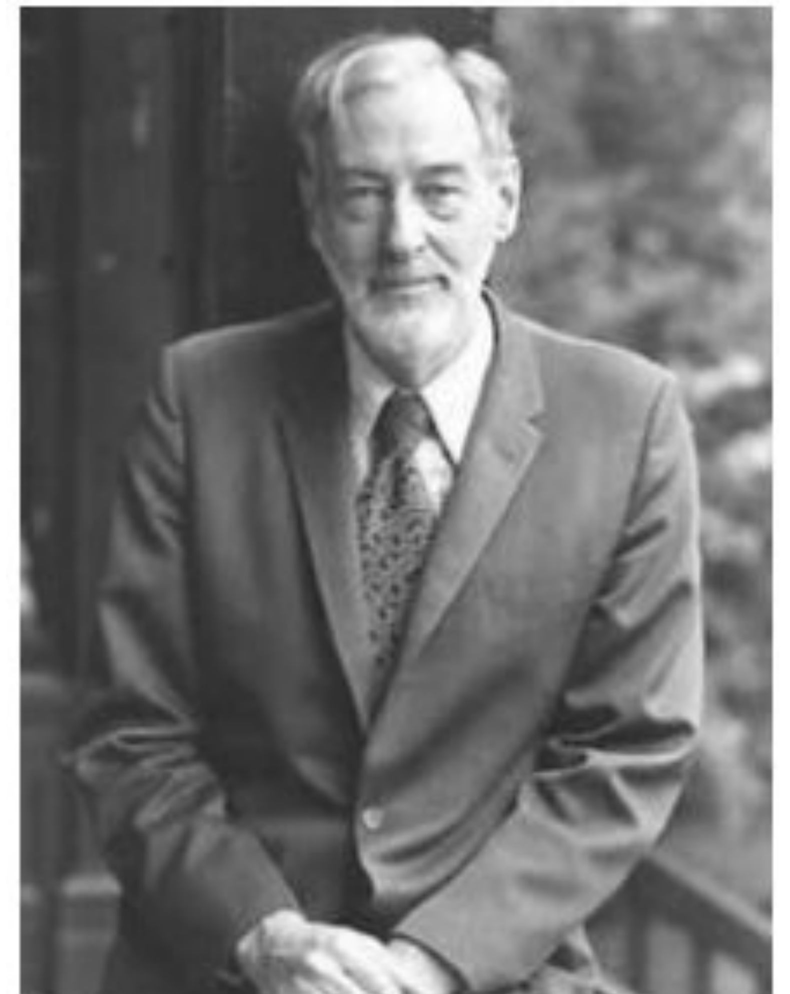
$$I = E(N-1) - E(N)$$

com o último valor de autoenergia ocupado;

- Formulado originalmente dentro da teoria HF;

- É possível ser reformulado no esquema de Kohn-Sham.

Tjalling Charles Koopmans
- **Prêmio Nobel de Economia**



Teorema de Koopmans: caso HF

- No método HF, a função de onda é aproximada pelo determinante de Slater

$$\Psi^{N}(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1, \sigma_1) & \phi_2(\mathbf{r}_1, \sigma_1) & \cdots & \phi_N(\mathbf{r}_1, \sigma_1) \\ \phi_1(\mathbf{r}_2, \sigma_2) & \phi_2(\mathbf{r}_2, \sigma_2) & \cdots & \phi_N(\mathbf{r}_2, \sigma_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N\sigma_N) & \phi_2(\mathbf{r}_N, \sigma_N) & \cdots & \phi_N(\mathbf{r}_N, \sigma_N) \end{vmatrix}$$

- A energia total do sistema de N partículas é dada por

$$E(N) = \langle \Psi^{N} | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Psi^{N} \rangle$$

Teorema de Koopmans: caso HF

- Para um sistema de N-1 corpos, seria preciso calcular um novo determinante de Slater com novos orbitais;
- Vamos desprezar esse efeito e supor que os demais orbitais não se alteram quando 1 elétron é removido, isto é:

$$\overset{N-1}{\Psi}(\vec{r}_1\sigma_1, \ldots, \vec{r}_{N-1}\sigma_{N-1}) =$$

$$= \frac{1}{\sqrt{(N-1)!}} \begin{vmatrix} \phi_1(\vec{r}_1, \sigma_1) & \phi_2(\vec{r}_1, \sigma_1) & \cdots & \phi_{N-1}(\vec{r}_1, \\ \phi_1(\vec{r}_2, \sigma_2) & \phi_2(\vec{r}_2, \sigma_2) & \cdots & \phi_{N-1}(\vec{r}_2, \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\vec{r}_{N-1}\sigma_{N-1}) & \phi_2(\vec{r}_{N-1}, \sigma_{N-1}) & \cdots & \phi_{N-1}(\vec{r}_{N-1} \end{vmatrix}$$

Sendo os orbitais $\phi_1, \phi_2, \ldots \phi_{N-1}$

os mesmos do cálculo anterior

Teorema de Koopmans: caso HF

- Dessa maneira, temos que $\begin{cases} E(N) = \langle \Psi^N | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Psi^N \rangle \\ E(N-1) = \langle \Psi^{N-1} | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Psi^{N-1} \rangle \end{cases}$

- Após o desenvolvimento das expressões acima, demonstra-se que

$$E(N) - E(N-1) = \epsilon_N$$

$$\boxed{I = E(N-1) - E(N) = -\epsilon_N}$$

- Observe que o resultado é considera a aproximação de não relaxação dos orbitais ϕ_i, i=1,2,3, …, N-1.
  - O resultado é aproximado.

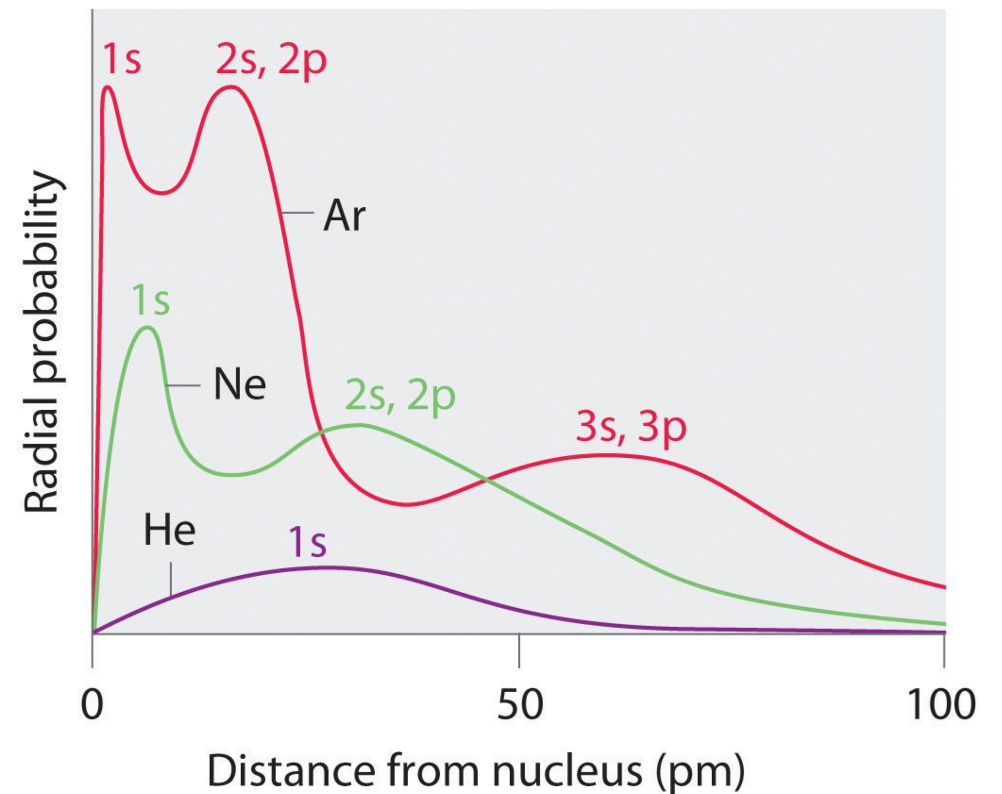
Teorema de Koopmans: caso KS

- A demonstração do teorema para o caso KS é baseada no seguinte resultado:

"Para pontos afastados de um sistema eletrônico finito, a densidade eletrônica assume a forma assintótica

$$n(\mathbf{r}) = Ae^{-2\alpha r} \text{"}$$

$$\alpha = \sqrt{2I}$$



Teorema de Koopmans: caso KS

- Para entender esse resultado, considere o problema exato de N elétrons

$$\left(\hat{T} + \hat{V}_{ext} + \hat{V}_{ee}\right) \Psi^N(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) = E(N)\Psi^N(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

- Tomando o limite r -> ∞, o elétron afastado não sofre repulsão eletrônica e se desacopla com os demais, i.e.,

$$\Psi^N(\mathbf{r}, \vec{r}_2, \dots, \mathbf{r}_N) = \phi(\mathbf{r})\Psi^{N-1}(\mathbf{r}_2, \dots, \mathbf{r}_N)$$

- Dessa maneira, o problema é dividido em duas partes

$$\left(\hat{T} + \hat{V}_{ext} + \hat{V}_{ee}\right) \Psi^{N-1}(\mathbf{r}_2, \dots, \mathbf{r}_N) = E(N-1)\Psi^{N-1}(\mathbf{r}_2, \dots, \mathbf{r}_N)$$

$$\left(-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r})\right) \phi(\mathbf{r}) = \varepsilon\phi(\mathbf{r}) \quad \text{com} \quad E(N) = E(N-1) + \varepsilon$$

Teorema de Koopmans: caso KS

- Considerando um potencial eletrostático Z_{ef}/r sobre o último elétron

$$\left(-\frac{\nabla^2}{2} + \frac{Z}{r}\right)\phi(\mathbf{r}) = \varepsilon\phi(\mathbf{r})$$

cujo autovalor de energia corresponde a

$$\phi(\mathbf{r}) = Ae^{-Zr}$$

$$\varepsilon = E(N) - E(N-1) = -I = -\frac{Z^2}{2}$$

$$\phi(\mathbf{r}) = Ae^{-\sqrt{2I}r}$$

Teorema de Koopmans: caso KS

- Assim, a densidade de pontos afastados da origem é

$$n(\mathbf{r}) = N \int d^3r_2 \ldots d^3r_N |\Psi^N(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2$$

$$n(\mathbf{r}) = N|\phi(\mathbf{r})|^2 = N|A|^2 e^{-2\sqrt{2I}r}$$

- O sistema KS tem a mesma densidade de carga que o sistema real, logo tem a mesmo comportamento assintótico

$$I = E(N-1) - E(N) = -\epsilon_N$$