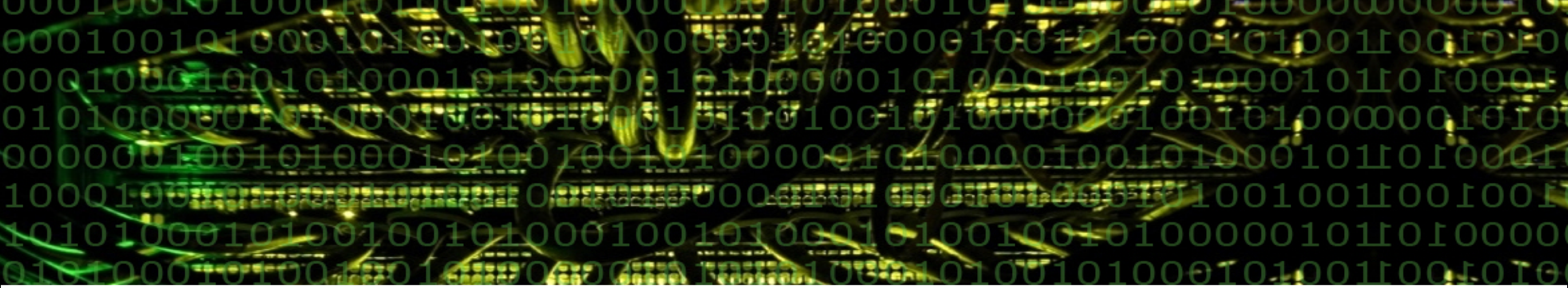

Introduction to DFT and Density Functionals

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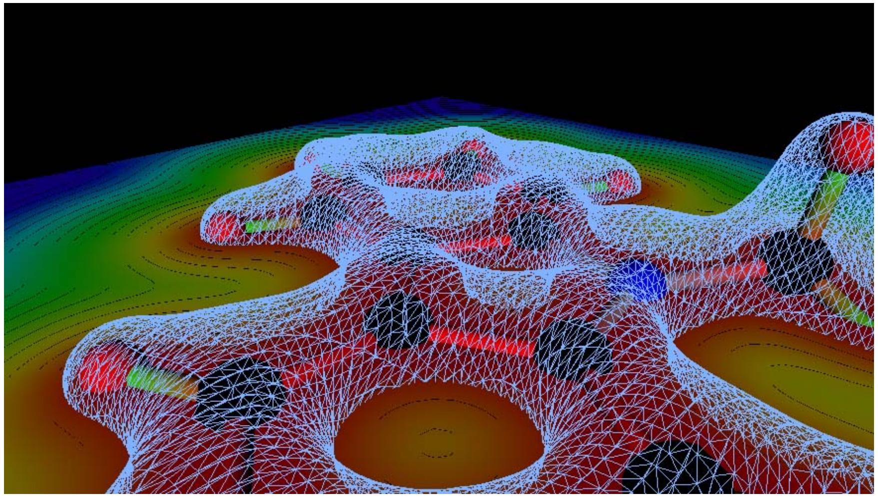
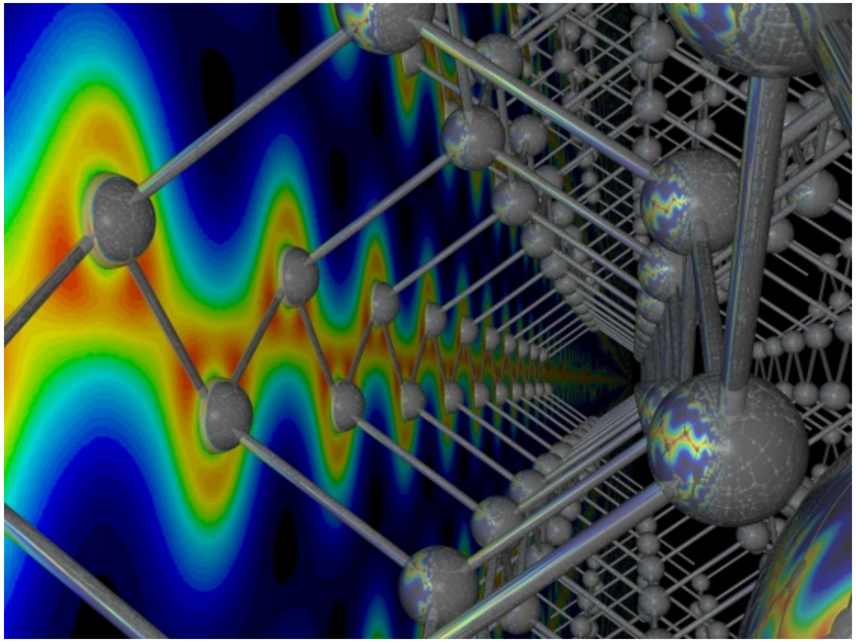
Examples

Carbazole molecule



Réf: Jean-François Brière (http://www.phys.umontreal.ca/~michel_cote/Images_Scientifiques/images.shtml)

Inside of diamant



Réf: Mike Towler (http://www.tcm.phy.cam.ac.uk/~mdt26/)

Condensed Matter

Schrödinger's equation:

$$i\hbar \frac{\partial}{\partial t}\left|\Psi\right\rangle = H\left|\Psi\right\rangle$$

Hamiltonian for electrons and atoms with coulomb interaction:

$$H = -\sum_{j}^{Ne} \frac{\hbar^2}{2m}\nabla_j^2 - \sum_{\alpha}^{Ni} \frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2$$

$$-\sum_{j}^{Ne}\sum_{\alpha}^{Ni}\frac{Z_\alpha e^2}{\left|r_j - R_\alpha\right|} + \sum_{j<k}^{Ne}\frac{e^2}{\left|r_j - r_k\right|} + \sum_{\alpha<\beta}^{Ni}\frac{Z_\alpha Z_\beta e^2}{\left|R_\alpha - R_\beta\right|}$$

Electrons

Using the Born-Oppenheimer approximation:

$$H\Psi = \underbrace{\frac{-\hbar^2}{2m}\sum_{l=1}^{N}\nabla_l^2\Psi}_{\text{Kinetic energy}} + \underbrace{\sum_{l=1}^{N}U_{\text{ion}}(\vec{r}_l)\Psi}_{\text{Potential energy}} + \underbrace{\tfrac{1}{2}\sum_{l,l'=1}^{N}\frac{e^2}{\left|\vec{r}_l - \vec{r}_{l'}\right|}\Psi}_{\text{Interaction energy}} = E\Psi$$

We are looking for a solution of the type of a wave function for many electrons:

$$\Psi(x_1, x_2, \ldots, x_N)$$

The problem is easy to write down …but the solution …

Electrons system

$$\Psi(x_1, x_2, \ldots, x_N)$$

Storage required:

$$x \rightarrow 10 \times 10 \times 10 = 1000 \text{ data}$$

$$10 \text{ electrons} \rightarrow 1000^{10} \text{ data} \rightarrow 10^{30} \times 16 \text{ bytes}$$

$$= 16 \times 10^{21} \text{ Gb}$$

Impracticable!!!

Dirac’s quote (1929)

« The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble »

Réf: *Quantum mechanics of many-electron systems*, Proceedings of the Royal Society of London, pp.714. (1929)

Dirac’s quote (1929)

« It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation. »

Réf: *Quantum mechanics of many-electron systems*, Proceedings of the Royal Society of London, pp.714. (1929)

Wavefunction approach: Hartree method

$$\Psi(x_1, x_2, \ldots, x_N) = \phi_1(x_1)\phi_2(x_2)\cdots\phi_N(x_N) = \prod_{l=1}^{N} \phi_l(x_l)$$

$$n(x) = \sum_{l=1}^{N} \phi_l^*(x)\phi_l(x)$$

Lagrange multipliers to assure that the φ_l remain orthogonal

$$E = \langle \Psi | H | \Psi \rangle - \sum_{l=1}^{N} \lambda_l \langle \phi_l | \phi_l \rangle$$

$$\frac{\partial E}{\partial \phi_l^*(x)} = \left[\frac{-\hbar^2}{2m} \nabla^2 + U_{\text{ion}}(x) + e^2 \int dx' \frac{n(x')}{|x - x'|} \right] \phi_l(x) - \lambda_l \phi_l(x) = 0$$

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + U_{\text{ion}}(x) + V_H(x) \right] \phi_l(x) = \lambda_l \phi_l(x)$$

Same equation for all φ_l

Hartree-Fock method

$$\Psi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \prod_{l=l}^{N} \phi_{Pl}(x_l) = \Phi_0(x_1, x_2, \ldots, x_N)$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{vmatrix}$$

Slater determinant

Particules are not independant, change the position of one and all the others are affected.

Pauli exclusion principle is respected.

Hartree-Fock method

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + U_{\text{ion}}(x) + V_H(x)\right]\phi_l(x)$$

$$\underbrace{-\sum_{j=1}^{N}\delta_{ss'}\phi_j(x)\int dx'\,\frac{\phi_j^*(x')\phi_l(x')}{|x-x'|}}_{\text{Exchange energy}} = \lambda_l\phi_l(x)$$

Because of the exchange term, the problem is much harder to resolve.

Results are better than those of the Hartree method but still not very satisfying.

Configuration Interaction method

$$\Psi(x_1, x_2, \ldots, x_N) = \sum_i C_i \Phi_i(x_1, x_2, \ldots, x_N)$$

Sum of Slater determinants
(configurations)

Must find the coefficients C_i

CI = configuration interaction

CIS = CI with single excitations only

CISD = CI with single and double excitations only

Correlation energy: contribution over that of Hartree-Fock

Wavefunction methods

Advantages:

- Control approximations
- Systematic approach (H, HF, CIS, …)
- Upper bound (variational principle)

Disadvantages:

- Very costly numerically

  (up to 20-30 electrons, forget solids!)

Progress in theoretical methods

John A. Pople

Nobel Prize 1998 in Chemistry:

"for his development of computational methods in quantum chemistry”

Walter Kohn

"for his development of the density-functional theory”

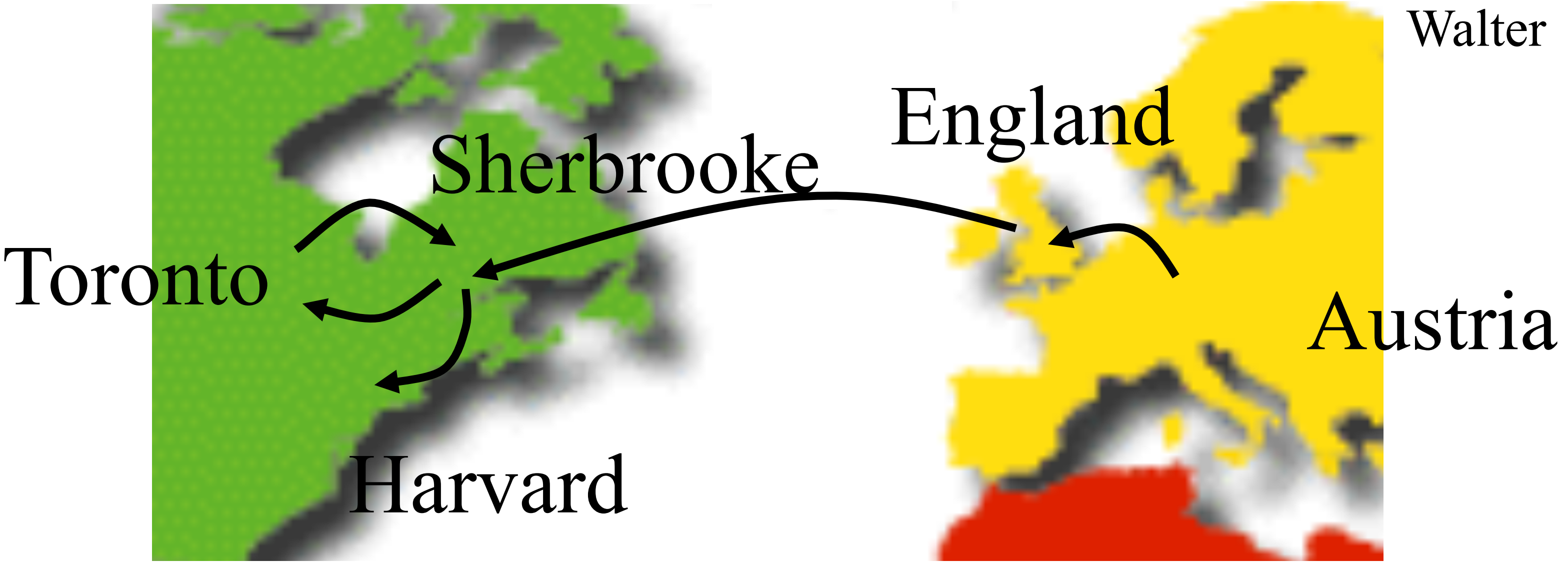
- efficient
- flexible
- precise
- parameter free

Walter Kohn and Canada

Nobel Prize in 1998 for Chemistry:
Development of *ab initio* methods

Density Functional Theory (WK)
(efficient, flexible, precise, parameters free)

Walter Kohn



England
Sherbrooke
Toronto
Austria
Harvard

Walter Kohn died April 16, 2016.

Milestones : first-principles approach

Precursor : Thomas-Fermi approximation (1927)

Inhomogeneous electron gas
P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)
Self-consistent equations including exchange and correlation effects
W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965)

Ceperley, Alder (1980); Perdew, Zunger (1981) : computation and parametrization of the exchange and correlation energy needed in the local density approximation

Most cited papers

Papers published in APS journals (PRL, PRA, PRB, .. RMP),
most cited by papers published in APS journals

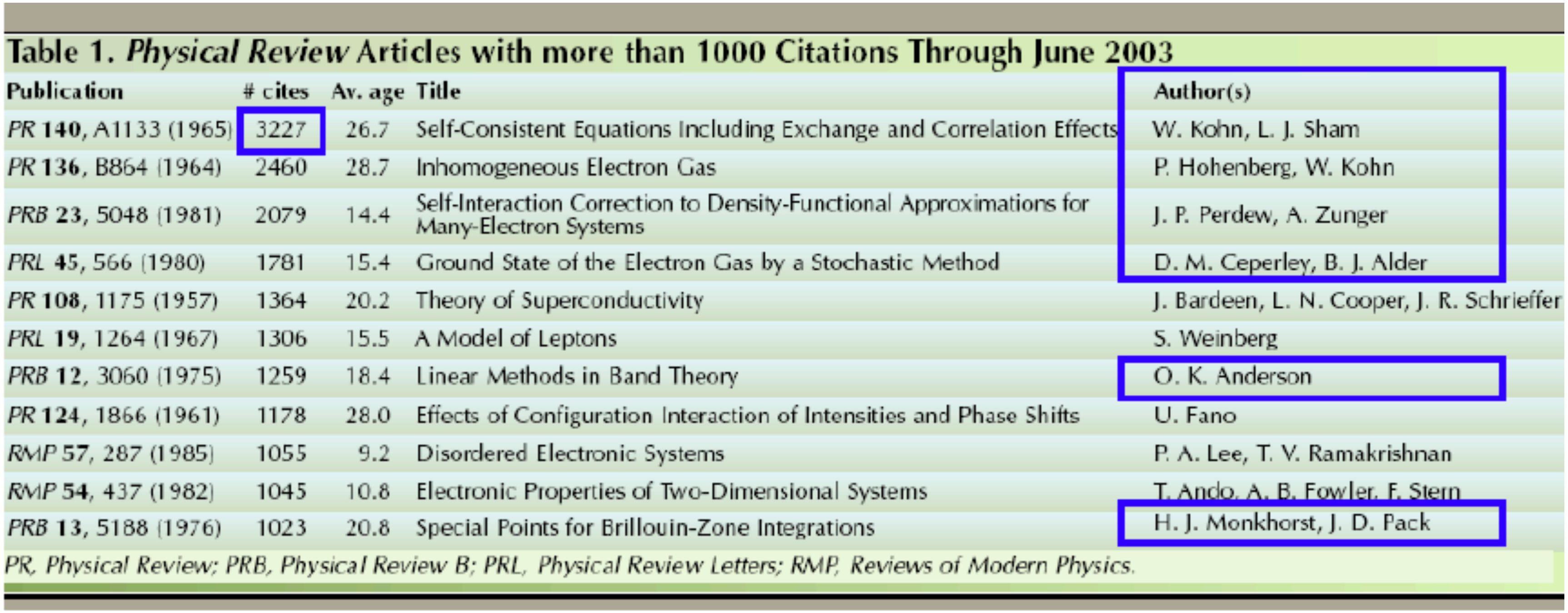


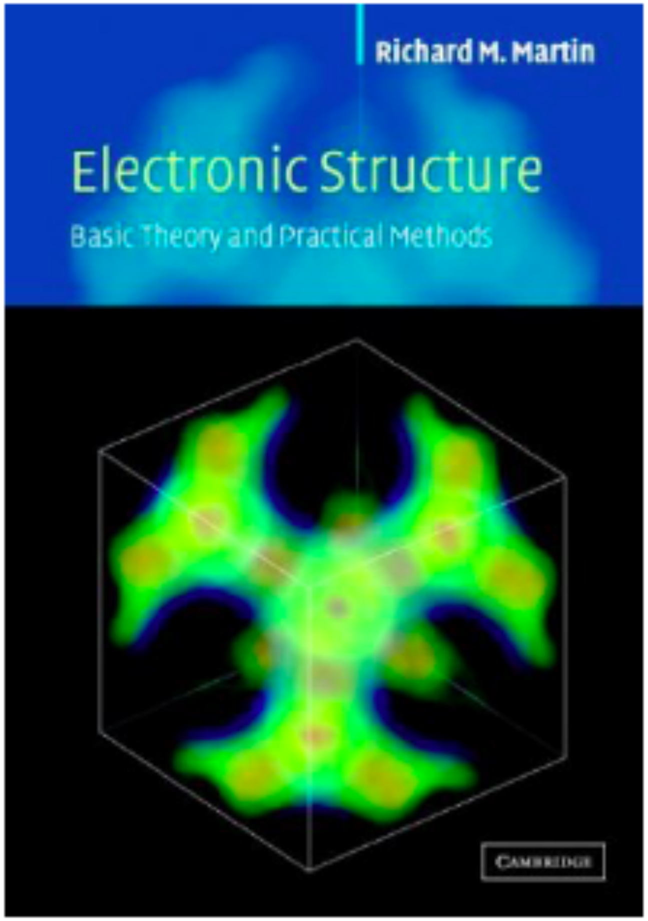
Table 1. ***Physical Review*** **Articles with more than 1000 Citations Through June 2003**

Publication	# cites	Av. age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL **45**, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR **108**, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL **19**, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB **12**, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR **124**, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP **57**, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP **54**, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB **13**, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

S. Redner, *Citation Statistics from 110 Years of Physical Review*, Physics Today, June 2005.
Today, according to Google Scholar: K&S, 40k; H&K, 35k; PBE functional, 60k !

A basic reference on DFT and applications to solids



Richard M. Martin

Cambridge University Press, 2004

Electronic Structure : Basic Theory and Practical Methods

(ISBN: 0521782856)

For details, see

http : //www.cambridge.org/uk/catalogue/catalogue.asp?isbn=0521782856

Functionals of the density

What is a functional?

It is a quantity that depends non on a variable but on a function.

$$f(x) = Ax^2$$ function

$$f[n] = \int n(x)v(x)dx$$ functionnal

Derivative

$$\frac{\partial f(x)}{\partial x} = \lim_{\alpha \to 0} \frac{f(x+\alpha) - f(x)}{\alpha}$$

$$\frac{\partial f[n]}{\partial n(x)} = \lim_{\alpha \to 0} \frac{f[n(x') + \alpha\delta(x'-x)] - f[n(x')]}{\alpha}$$

function of x

Density functional theory:
First Hononberg-Kohn theorem

Honenberg et Kohn, Physical Review, vol 136, B864, (1964)

Assume:
$$V(r) \to \Psi \to n(r)$$
$$V'(r) \to \Psi' \to n(r)$$

$$E' = \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle = \langle \Psi | H - V(r) + V'(r) | \Psi \rangle$$

$$E' < E + \int [V'(r) - V(r)] n(r) dr$$

Samething but starting from *E:*

$$E < E' + \int [V(r) - V'(r)] n(r) dr$$

Combine:

$$E' + E < E' + E$$ Contradiction!!!

$$n(r) \leftrightarrow V(r) \leftrightarrow \Psi$$

First Hohenberg-Kohn theorem

The <u>ground state</u> density n(**r**) of a many-electron system determines uniquely the external potential V(**r**), modulo one global constant.

Consequence : **formally**, the density can be considered as the fundamental variable of the formalism, instead of the potential.

$$\begin{tikzcd}
V_{ext}(\mathbf{r}) \arrow[d, Rightarrow] \arrow[r, Leftarrow, "\mathrm{HK}"] & n_0(\mathbf{r}) \\
\Psi_i(\{\mathbf{r}\}) \arrow[r, Rightarrow] & \Psi_0(\{\mathbf{r}\}) \arrow[u, Rightarrow]
\end{tikzcd}$$

No need for wavefunctions or Schrödinger equation !

The constrained-search approach to DFT

M. Levy, Proc. Nat. Acad. Sci. USA, 76, 6062 (1979)

Use the extremal principle of QM.

$$E_{\mathrm{V}} = \min_{\Psi}\left\{\langle\Psi|\hat{H}_{\mathrm{V}}|\Psi\rangle\right\} = \min_{n}\left\{\min_{\Psi\to n}\left\{\langle\Psi|\hat{H}_{\mathrm{V}}|\Psi\rangle\right\}\right\}$$

$$= \min_{n}\left\{\min_{\Psi\to n}\left\{\langle\Psi|\hat{T}+\hat{V}_{\mathrm{int}}+\hat{V}|\Psi\rangle\right\}\right\}$$

$$= \min_{n}\left\{\min_{\Psi\to n}\left\{\langle\Psi|\hat{T}+\hat{V}_{\mathrm{int}}|\Psi\rangle+\int n(\mathbf{r})V(\mathbf{r})d\mathbf{r}\right\}\right\}$$

$$= \min_{n}\left\{F[n]+\int n(\mathbf{r})V(\mathbf{r})d\mathbf{r}\right\} = \min_{n}\left\{E_{V}[n]\right\}$$

where $F[n] = \min_{\Psi\to n}\left\{\langle\Psi|\hat{T}+\hat{V}_{\mathrm{int}}|\Psi\rangle\right\}$ is a universal functional of the density ...

Not known explicitely !

The Kohn & Sham approach

The exchange-correlation energy

$F[n]$: large part of the total energy, hard to approximate

Kohn & Sham (Phys. Rev. **140**, A1133 (1965)) :
mapping of the interacting system on a non-interacting system

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

If one considers a non-interacting electronic system :

$$T_s[n] = \min_{\Psi \to n} \left\{ \langle \Psi | \hat{T} | \Psi \rangle \right\}$$

Kinetic energy functional of the density

Exchange-correlation functional of the density :

$$E_{xc}[n] = F[n] - T_s[n] - \frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

Not known explicitely !
But let’s suppose
we know it

The Kohn-Sham potential

So, we have to minimize: (under constraint of total electron number)

$$E_V\left[n\right] = T_s\left[n\right] + \int V(\mathbf{r})n(\mathbf{r})\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + E_{\mathrm{xc}}\left[n\right]$$

Introduction of Lagrange multipliers

$$0 = \delta\left(E_V\left[n\right] - \lambda\left\{\int n(\mathbf{r})\mathrm{d}\mathbf{r} - \mathbf{N}\right\}\right) = \int\left(\frac{\delta T_s\left[n\right]}{\delta n} + V(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{\left|\mathbf{r}_1 - \mathbf{r}\right|}\mathrm{d}\mathbf{r}_1 + \frac{\delta E_{\mathrm{xc}}\left[n\right]}{\delta n(\mathbf{r})} - \lambda\right)\delta n(\mathbf{r})\mathrm{d}\mathbf{r}$$

If one considers the minimization for non-interacting electrons in a potential $V_{\mathrm{KS}}(\mathbf{r})$, with the same density $n(\mathbf{r})$, one gets

$$0 = \int\left(\frac{\delta T_s\left[n\right]}{\delta n} + V_{\mathrm{KS}}(\mathbf{r}) - \lambda\right)\delta n(\mathbf{r})\mathrm{d}\mathbf{r}$$

Identification :

$$V_{\mathrm{KS}}(\mathbf{r}) = V(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{\left|\mathbf{r}_1 - \mathbf{r}\right|}\mathrm{d}\mathbf{r}_1 + \frac{\delta E_{\mathrm{xc}}\left[n\right]}{\delta n(\mathbf{r})}$$

The Kohn-Sham potential

The Kohn-Sham orbitals and eigenvalues

Non-interacting electrons in the Kohn-Sham potential :

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\,\psi_i(\mathbf{r})$$

Density $n(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$

$$V_{\mathrm{KS}}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \boxed{\int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|}\mathrm{d}\mathbf{r}_1} + \boxed{\frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}}$$

Hartree potential Exchange-correlation potential

To be solved self-consistently !

Note : by construction, at self-consistency, and supposing the exchange-correlation functional to be exact, the density will be the exact density, the total energy will be the exact one, but Kohn-Sham wavefunctions and eigenenergies correspond to a fictitious set of independent electrons, so they do not correspond to any exact quantity.

Minimum principle for the energy

Using the variational principle for non-interacting electrons, one can show that the solution of the Kohn-Sham self-consistent system of equations is equivalent to the minimisation of

$$E_{\mathrm{KS}}\left[\left\{\psi_i\right\}\right] = \sum_i \left\langle \psi_i \right| -\frac{1}{2}\nabla^2 \left| \psi_i \right\rangle + \int V_{ext}(\mathbf{r})n(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\,\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + E_{\mathrm{xc}}\left[n\right]$$

under constraints of orthonormalization $\left\langle \psi_i \middle| \psi_j \right\rangle = \delta_{ij}$

for the occupied orbitals.

Density Functional Theory : approximations

An exact result for the exchange-correlation energy

(without demonstration)

The exchange-correlation energy, functional of the density is the integral over the whole space of the density times the local exchange-correlation energy per particle

$$E_{\mathrm{xc}}\left[n\right] = \int n(\mathbf{r}_1)\varepsilon_{xc}(\mathbf{r}_1;n)\,\mathrm{d}\mathbf{r}_1$$

while the local exchange-correlation energy per particle is the electrostatic interaction energy of a particle with its DFT exchange-correlation hole.

$$\varepsilon_{xc}(\mathbf{r}_1;n) = \int \frac{1}{2}\frac{\overline{n^{xc}}(\mathbf{r}_2|\mathbf{r}_1;n)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,\mathrm{d}\mathbf{r}_2$$

Sum rule : $\int \overline{n^{xc}}(\mathbf{r}_2|\mathbf{r}_1;n)\,\mathrm{d}\mathbf{r}_2 = -1$

The local density approximation (I)

Hypothesis :

- the local XC energy per particle only depend on the local density
- and is equal to the local XC energy per particle of an homogeneous electron gas of same density (in a neutralizing background - « jellium »)

$$\varepsilon_{xc}^{LDA}(\mathbf{r}_1; n) = \varepsilon_{xc}^{hom}(\, n(\mathbf{r}_1)\,)$$

Gives excellent numerical results ! Why ?

1) Sum rule is fulfilled

2) Characteristic screening length indeed depend on local density

The local density approximation (II)

Actual function : exchange part (x) + correlation part (c)

$$\varepsilon_x^{\mathrm{hom}}(n) = Cn^{1/3} \qquad \text{with} \qquad C = -\frac{3}{4\pi}\left(3\pi^2\right)^{1/3}$$

for the correlation part, one resorts to accurate numerical simulations beyond DFT (e.g. Quantum Monte Carlo)

Corresponding exchange-correlation potential $V_{\mathrm{xc}}(\mathbf{r}) = \dfrac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}$

$$V_{\mathrm{xc}}^{\mathrm{approx}}(\mathbf{r}) = \mu_{\mathrm{xc}}\big(n(\mathbf{r})\big) \qquad \mu_{xc}(n) = \frac{\mathrm{d}\left(n\varepsilon_{xc}^{approx}(n)\right)}{\mathrm{d}n}$$

$$\mu_x(n) = C\frac{4}{3}n^{1/3} = \frac{4}{3}\varepsilon_x^{\mathrm{hom}}(n)$$

The local density approximation (III)

To summarize :

$$E^{LDA}\left[n\right] = T_s\left[n\right] + \int V_{ext}(\mathbf{r})n(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + E_{xc}^{LDA}\left[n\right]$$

or

$$E^{LDA}\left[\left\{\psi_i\right\}\right] = \sum_i \left\langle \psi_i \right| -\frac{1}{2}\nabla^2 \left|\psi_i\right\rangle + \int V_{ext}(\mathbf{r})n(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

$$+ \int n(\mathbf{r}_1)\varepsilon_{xc}^{LDA}(n(\mathbf{r}_1))\,\mathrm{d}\mathbf{r}_1$$

and

$$V_{\mathrm{KS}}^{LDA}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{\left|\mathbf{r}_1 - \mathbf{r}\right|}\mathrm{d}\mathbf{r}_1 + \mu_{xc}^{\mathrm{hom}}(n(\mathbf{r}))$$

Beyond the local density approximation

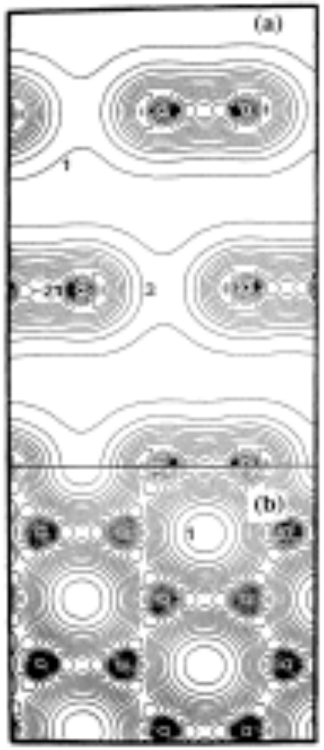
Generalized gradient approximations (GGA)

$$E_{\mathrm{xc}}^{\mathrm{approx}}\left[n\right] = \int n(\mathbf{r}_1)\varepsilon_{\mathrm{xc}}^{\mathrm{approx}}(n(\mathbf{r}_1),\left|\nabla n(\mathbf{r}_1)\right|,\nabla^2 n(\mathbf{r}_1))\,\mathrm{d}\mathbf{r}_1$$

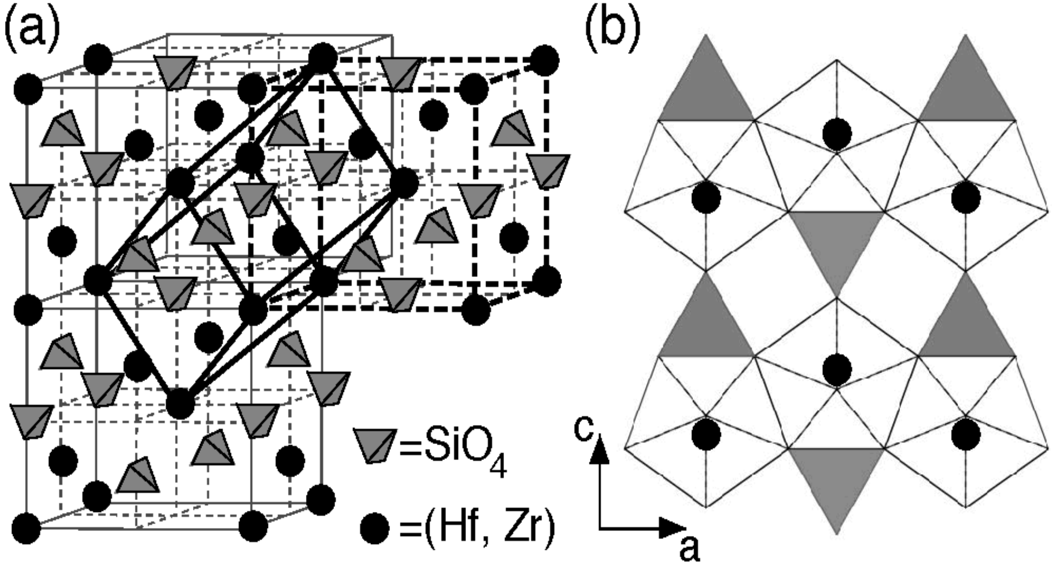
No model system like the homogeneous electron gas !
Many different proposals, including one from Perdew, Burke and Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996), often abbreviated « PBE ».
Others : PW86, PW91, LYP ...

Also : « hybrid » functionals (B3LYP),
« exact exchange » functional,
« self-interaction corrected » functionals ...

Example



Charge density of graphite



	$HfSiO_4$		$ZrSiO_4$	
	Th.	Expt.	Th.	Expt.
a	6.61	6.57	6.54	6.61
c	5.97	5.96	5.92	6.00
u	0.0672	0.0655	0.0645	0.0646
v	0.1964	0.1948	0.1945	0.1967
Volume	130.42	128.63	126.60	131.08
d(Si-O)	1.62	1.61	1.61	1.62
d(M-O)	2.14	2.10	2.10	2.13
	2.27	2.24	2.24	2.27
$\angle$(O-Si-O)	97°	97°	97°	97°
	116°	117°	116°	116°

Accuracy, typical usage.

If covalent bonds, metallic bonds, ionic bonds :

2-3% for the geometry (bond lengths, cell parameters)
0.2 eV for the bonding energies (GGA)
problem with the band gap

For weak bonding situations (Hydrogen bonding, van derWaals), worse

Treatment of a few thousand atoms is doable on powerful parallel computers
Up to 50-100 atoms is OK on a PC.

The band gap problem

The DFT bandgap problem (I)

- DFT is a ground state theory
  => no direct interpretation of Kohn-Sham eigenenergies ε_i in

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + V_{xc}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- However { ε_i } are similar to quasi-particle band structure :
  LDA / GGA results for valence bands are accurate ... but
  NOT for the band gap $E_g^{KS} = \varepsilon_c - \varepsilon_v$

- The band gap can alternatively be obtained from total energy differences

[correct expression !]

$$E_g = E(N+1) + E(N-1) - 2\,E(N) = \left\{E(N+1) - E(N)\right\} - \left\{E(N) - E(N-1)\right\}$$

in the limit N → ∞
(where E(N) is the total energy of the N - electron system)

The DFT bandgap problem (II)

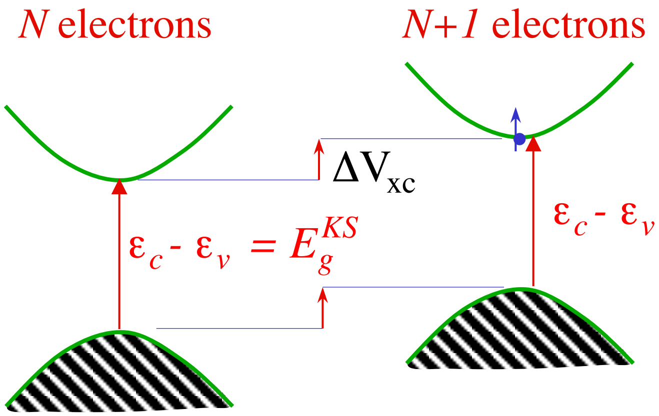
- For LDA & GGA, the *XC* potential is a continuous functional of the number of electrons

$$\varepsilon_i = \frac{\partial E}{\partial f_i} \qquad \textit{[Janak's theorem]}$$

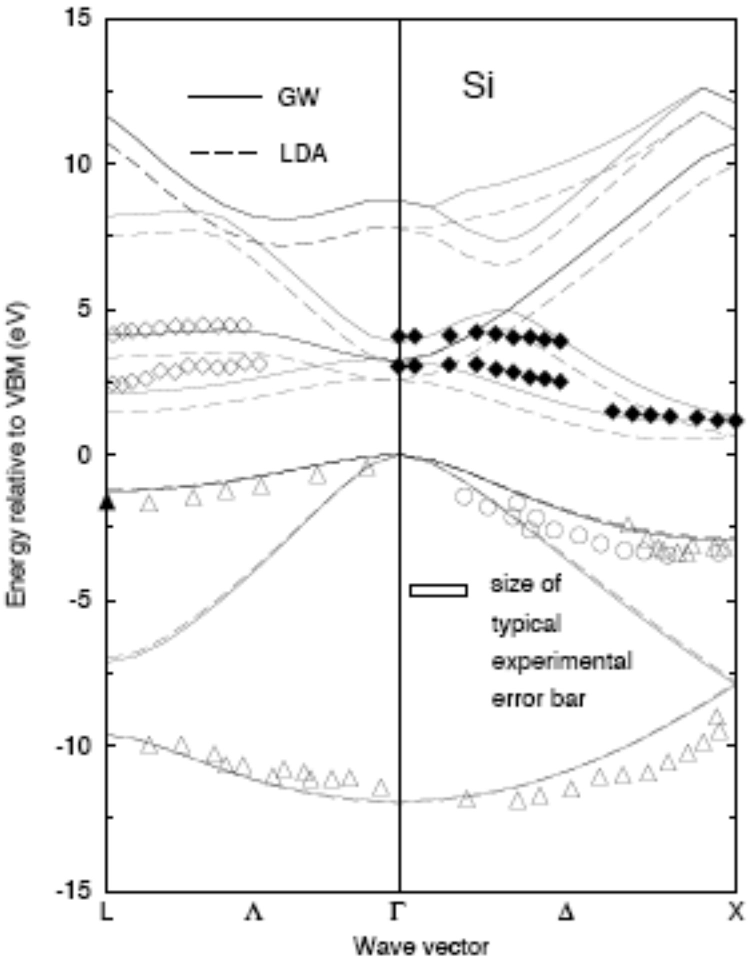
$$\Rightarrow \quad E_g^{KS} = \varepsilon_c - \varepsilon_v \underset{N\to\infty}{=} E_g = E(N+1) + E(N-1) - 2E(N)$$

- In general, the *XC* potential might be discontinuous with the number of particle

$$e.g. \quad xOEP \qquad\qquad E_g^{KS} \neq E_g$$



The DFT bandgap problem (III)



Comparison of LDA and GW band Structures with photoemission and Inverse photoemission experiments for Silicon.

From "Quasiparticle calculations in solids", by Aulbur WG, Jonsson L, Wilkins JW, in Solid State Physics 54, 1-218 (2000)

Accuracy:

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

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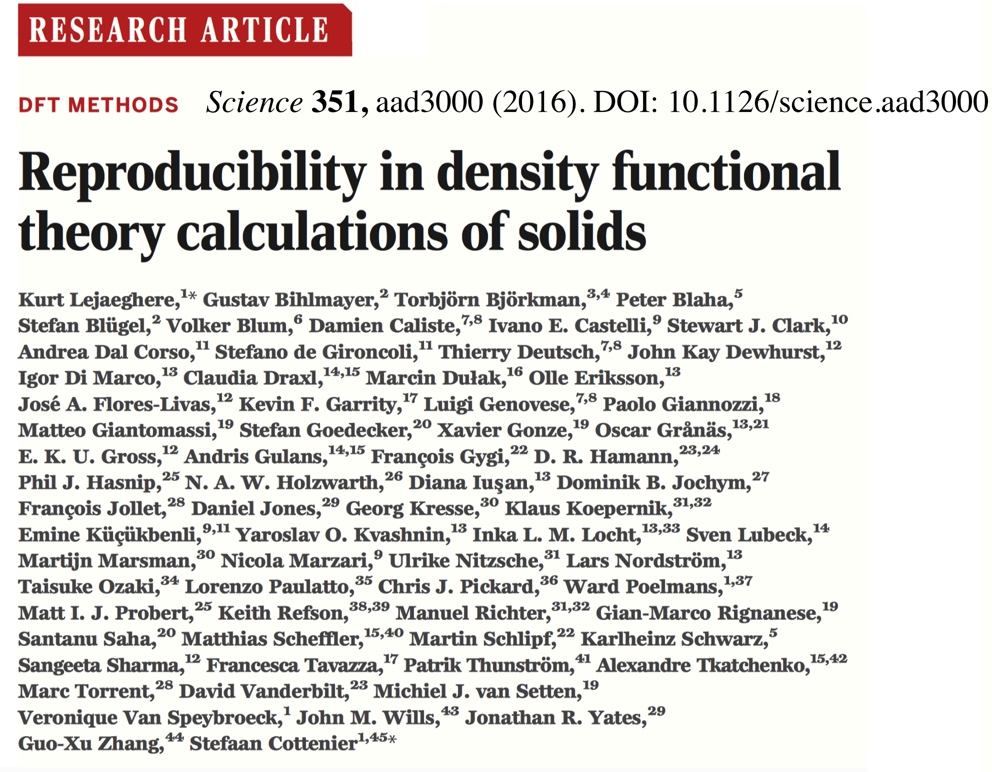
44 strongly and 5 weakly bound solids

TABLE II. The ME, MAE, MRE, MARE, and MAXRE on the testing set of 44 strongly bound solids for the lattice constant a_0, bulk modulus B_0, and cohesive energy E_{coh}. The units of the ME and MAE are Å, GPa, and eV/atom for a_0, B_0, and E_{coh}, respectively, and % for the MRE, MARE, and MAXRE. The solid for which the MAXRE occurs is indicated in parentheses. All results were obtained non-self-consistently using PBE orbitals/density. Within each group, the functionals are ordered by increasing value of the MARE of a_0. For hybrid functionals, the fraction α_x of HF exchange is indicated in parentheses.

	a_0					B_0					E_{coh}				
Functional	ME	MAE	MRE	MARE	MAXRE	ME	MAE	MRE	MARE	MAXRE	ME	MAE	MRE	MARE	MAXRE
LDA															
LDA[80]	−0.071	0.071	−1.5	1.5	−4.9 (Ba)	10.1	11.5	8.1	9.4	32.8 (Ni)	0.77	0.77	17.2	17.2	38.7 (Ni)
GGA															
SG4[60]	0.005	0.026	0.0	0.6	−1.9 (V)	1.7	7.9	−2.2	7.8	−25.9 (Rb)	0.19	0.28	3.5	7.0	19.5 (Ni)
WC[81]	0.002	0.029	0.0	0.6	−2.5 (Ba)	−0.2	7.6	−2.6	7.4	−23.8 (Rb)	0.22	0.26	4.2	6.2	20.1 (Ni)
SOGGA[82]	−0.012	0.027	−0.3	0.6	−2.3 (Ba)	4.1	8.9	0.6	7.4	23.6 (Ni)	0.39	0.41	8.8	9.2	26.8 (Ni)
PBEsol[83]	−0.005	0.030	−0.1	0.6	−2.3 (Sr)	0.7	7.8	−1.4	7.0	19.5 (Ni)	0.29	0.31	6.1	6.9	22.8 (Ni)
AM05[84]	0.014	0.037	0.2	0.8	2.1 (NaF)	−0.3	8.8	−4.0	9.2	−25.9 (Rb)	0.30	0.45	7.6	12.6	90.4 (LiH)
PBEint[85]	0.026	0.039	0.5	0.8	2.5 (NaF)	−3.0	8.4	−5.3	8.7	−25.5 (Rb)	0.10	0.20	1.5	4.7	16.4 (Ni)
PBEalpha[86]	0.021	0.042	0.4	0.9	2.0 (Sn)	−6.0	8.4	−5.0	7.6	−21.2 (Ge)	0.10	0.18	1.8	4.1	14.5 (Ni)

Pseudopotentials:



RESEARCH ARTICLE

DFT METHODS *Science* **351,** aad3000 (2016). DOI: 10.1126/science.aad3000

Reproducibility in density functional theory calculations of solids

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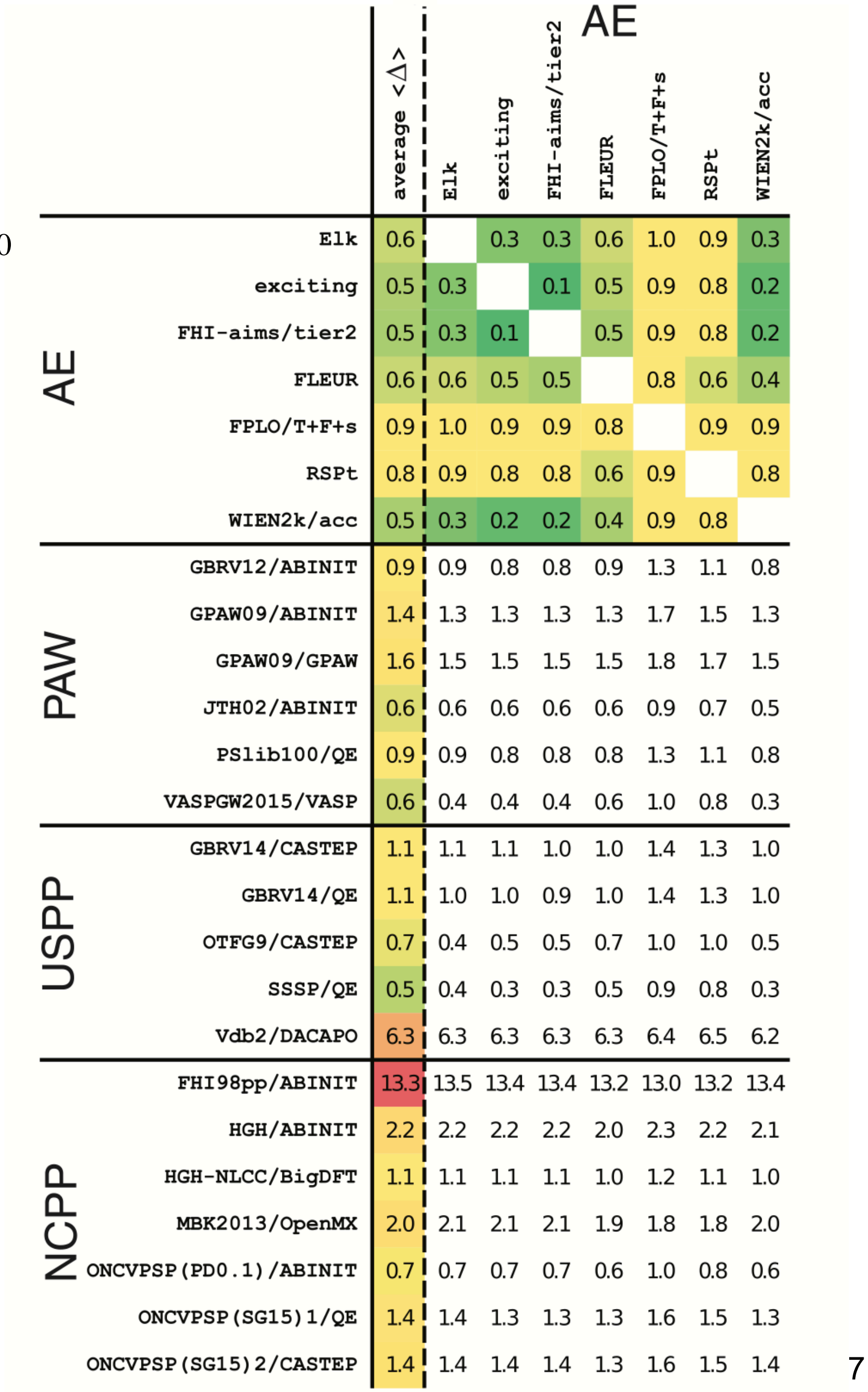
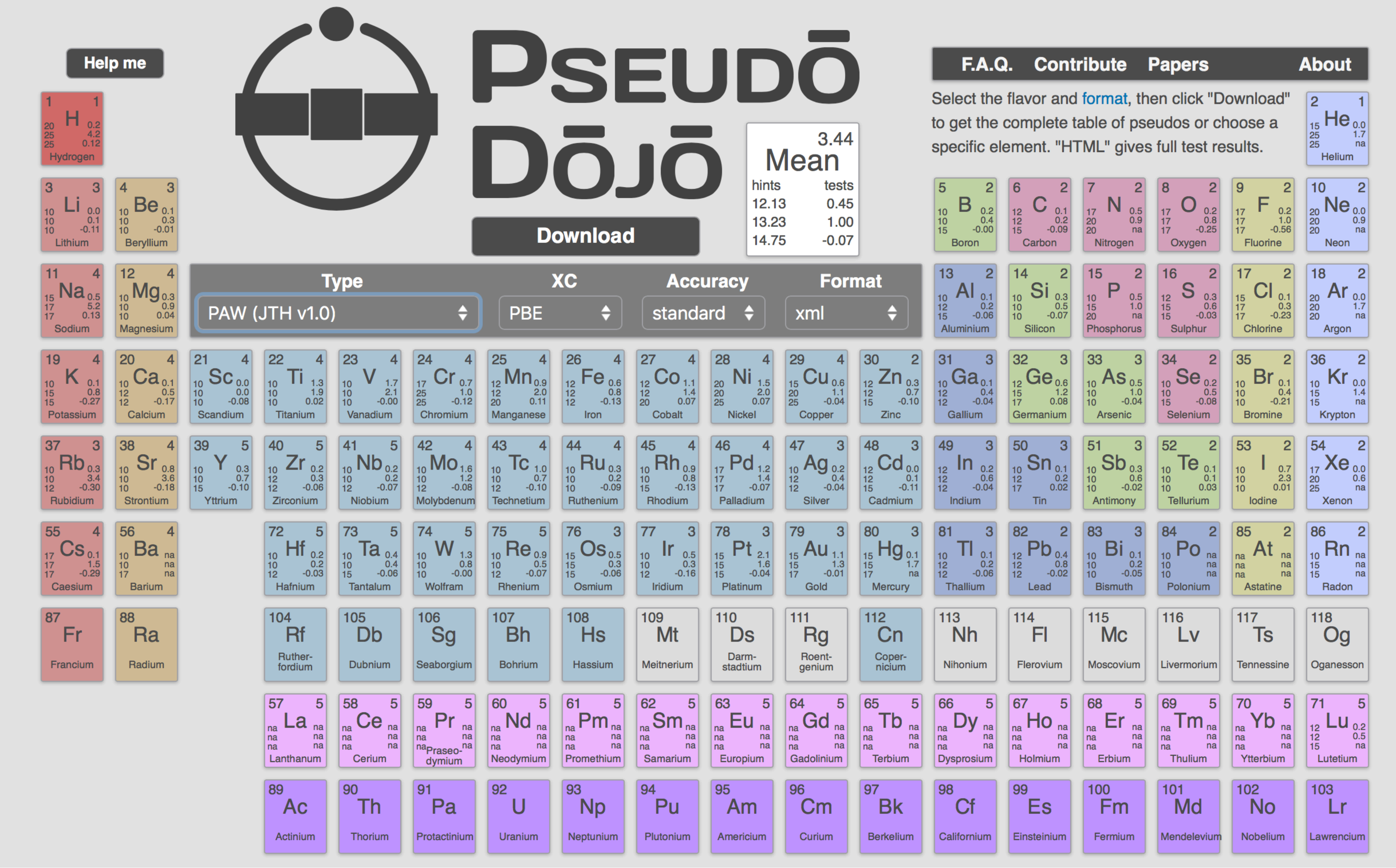
$$\Delta_i(a,b) = \sqrt{\frac{\int_{0.94V_{0,i}}^{1.06V_{0,i}} \left(E_{b,i}(V) - E_{a,i}(V)\right)^2 dV}{0.12V_{0,i}}}$$

https://molmod.ugent.be/deltacodesdft



			AE						
		average <Δ>	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
AE	Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
	FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
	RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
	WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW	GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8
	GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3
	GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5
	PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
	VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3
USPP	GBRV14/CASTEP	1.1	1.1	1.1	1.0	1.0	1.4	1.3	1.0
	GBRV14/QE	1.1	1.0	1.0	0.9	1.0	1.4	1.3	1.0
	OTFG9/CASTEP	0.7	0.4	0.5	0.5	0.7	1.0	1.0	0.5
	SSSP/QE	0.5	0.4	0.3	0.3	0.5	0.9	0.8	0.3
	Vdb2/DACAPO	6.3	6.3	6.3	6.3	6.3	6.4	6.5	6.2
NCPP	FHI98pp/ABINIT	13.3	13.5	13.4	13.4	13.2	13.0	13.2	13.4
	HGH/ABINIT	2.2	2.2	2.2	2.2	2.0	2.3	2.2	2.1
	HGH-NLCC/BigDFT	1.1	1.1	1.1	1.1	1.0	1.2	1.1	1.0
	MBK2013/OpenMX	2.0	2.1	2.1	2.1	1.9	1.8	1.8	2.0
	ONCVPSP(PD0.1)/ABINIT	0.7	0.7	0.7	0.7	0.6	1.0	0.8	0.6
	ONCVPSP(SG15)1/QE	1.4	1.4	1.3	1.3	1.3	1.6	1.5	1.3
	ONCVPSP(SG15)2/CASTEP	1.4	1.4	1.4	1.4	1.3	1.6	1.5	1.4

Pseudopotentials: www.pseudo-dojo.org



Select the flavor and format, then click "Download" to get the complete table of pseudos or choose a specific element. "HTML" gives full test results.

3.44	Mean
hints	tests
12.13	0.45
13.23	1.00
14.75	-0.07

Type: PAW (JTH v1.0)
XC: PBE
Accuracy: standard
Format: xml

1	H	1	20 25 25	0.2 4.2 0.12	Hydrogen
2	He	1	15 25 25	0.0 1.7 na	Helium
3	Li	3	10 10 10	0.0 0.1 -0.11	Lithium
4	Be	3	10 10 10	0.1 0.3 -0.01	Beryllium
5	B	2	10 10 15	0.2 0.4 -0.00	Boron
6	C	2	12 12 15	0.1 0.2 -0.09	Carbon
7	N	2	17 20 20	0.5 0.9 na	Nitrogen
8	O	2	17 17 17	0.2 0.8 -0.25	Oxygen
9	F	2	17 17 17	0.2 1.0 -0.56	Fluorine
10	Ne	2	20 20 20	0.0 0.9 na	Neon
11	Na	4	15 17 17	0.5 5.2 0.13	Sodium
12	Mg	4	10 10 10	0.3 0.9 0.04	Magnesium
13	Al	2	10 12 15	0.1 0.2 -0.06	Aluminium
14	Si	2	10 10 10	0.3 0.5 -0.07	Silicon
15	P	2	10 15 20	0.5 1.0 na	Phosphorus
16	S	2	12 15 15	0.3 0.6 -0.03	Sulphur
17	Cl	2	15 17 17	0.1 0.3 -0.23	Chlorine
18	Ar	2	20 20 20	0.0 1.7 na	Argon
19	K	4	10 15 15	0.1 0.8 -0.27	Potassium
20	Ca	4	10 12 12	0.1 0.5 -0.17	Calcium
21	Sc	4	10 10 10	0.0 0.0 -0.08	Scandium
22	Ti	4	10 10 10	1.3 1.9 0.02	Titanium
23	V	4	10 10 10	1.7 2.1 -0.00	Vanadium
24	Cr	4	17 25 25	0.7 1.0 -0.12	Chromium
25	Mn	4	12 12 20	0.9 2.0 0.11	Manganese
26	Fe	4	12 12 12	0.6 0.8 -0.13	Iron
27	Co	4	12 12 20	1.1 1.4 0.07	Cobalt
28	Ni	4	20 20 25	1.5 2.0 0.07	Nickel
29	Cu	4	15 20 25	0.6 1.1 -0.04	Copper
30	Zn	2	12 12 15	0.3 0.7 -0.10	Zinc
31	Ga	3	10 12 12	0.1 0.4 -0.04	Gallium
32	Ge	3	12 15 17	0.6 1.2 0.08	Germanium
33	As	3	10 10 10	0.5 1.0 -0.04	Arsenic
34	Se	2	10 10 15	0.2 0.5 -0.08	Selenium
35	Br	2	10 10 10	0.1 0.4 -0.21	Bromine
36	Kr	2	10 15 15	0.0 1.4 na	Krypton
37	Rb	3	10 10 12	0.3 3.4 -0.30	Rubidium
38	Sr	4	10 10 10	0.8 3.6 -0.18	Strontium
39	Y	5	10 10 15	0.3 0.7 -0.10	Yttrium
40	Zr	5	10 12 12	0.2 0.3 -0.06	Zirconium
41	Nb	5	10 10 12	0.2 0.2 -0.07	Niobium
42	Mo	4	10 10 12	1.6 1.2 -0.08	Molybdenum
43	Tc	4	10 10 12	1.0 0.7 -0.10	Technetium
44	Ru	4	10 10 10	0.3 0.2 -0.09	Ruthenium
45	Rh	4	10 10 15	0.9 0.8 -0.13	Rhodium
46	Pd	4	17 17 17	1.2 1.4 -0.07	Palladium
47	Ag	3	10 12 12	0.2 0.4 -0.04	Silver
48	Cd	3	12 12 15	0.0 0.1 -0.11	Cadmium
49	In	3	12 12 12	0.2 0.6 -0.04	Indium
50	Sn	3	10 12 17	0.1 0.2 0.02	Tin
51	Sb	3	10 10 10	0.3 0.6 -0.02	Antimony
52	Te	2	10 10 10	0.1 0.1 0.03	Tellurium
53	I	2	10 10 10	0.7 2.3 0.01	Iodine
54	Xe	2	17 20 25	0.0 0.6 na	Xenon
55	Cs	4	17 17 17	0.1 1.5 -0.29	Caesium
56	Ba	4	10 10 17	na na na	Barium
57	La	5	na na na	na na na	Lanthanum
58	Ce	5	na na na	na na na	Cerium
59	Pr	5	na na na	na na na	Praseo-dymium
60	Nd	5	na na na	na na na	Neodymium
61	Pm	5	na na na	na na na	Promethium
62	Sm	5	na na na	na na na	Samarium
63	Eu	5	na na na	na na na	Europium
64	Gd	5	na na na	na na na	Gadolinium
65	Tb	5	na na na	na na na	Terbium
66	Dy	5	na na na	na na na	Dysprosium
67	Ho	5	na na na	na na na	Holmium
68	Er	5	na na na	na na na	Erbium
69	Tm	5	na na na	na na na	Thulium
70	Yb	5	na na na	na na na	Ytterbium
71	Lu	5	12 12 15	0.2 0.5 na	Lutetium
72	Hf	5	10 10 12	0.2 0.2 -0.03	Hafnium
73	Ta	5	10 10 15	0.4 0.4 -0.06	Tantalum
74	W	5	10 10 10	1.3 0.8 -0.00	Wolfram
75	Re	5	10 10 12	0.9 0.5 -0.07	Rhenium
76	Os	3	15 15 15	0.5 0.3 -0.06	Osmium
77	Ir	3	10 10 12	0.5 0.3 -0.16	Iridium
78	Pt	3	15 15 15	2.1 1.6 -0.04	Platinum
79	Au	3	15 15 17	1.1 1.3 -0.01	Gold
80	Hg	3	15 15 17	0.1 1.7 na	Mercury
81	Tl	3	10 12 12	0.1 0.2 -0.06	Thallium
82	Pb	2	12 12 12	0.4 0.8 -0.02	Lead
83	Bi	3	10 10 10	0.1 0.2 -0.05	Bismuth
84	Po	2	10 10 10	na na na	Polonium
85	At	2	na na na	na na na	Astatine
86	Rn	2	10 15 15	na na na	Radon
87	Fr				Francium
88	Ra				Radium
89	Ac				Actinium
90	Th				Thorium
91	Pa				Protactinium
92	U				Uranium
93	Np				Neptunium
94	Pu				Plutonium
95	Am				Americium
96	Cm				Curium
97	Bk				Berkelium
98	Cf				Californium
99	Es				Einsteinium
100	Fm				Fermium
101	Md				Mendelevium
102	No				Nobelium
103	Lr				Lawrencium
104	Rf				Ruther-fordium
105	Db				Dubnium
106	Sg				Seaborgium
107	Bh				Bohrium
108	Hs				Hassium
109	Mt				Meitnerium
110	Ds				Darm-stadtium
111	Rg				Roent-genium
112	Cn				Coper-nicium
113	Nh				Nihonium
114	Fl				Flerovium
115	Mc				Moscovium
116	Lv				Livermorium
117	Ts				Tennessine
118	Og				Oganesson

The band gap problem

The DFT bandgap problem (I)

- DFT is a ground state theory

  => no direct interpretation of Kohn-Sham eigenenergies ε_i in

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} \mathrm{d}\mathbf{r}_1 + V_{\mathrm{xc}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- However { ε_i } are similar to quasi-particle band structure :

  LDA / GGA results for valence bands are accurate ... but

  NOT for the band gap $E_g^{KS} = \varepsilon_c - \varepsilon_v$

- The band gap can alternatively be obtained from total energy differences

[correct expression !]

$$E_g = E(N+1) + E(N-1) - 2\,E(N) = \left\{E(N+1) - E(N)\right\} - \left\{E(N) - E(N-1)\right\}$$

in the limit N $\rightarrow \infty$

(where E(N) is the total energy of the N - electron system)

The DFT bandgap problem (II)

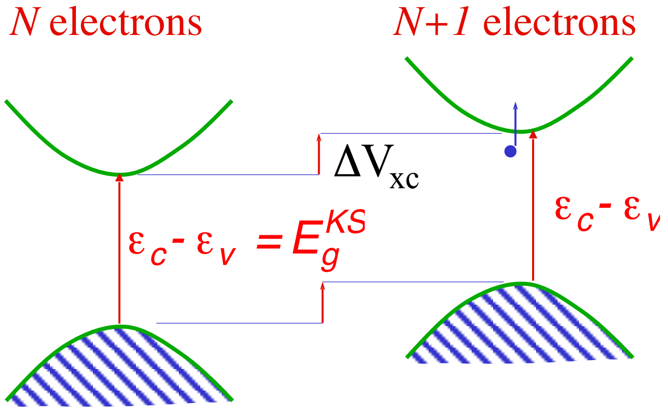
- For LDA & GGA, the *XC* potential is a continuous functional of the number of electrons

$$\varepsilon_i = \frac{\partial E}{\partial f_i} \qquad \text{[Janak's theorem]}$$

$$\Rightarrow \quad E_g^{KS} = \varepsilon_c - \varepsilon_v \underset{N \to \infty}{=} E_g = E(N+1) + E(N-1) - 2E(N)$$

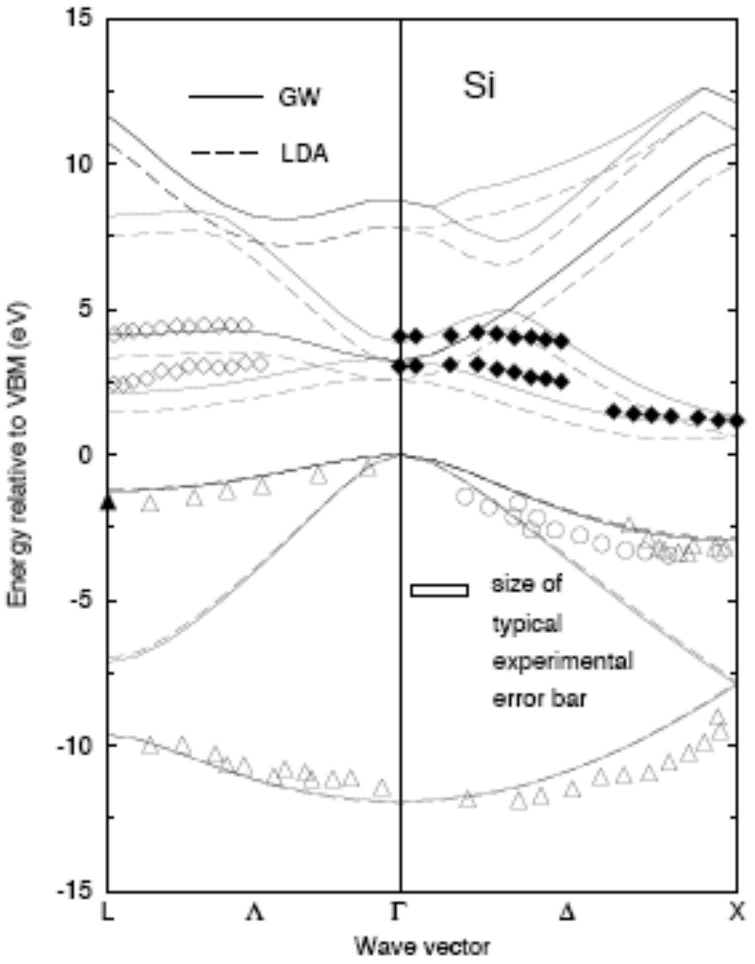
- In general, the *XC* potential might be discontinuous with the number of particle

$$E_g^{KS} \neq E_g$$



$$\Delta_{\mathrm{xc}} = \left(\left. \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\boldsymbol{r})} \right|_{N+1} - \left. \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\boldsymbol{r})} \right|_{N} \right) + \mathcal{O}\left(\frac{1}{N} \right)$$

The DFT bandgap problem (III)



Comparison of LDA and GW band
Structures with photoemission and
Inverse photoemission experiments
for Silicon.

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in Solid State Physics 54, 1-218 (2000)

Relation to Many-body methods : the Sham-Schlüter equation

Kohn-Sham hamiltonian:
$$h_{KS} = -\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\vec{\mathbf{r}})$$

KS potential:
(choose such that it reproduces the interacting density)
$$V_{KS}(\vec{\mathbf{r}}) = V_{ext}(\vec{\mathbf{r}}) + V_H(\vec{\mathbf{r}}) + V_{xc}(\vec{\mathbf{r}})$$

KS Green function:
$$G_{KS}(\vec{\mathbf{r}},\vec{\mathbf{r}'},\omega) = \sum_n \frac{\psi_n(\vec{\mathbf{r}})\psi_n^*(\vec{\mathbf{r}'})}{\omega - \epsilon_n^{KS} + i\delta\,\mathrm{sign}(\epsilon_n^{KS})}$$

$$n(\vec{\mathbf{r}}) = n_{KS}(\vec{\mathbf{r}}) = -i\int \frac{\mathrm{d}\omega}{2\pi} G_{KS}(\vec{\mathbf{r}},\vec{\mathbf{r}},\omega)\,\mathrm{e}^{i0^+}$$

Relation to Many-body methods : the Sham-Schlüter equation

Define interaction: $\tilde{\Sigma}(\vec{\mathbf{r}},\vec{\mathbf{r}}',\omega) \equiv \Sigma_{xc}(\vec{\mathbf{r}},\vec{\mathbf{r}}',\omega) - \delta(\vec{\mathbf{r}}-\vec{\mathbf{r}}')V_{xc}(\vec{\mathbf{r}})$

Interacting hamiltonian: $h = h_{KS} + \tilde{\Sigma}(\vec{\mathbf{r}},\vec{\mathbf{r}}',\omega)$

Dyson equation: $G = G_{KS} + G_{KS}\tilde{\Sigma}G$

$$\int \frac{\mathrm{d}\omega}{2\pi} G = \int \frac{\mathrm{d}\omega}{2\pi} G_{KS} + \int \frac{\mathrm{d}\omega}{2\pi} G_{KS}\tilde{\Sigma}G$$

$$n(\vec{\mathbf{r}}) = n_{KS}(\vec{\mathbf{r}}) + \int \frac{\mathrm{d}\omega}{2\pi} G_{KS}\tilde{\Sigma}G$$

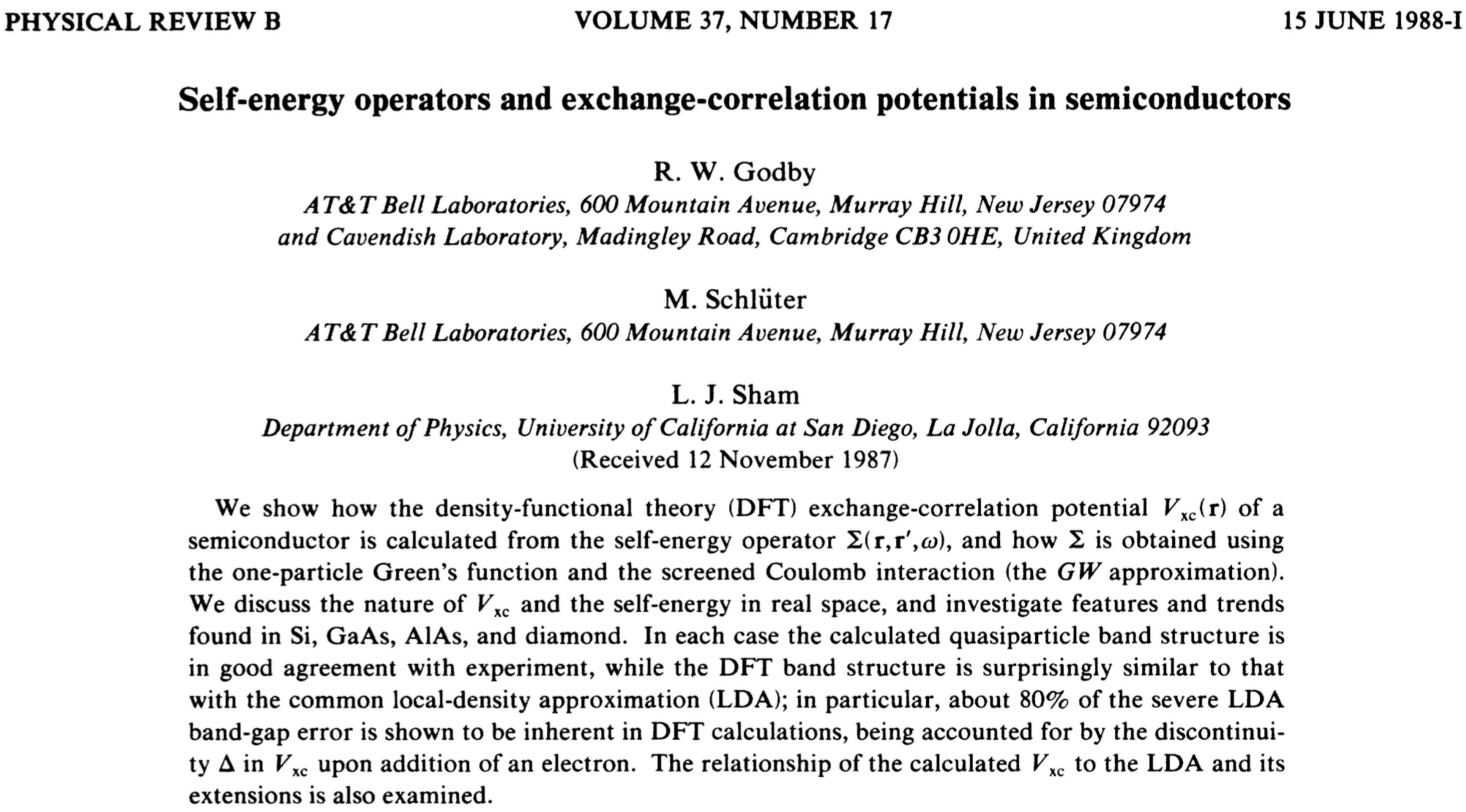
Relation to Many-body methods : the Sham-Schlüter equation

$$0 = \int \frac{\mathrm{d}\omega}{2\pi} G_{KS} \widetilde{\Sigma} G$$

$$\int \mathrm{d}\vec{\mathbf{r}}' V_{KS}(\vec{\mathbf{r}}') \int \mathrm{d}\omega \, G_{KS}(\vec{\mathbf{r}}, \vec{\mathbf{r}}', \omega) G(\vec{\mathbf{r}}', \vec{\mathbf{r}}, \omega)$$

$$= \int \mathrm{d}\vec{\mathbf{r}}' \int \mathrm{d}\vec{\mathbf{r}}'' \int \mathrm{d}\omega \, G_{KS}(\vec{\mathbf{r}}, \vec{\mathbf{r}}', \omega) \widetilde{\Sigma}(\vec{\mathbf{r}}', \vec{\mathbf{r}}'', \omega) G(\vec{\mathbf{r}}'', \vec{\mathbf{r}}, \omega)$$

Relation to Many-body methods : the Sham-Schlüter equation



PHYSICAL REVIEW B **VOLUME 37, NUMBER 17** **15 JUNE 1988-I**

Self-energy operators and exchange-correlation potentials in semiconductors

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(Received 12 November 1987)

We show how the density-functional theory (DFT) exchange-correlation potential $V_{xc}(\mathbf{r})$ of a semiconductor is calculated from the self-energy operator $\Sigma(\mathbf{r},\mathbf{r}',\omega)$, and how Σ is obtained using the one-particle Green's function and the screened Coulomb interaction (the GW approximation). We discuss the nature of V_{xc} and the self-energy in real space, and investigate features and trends found in Si, GaAs, AlAs, and diamond. In each case the calculated quasiparticle band structure is in good agreement with experiment, while the DFT band structure is surprisingly similar to that with the common local-density approximation (LDA); in particular, about 80% of the severe LDA band-gap error is shown to be inherent in DFT calculations, being accounted for by the discontinuity Δ in V_{xc} upon addition of an electron. The relationship of the calculated V_{xc} to the LDA and its extensions is also examined.

Relation to Many-body methods : the Sham-Schlüter equation

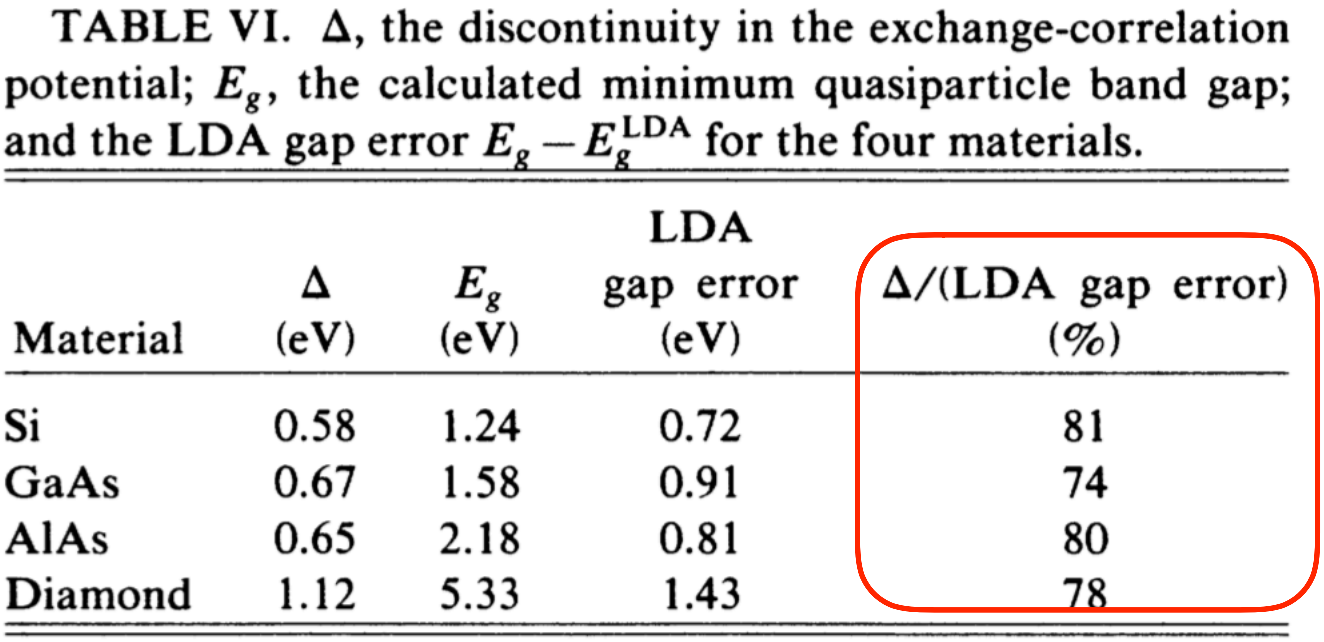

TABLE VI. Δ, the discontinuity in the exchange-correlation potential; E_g, the calculated minimum quasiparticle band gap; and the LDA gap error $E_g - E_g^{\mathrm{LDA}}$ for the four materials.

Material	Δ (eV)	E_g (eV)	LDA gap error (eV)	Δ/(LDA gap error) (%)
Si	0.58	1.24	0.72	81
GaAs	0.67	1.58	0.91	74
AlAs	0.65	2.18	0.81	80
Diamond	1.12	5.33	1.43	78

$E_g^{GW} - E_g^{SS}$ $\curvearrowright$

E_g^{GW}

$\curvearrowleft$ $E_g^{GW} - E_g^{LDA}$

Thank you for your attention.
Questions?