JNTE - 2022
Journées Nationales de Thermoélectricité
Institut des Sciences Chimiques de Rennes

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Ecole Nationale Supérieure de Chimie de Rennes

Modélisation et simulation *in silico*

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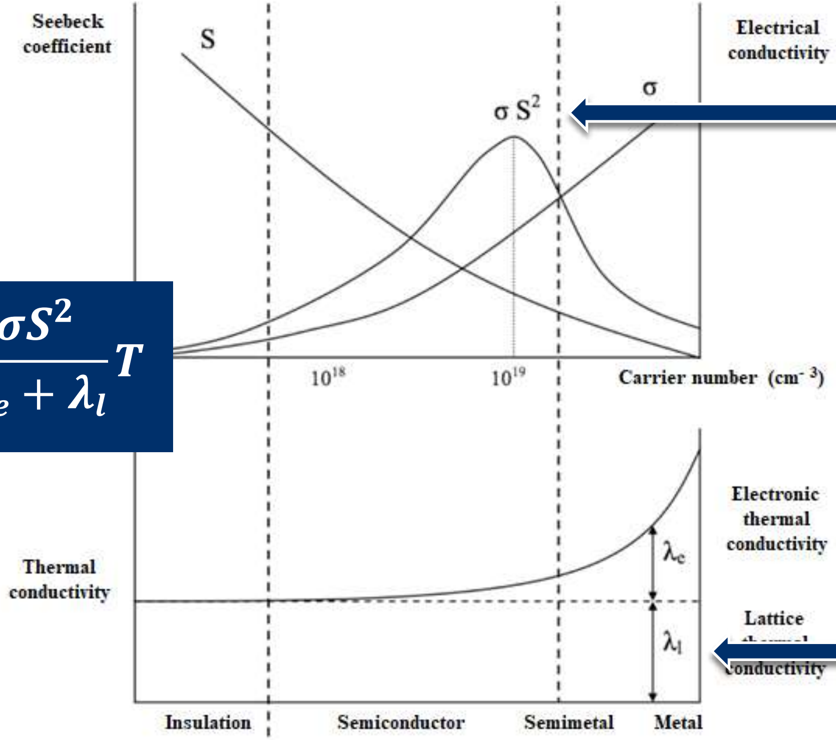
20 écoles de chimie

afaq ISO 9001 Qualité AFNOR CERTIFICATION

IMPROVING THE FIGURE OF MERIT

$$ZT = \frac{\sigma S^2}{\lambda_e + \lambda_l} T$$



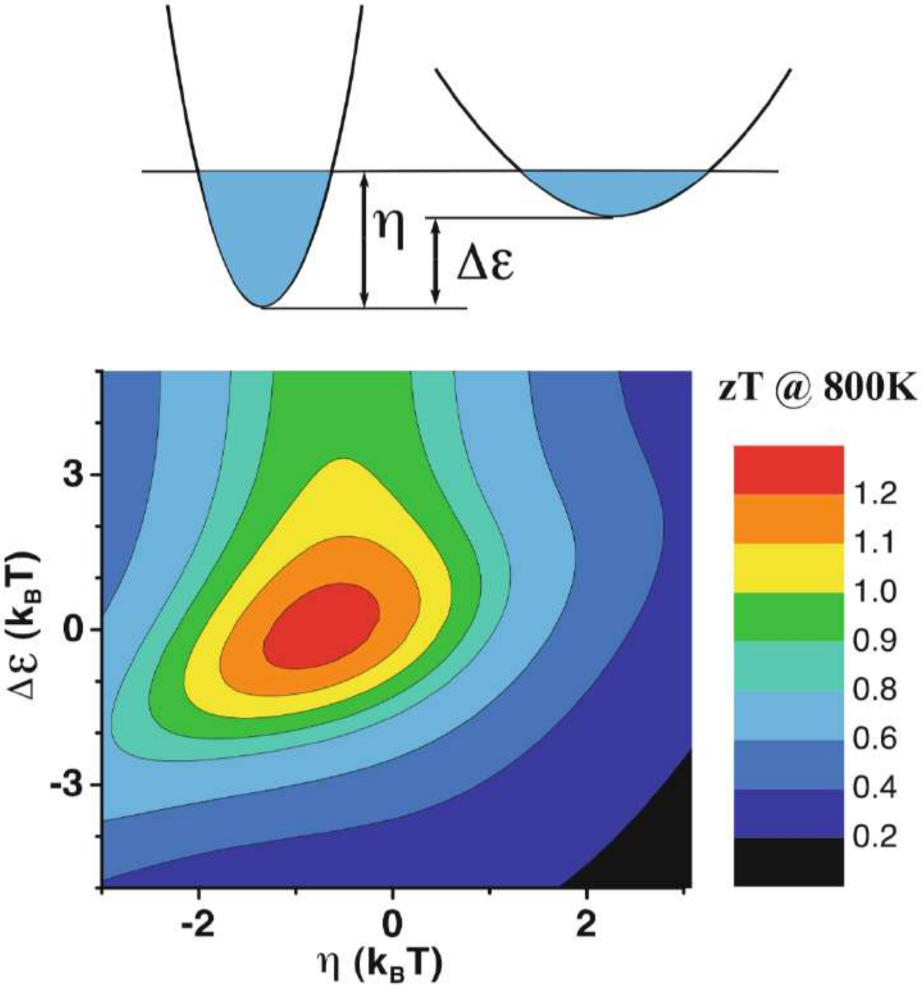
Increasing power factor

Decreasing lattice thermal conductivity

BAND ENGINEERING

$$S = \frac{8\pi^2 k_b^2 T}{3qh^2} m_d^* \left(\frac{\pi}{3n}\right)^{2/3}$$

$$m_d^* = N_v^{2/3} m_b^*$$



G. J. Snyder et al, *Adv. Mater.* **2012**, 24, 6125

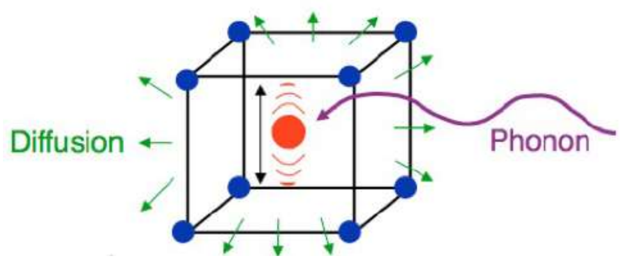
Thermoelectric Nanomaterials Materials Design and Applications, Eds. T. Mori & K. Koumoto, Springer-Verlag Berlin Heidelberg 2013

DECREASING LATTICE THERMAL CONDUCTIVITY

PHONON GLASS ELECTRON CRYSTAL

Search for compounds with:

- Complex crystal structure
- Large unit cell
- Heavy atoms
- Low electronegativity differences between the constituent atoms



G. Slack *CRC Handbook of Thermoelectrics* (Ed D. M. Rowe) CRC, Boca Raton, U.S. pp 407-440 (1995)

NANOSTRUCTURING

M. S. Dresselhaus et al, *Adv. Mater.* **2007**, 19, 1043

M. G. Kanatzidis et al, *Energy Environ. Sci.* **2014**, 7, 251

Theory Can Help but...

- Why DFT?
- Key parameters?
- What are the limitations?
- What about phonons?
- Computing transport properties?

"Anyone can do calculations nowadays.
Anyone can also operate a scalpel.
That doesn't mean all our medical problems are solved."

Karl Irikura

Conducting a Computational Project

These questions should be answered:

- What do you want to know?
- How accurate does the prediction need to be?
- How much time can be devoted to the problem?
- What approximations are being made?

The answers to these questions will determine the type of calculation, model and basis set to be used.

Computational models

- A model is a system of equations, or computations used to determine the energetics of a molecule
- Different models use different approximations (or levels of theory) to produce results of varying levels of accuracy.
- There is a trade off between accuracy and computational time.
- There are two main types of models; those that use Schrödinger's equation (or simplifications of it) and those that do not.

The Schrödinger's Equation

$$\hat{H} = -\sum_{\mu}\frac{1}{2M_{\mu}}\nabla_{\mu}^{2} - \sum_{i}\frac{1}{2}\nabla_{i}^{2} + \sum_{i,j>i}\frac{1}{r_{ij}} - \sum_{i,\mu}\frac{Z_{\mu}}{r_{i\mu}} + \sum_{\mu,\nu>\mu}\frac{Z_{\mu}Z_{\nu}}{R_{\mu\nu}}$$

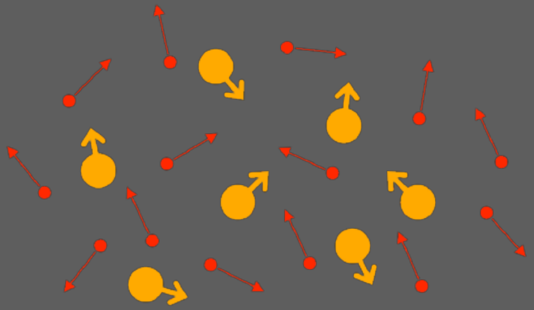
Impossible to solve exactly!

Many-electron problem

Old and extremely hard problem!

Approximations are required.

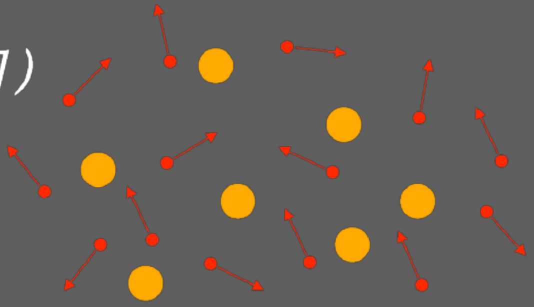
Born–Oppenheimer



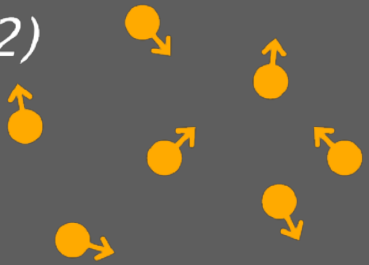
$$\frac{m_n}{m_e} >> 1$$

⇒Nuclei are much slower than electrons

(1)



(2)



electronic/nuclear decoupling

The electronic Schrödinger's Equation

$$\hat{H} = -\sum_{\mu}\cancel{\frac{1}{2M_\mu}}\nabla_\mu^{\,2} - \sum_{i}\frac{1}{2}\nabla_i^{\,2} + \sum_{i,j>i}\frac{1}{r_{ij}} \boxed{-\sum_{i,\mu}\frac{Z_\mu}{r_{i\mu}} + \sum_{\mu,\nu>\mu}\frac{Z_\mu Z_\nu}{R_{\mu\nu}}}$$

$$\hat{H}^{el}_{\{\vec{R}_\mu\}} = -\sum_{i}\frac{1}{2}\nabla_i^{\,2} + \sum_{i,j>i}\frac{1}{r_{ij}} + V^{ext}_{\{\vec{R}_\mu\}}(\{\vec{r}_i\})$$

$$\hat{H}^{el}_{\{\vec{R}_\mu\}}\Psi^{el}_{n,\{\vec{R}_\mu\}}(\{\vec{r}_i\}) = E^{el}_{n}(\{\vec{R}_\mu\})\Psi^{el}_{n,\{\vec{R}_\mu\}}(\{\vec{r}_i\})$$

The electronic Schrödinger's Equation

$$\hat{H} = -\sum \cancel{\frac{1}{2M_\mu}}\nabla_\mu^{\;2} - \sum \frac{1}{2}\nabla_i^{\;2} + \sum \frac{1}{r_{ij}} \boxed{-\sum \frac{Z_\mu}{r_{i\mu}} + \sum \frac{Z_\mu Z_\nu}{R_{\mu\nu}}}$$

Approximations are still required.
Different approaches:

- Quantum Chemistry (Hartree-Fock, CI…)
- Quantum Monte Carlo
- Perturbation theory (propagators)
- Density Functional Theory (DFT)

$$\hat{H}^{el}_{\{\vec{R}_\mu\}} \Psi^{el}_{n,\{\vec{R}_\mu\}}(\{\vec{r}_i\}) = E^{el}(\{\vec{R}_\mu\}) \Psi^{el}_{n,\{\vec{R}_\mu\}}(\{\vec{r}_i\})$$

Impossible to solve exactly!

"Anyone who wants to harvest in his lifetime cannot wait for the ab initio theory of weather"
HG von Schnering

Motivations for DFT

- The wave function itself is essentially uninterpretable.
- Reduce problem size
- Wave function based methods quickly become intractable for large systems, even with continued improvement in computing power, due to the coupled motion of the electrons.
- A desire to work with some physical observable rather than probability amplitude.

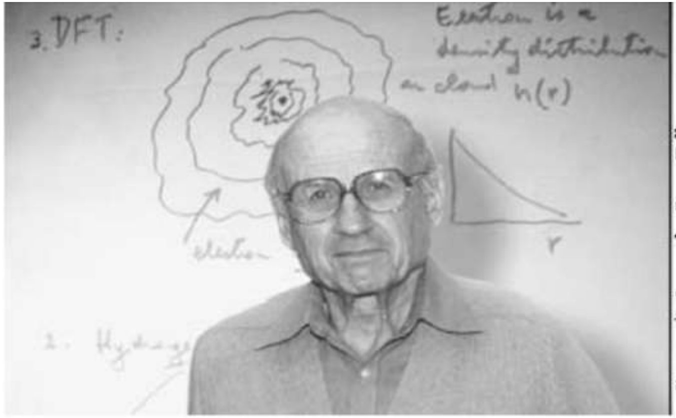
Why is DFT so popular?

- **Transferability**. We can use the same codes/methods for very different materials
- **Simplicity**. The Kohn-Sham equations are conceptually very similar to the Schrödinger equation for a single electron in an external potential
- **Reliability**. Often we can predict materials properties with high accuracy, sometimes even before experiments
- **Software sharing**. The development of DFT has become a global enterprise, e.g. open source and collaborative software development
- **Robust platform**. Often the shortcomings of DFT can be cured by using more sophisticated approaches, which still use DFT as their starting point

The basics of Density Functional Theory

All properties of the many-body system are determined by the ground state density $n_0(r)$

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



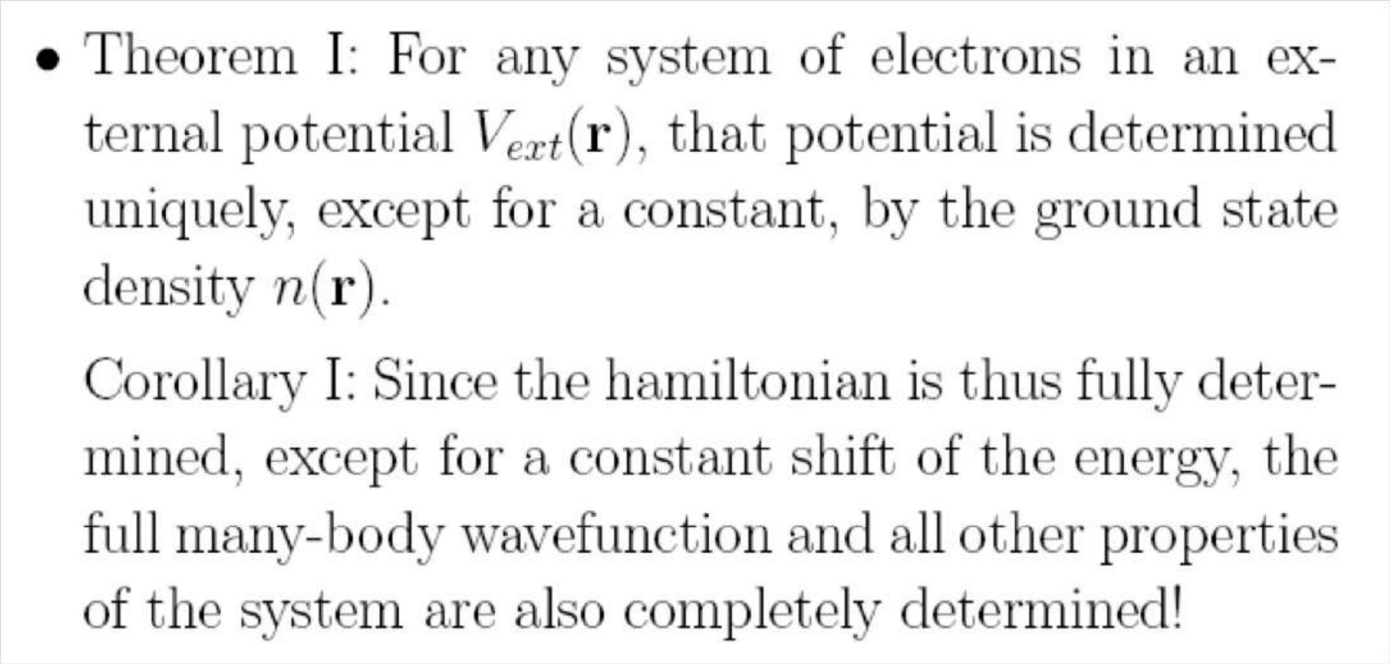
Composite Image by Dave Folks

W. Kohn, chemistry Nobel prize 1998

Each property is a functional of the ground state density $n_0(r)$ which is written as $f\,[n_0]$

A functional $f\,[n_0]$ maps a function to a result: $n_0(r) \rightarrow f$

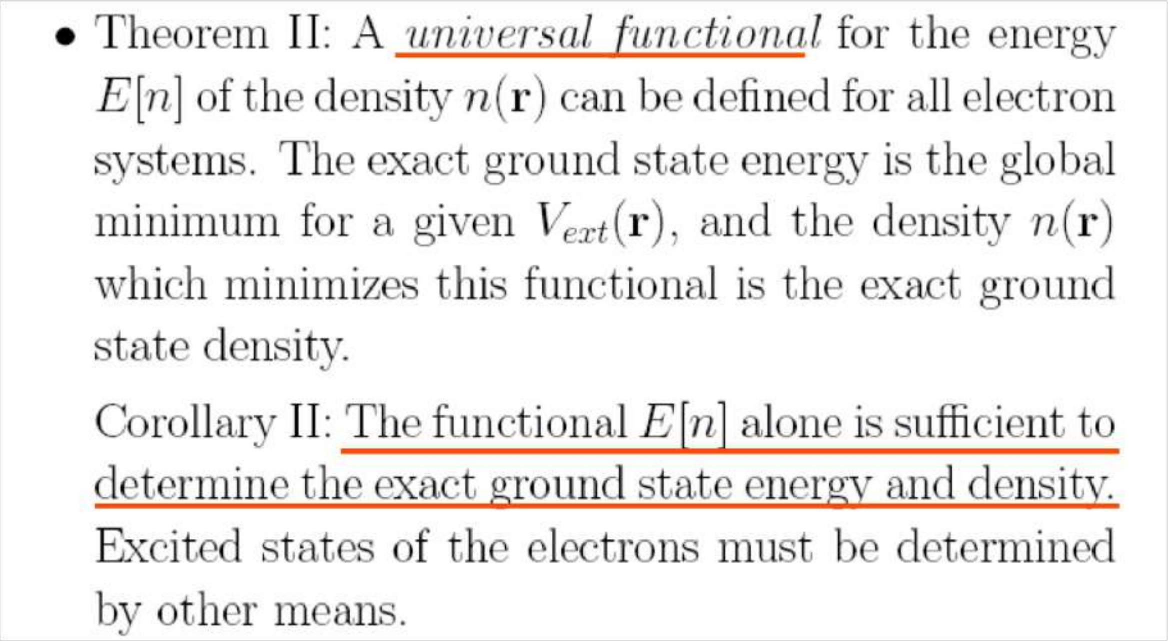
The Hohenberg-Kohn Theorems



- Theorem I: For any system of electrons in an external potential $V_{ext}(\mathbf{r})$, that potential is determined uniquely, except for a constant, by the ground state density $n(\mathbf{r})$.

  Corollary I: Since the hamiltonian is thus fully determined, except for a constant shift of the energy, the full many-body wavefunction and all other properties of the system are also completely determined!

The Hohenberg-Kohn Theorems



- Theorem II: A *universal functional* for the energy $E[n]$ of the density $n(\mathbf{r})$ can be defined for all electron systems. The exact ground state energy is the global minimum for a given $V_{ext}(\mathbf{r})$, and the density $n(\mathbf{r})$ which minimizes this functional is the exact ground state density.

  Corollary II: The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density. Excited states of the electrons must be determined by other means.

Minimizing E[n] for a given $V_{ext}(r) \rightarrow n_0(r)$ and E *variational principle*

In principle, one can find all other properties and they are functionals of $n_0(r)$.

The Kohn-Sham Ansatz

- Kohn-Sham (1965) – Replace original many-body problem with an independent electron problem – that can be solved!
- The ground state density is required to be the same as the exact density $n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$

$$E_{KS} = \underbrace{\frac{1}{2} \sum_{\sigma} \sum_{i=1} |\nabla \psi_i^{\sigma}|^2 + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II}} + \underbrace{E_{xc}[n]}.$$

Equations for independent particles - **soluble**

Exchange-Correlation Functional – Exact theory but **unknown** functional!

- **The new paradigm – find useful, approximate functionals**

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

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

Exchange-correlation potential

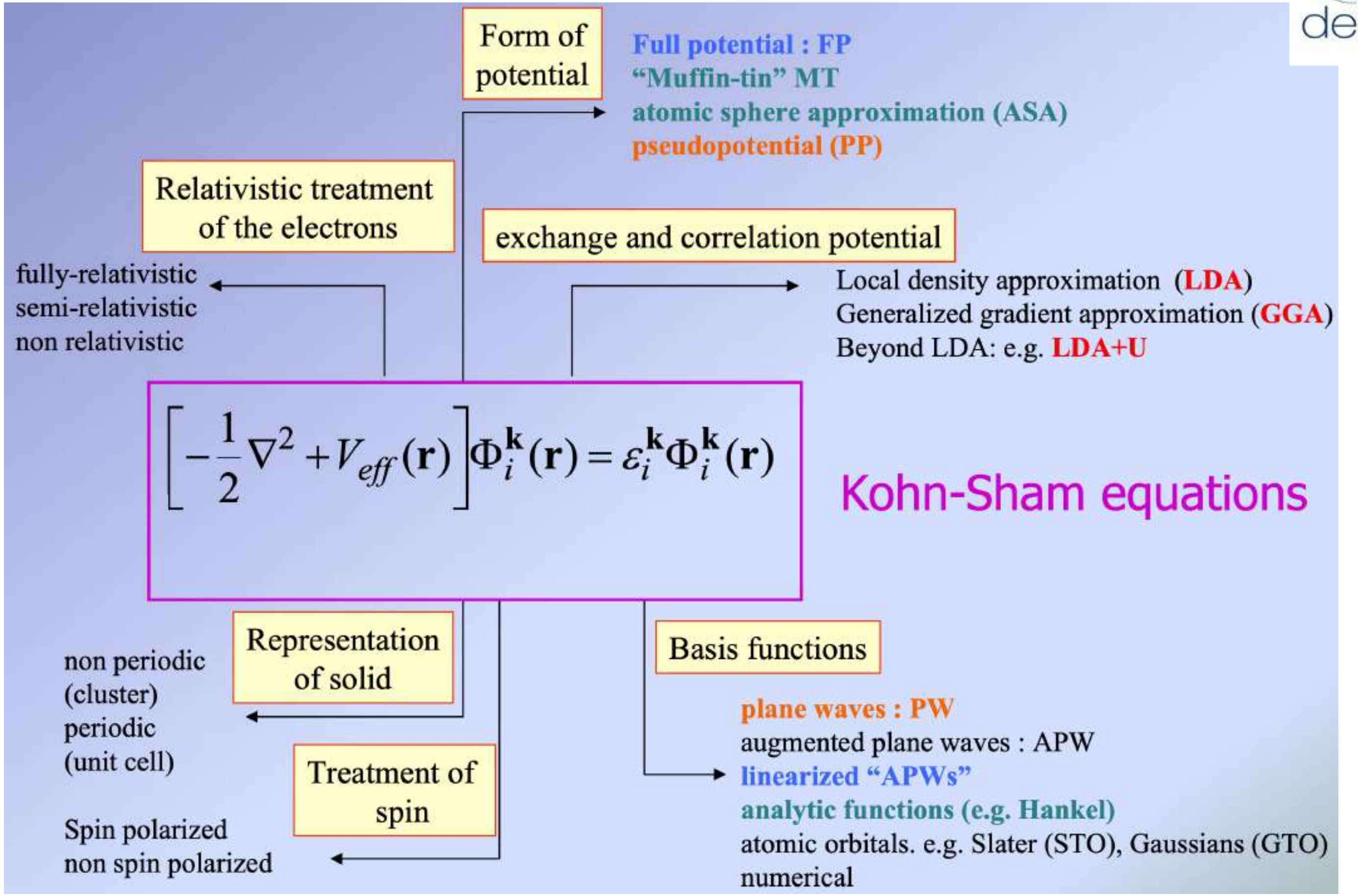
Hartree potential

To be solved self-consistently !

➪ 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

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

Overview of DFT concepts



Form of potential

Full potential : FP
“Muffin-tin” MT
atomic sphere approximation (ASA)
pseudopotential (PP)

Relativistic treatment of the electrons

fully-relativistic
semi-relativistic
non relativistic

exchange and correlation potential

Local density approximation (**LDA**)
Generalized gradient approximation (**GGA**)
Beyond LDA: e.g. **LDA+U**

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right]\Phi_i^{\mathbf{k}}(\mathbf{r}) = \varepsilon_i^{\mathbf{k}}\Phi_i^{\mathbf{k}}(\mathbf{r})$$

Kohn-Sham equations

Representation of solid

non periodic
(cluster)
periodic
(unit cell)

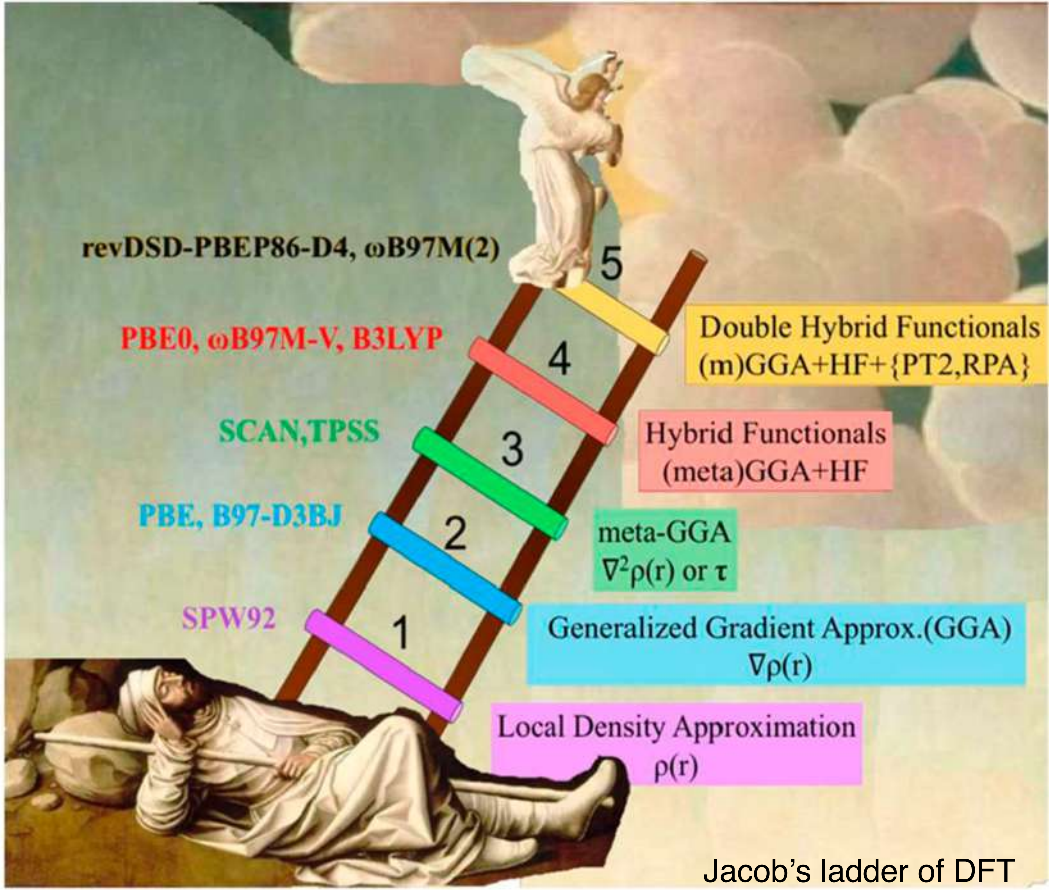
Treatment of spin

Spin polarized
non spin polarized

Basis functions

plane waves : PW
augmented plane waves : APW
linearized “APWs”
analytic functions (e.g. Hankel)
atomic orbitals. e.g. Slater (STO), Gaussians (GTO)
numerical

XC functionals



Jacob's ladder of DFT

B2GP-PLYP

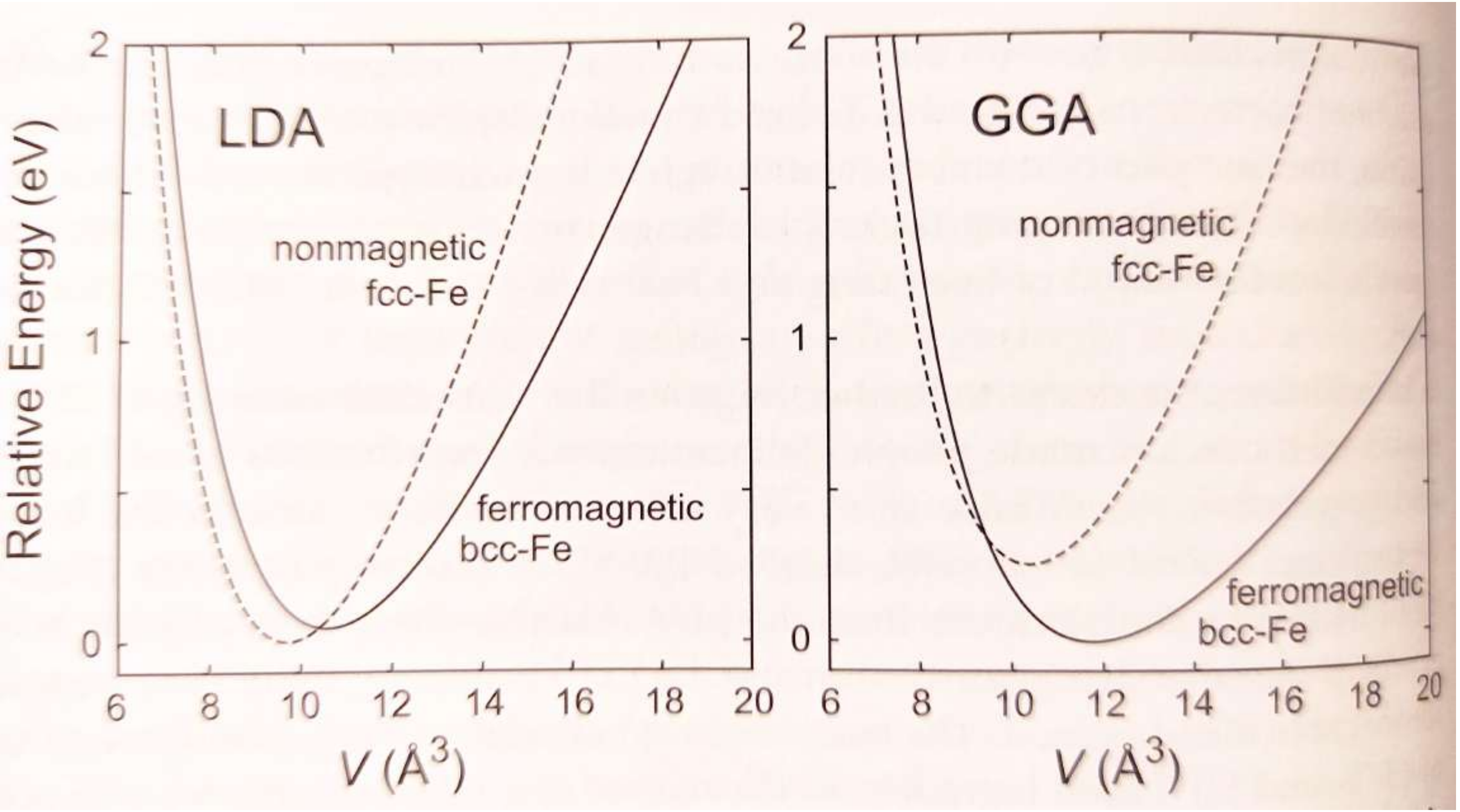
B3LYP, PBE0, HSE

TPSS, tHCTH, Mo6L, SCAN

BP86, PBE, PW91, BLYP...

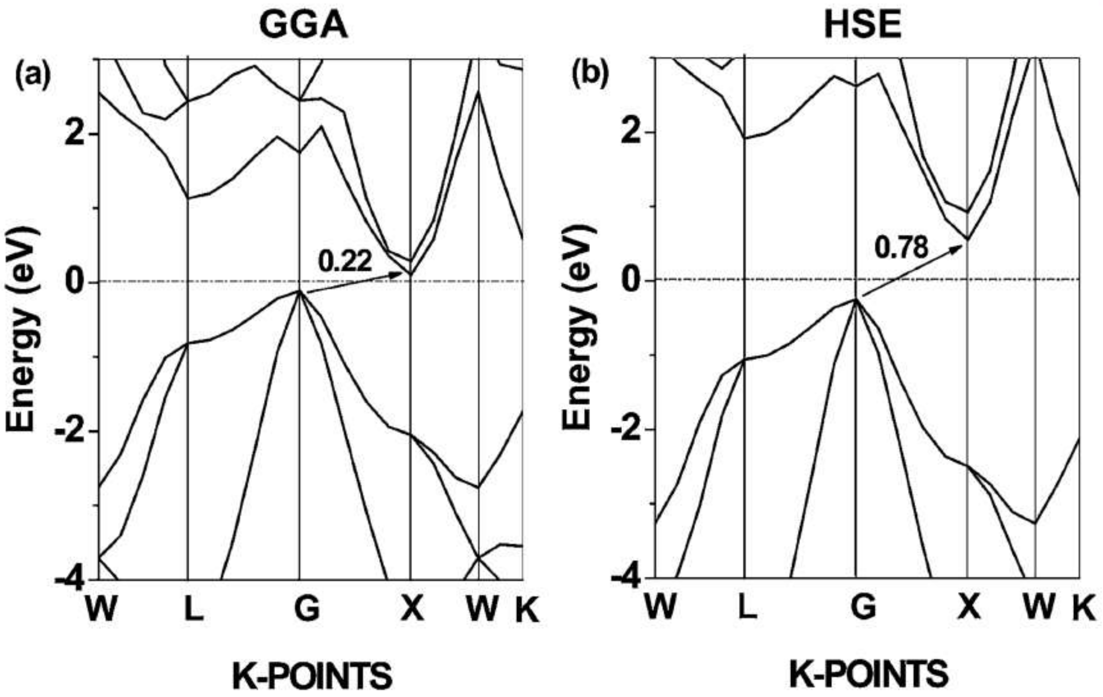
VWN

The case of Fe



Influence of XC on band gaps

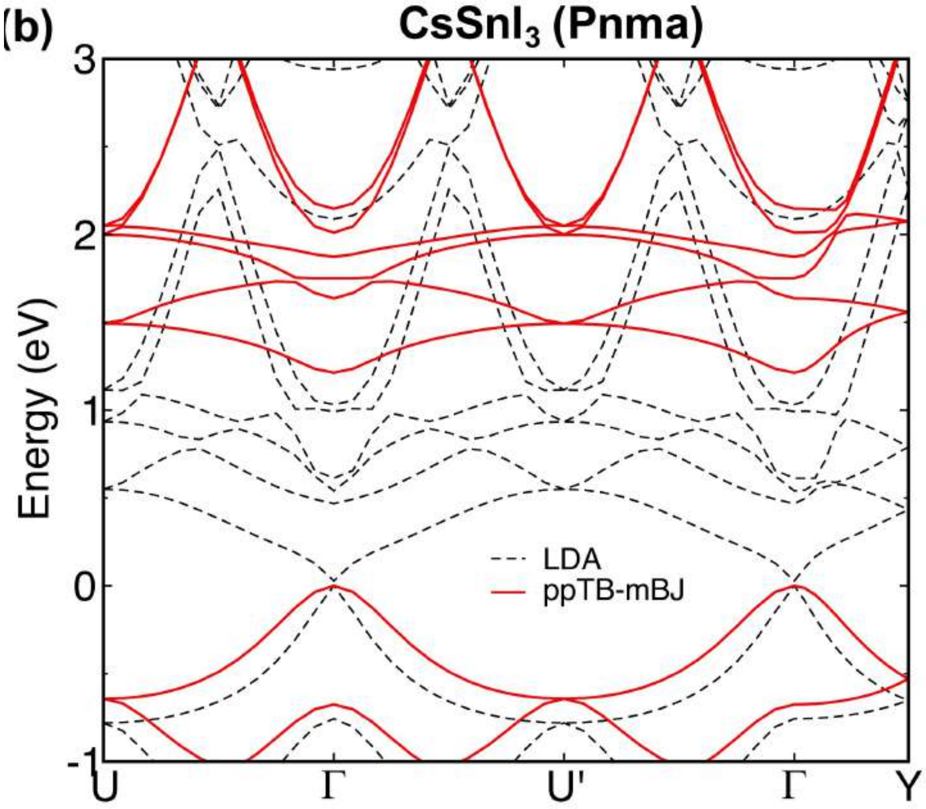
Mg_2Si

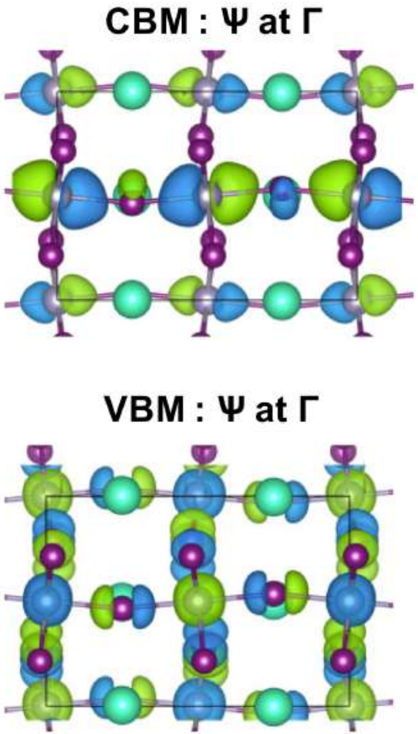


→ *LDA & GGA functionals underestimate band gaps*

J. Mater. Chem. C, 2015, 3, 530–537

Influence of XC on band gaps

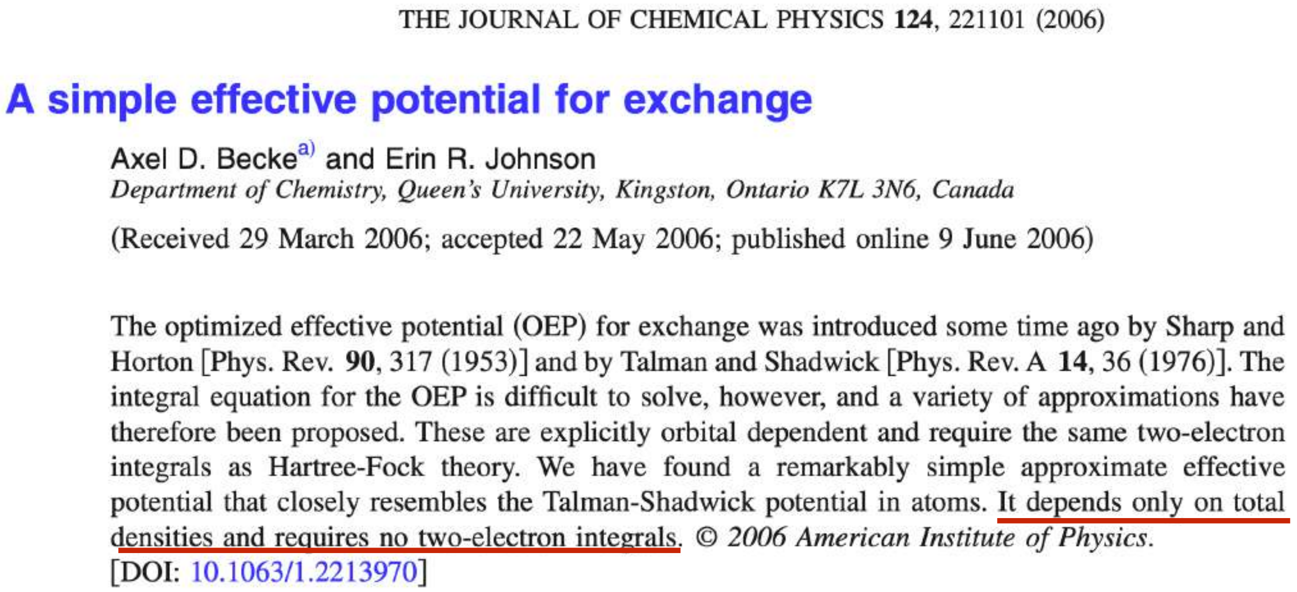




➔ *mBJ potential*

Phys. Rev. B 99, 035139 (2019)

The Becke-Johnson potential



THE JOURNAL OF CHEMICAL PHYSICS **124**, 221101 (2006)

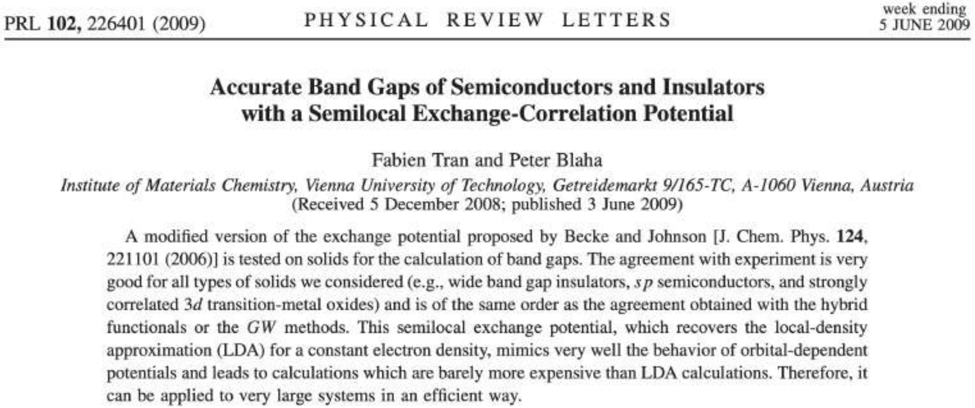
A simple effective potential for exchange

Axel D. Becke[a] and Erin R. Johnson
Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

(Received 29 March 2006; accepted 22 May 2006; published online 9 June 2006)

The optimized effective potential (OEP) for exchange was introduced some time ago by Sharp and Horton [Phys. Rev. **90**, 317 (1953)] and by Talman and Shadwick [Phys. Rev. A **14**, 36 (1976)]. The integral equation for the OEP is difficult to solve, however, and a variety of approximations have therefore been proposed. These are explicitly orbital dependent and require the same two-electron integrals as Hartree-Fock theory. We have found a remarkably simple approximate effective potential that closely resembles the Talman-Shadwick potential in atoms. It depends only on total densities and requires no two-electron integrals.
[DOI: 10.1063/1.2213970]

The Becke-Johnson potential



PRL **102,** 226401 (2009) PHYSICAL REVIEW LETTERS week ending 5 JUNE 2009

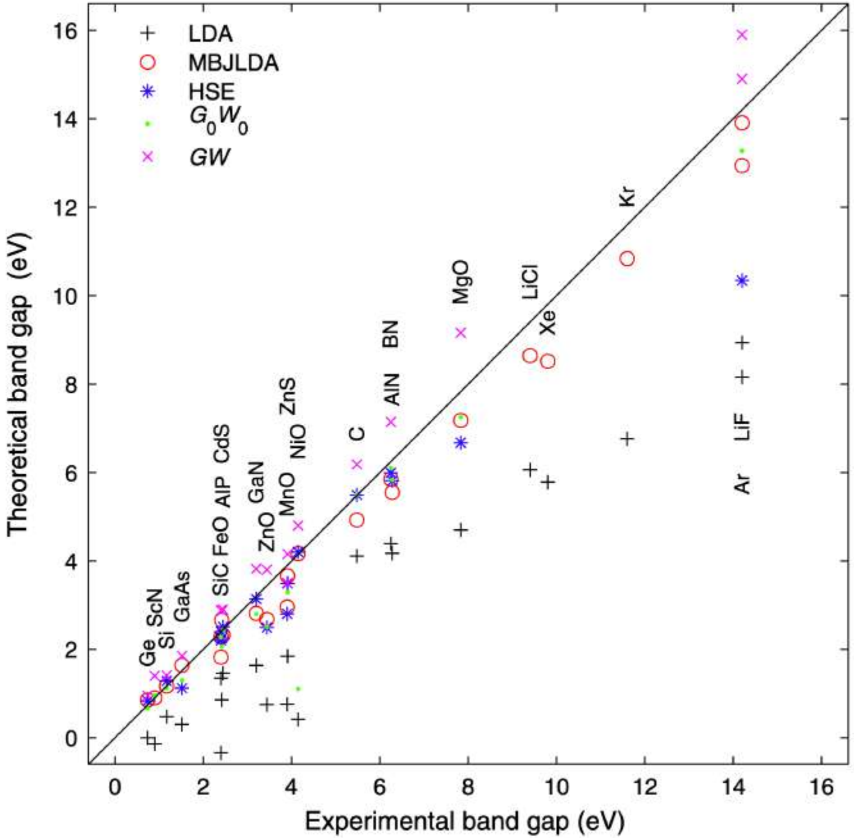
Accurate Band Gaps of Semiconductors and Insulators with a Semilocal Exchange-Correlation Potential

Fabien Tran and Peter Blaha

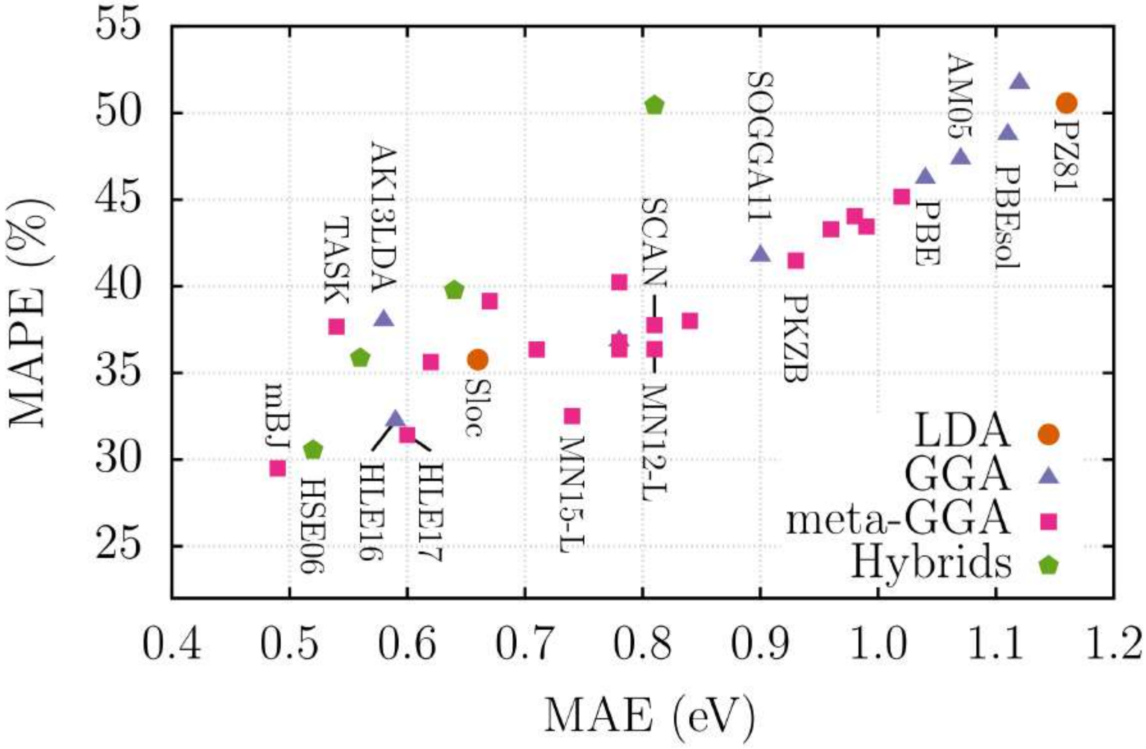
Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165-TC, A-1060 Vienna, Austria

(Received 5 December 2008; published 3 June 2009)

A modified version of the exchange potential proposed by Becke and Johnson [J. Chem. Phys. **124**, 221101 (2006)] is tested on solids for the calculation of band gaps. The agreement with experiment is very good for all types of solids we considered (e.g., wide band gap insulators, *sp* semiconductors, and strongly correlated 3*d* transition-metal oxides) and is of the same order as the agreement obtained with the hybrid functionals or the *GW* methods. This semilocal exchange potential, which recovers the local-density approximation (LDA) for a constant electron density, mimics very well the behavior of orbital-dependent potentials and leads to calculations which are barely more expensive than LDA calculations. Therefore, it can be applied to very large systems in an efficient way.

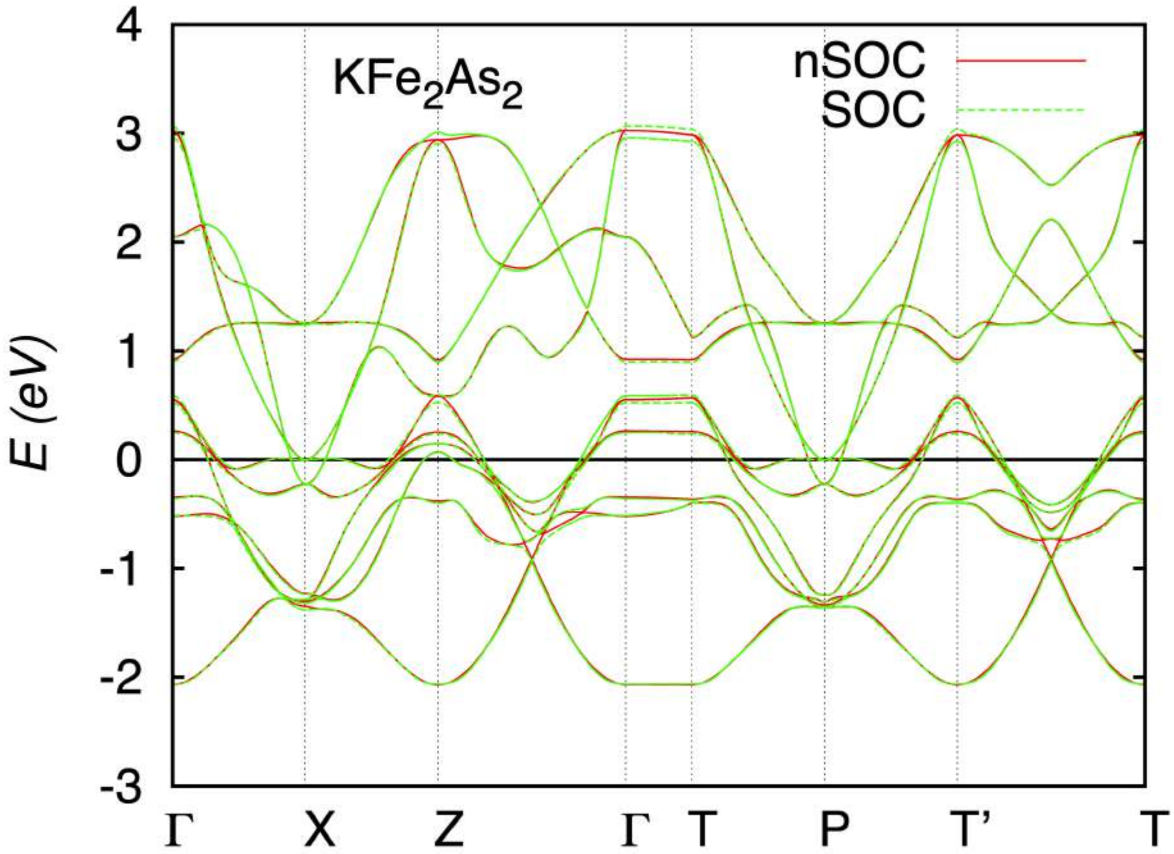


The Becke-Johnson potential



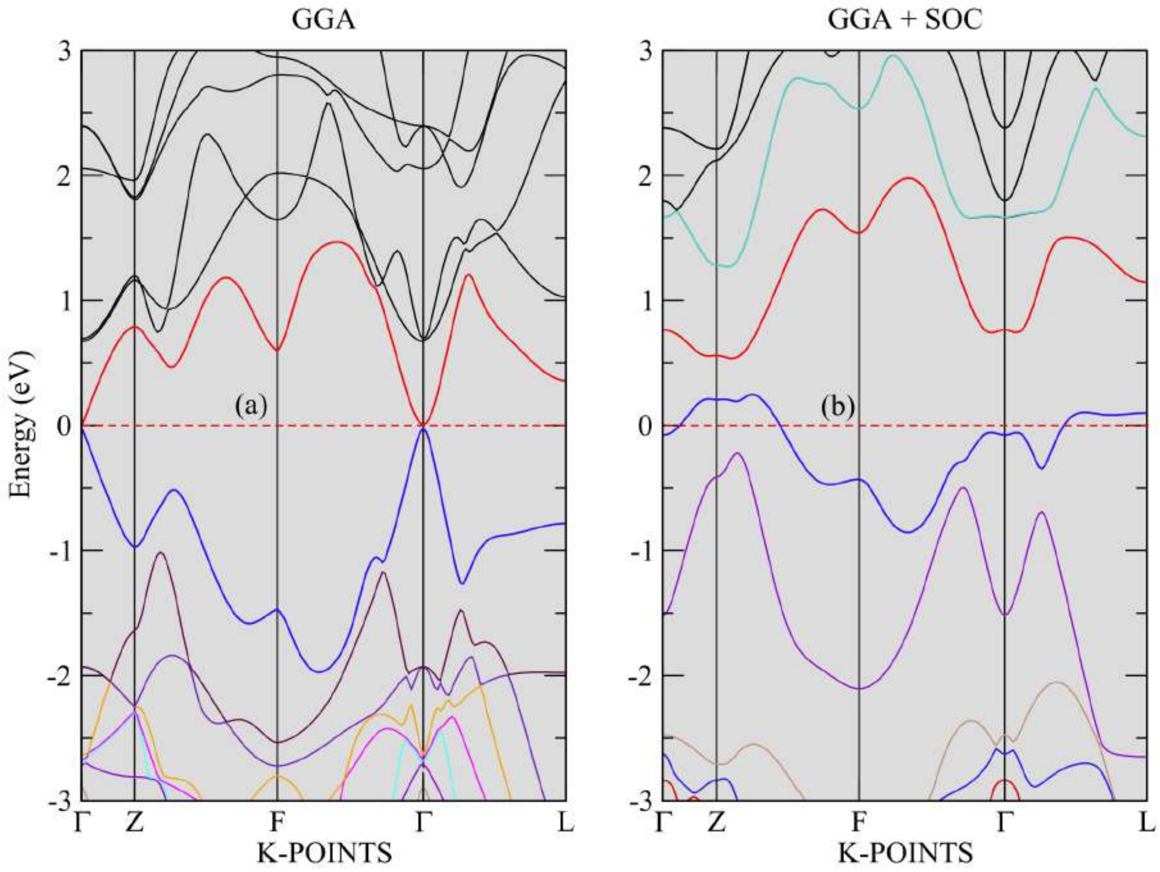
npj Computational Materials (2020) 96

Relativistic effects



- *Not much effect for "light" atoms*

Relativistic effects

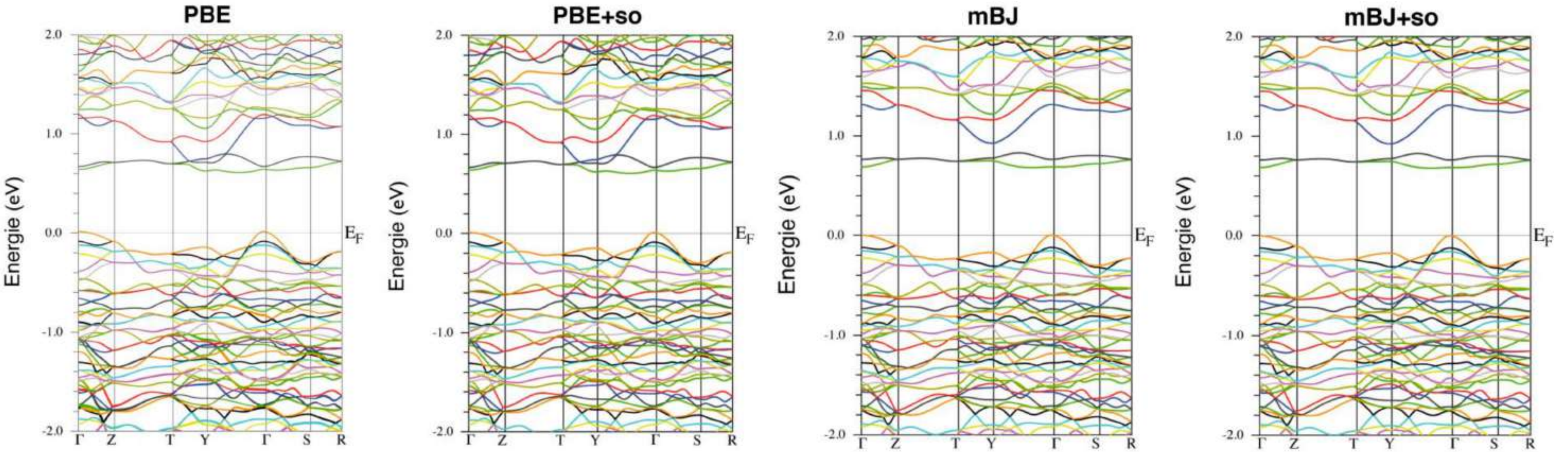


Bi_2Se_3

- *Can be important for “heavy” atoms*

AIP Advances **10**, 095018 (2020)

Relativistic effects



PBE

PBE+so

mBJ

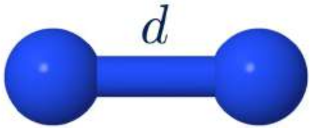
mBJ+so

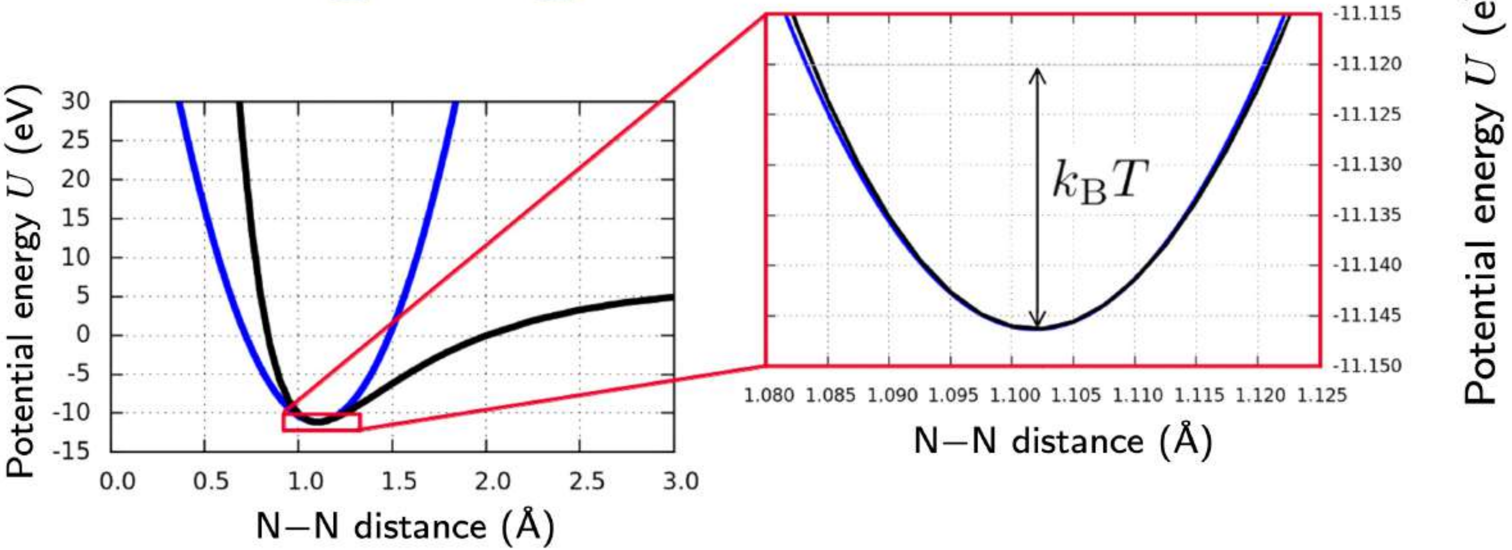
$Ag_4Mo_9Se_{11}$

J. Mater. Chem. C, 2017, 5, 12097

Harmonic approximation

N_2 molecule

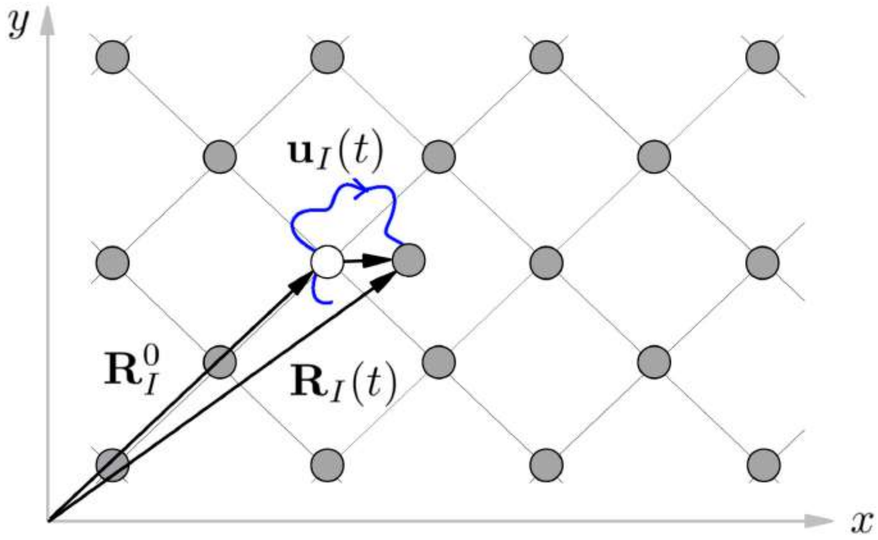




$$U(d) = U_0 + \frac{1}{2}K(d-d_0)^2 \longrightarrow \frac{\partial U}{\partial d} = K(d-d_0)$$

	Experiment	Harmonic	Anharmonic
ν_0 (meV)	300	288	305

Vibrational eigenmodes and eigenvalues



Taylor expansion of potential energy surface for small displacements

$$U = U_0 + \cancel{\sum_{I\alpha} u_{I\alpha} \frac{\partial U}{\partial R_{I\alpha}}} + \frac{1}{2}\sum_{I\alpha,J\beta} \underbrace{\boxed{\frac{\partial^2 U}{\partial R_{I\alpha}\partial R_{J\beta}}}}_{K_{I\alpha,J\beta}} u_{I\alpha}u_{J\beta} + \cancel{\mathcal{O}(u^3)}$$

matrix of force constants

Calculations of vibrational frequencies

1) Frozen-phonon method

$$\frac{\partial^2 U}{\partial R_{I\alpha}^2} \simeq \frac{U(R_{I\alpha}^0 + u) - 2U_0 + U(R_{I\alpha}^0 - u)}{u^2}$$

or alternatively using the forces

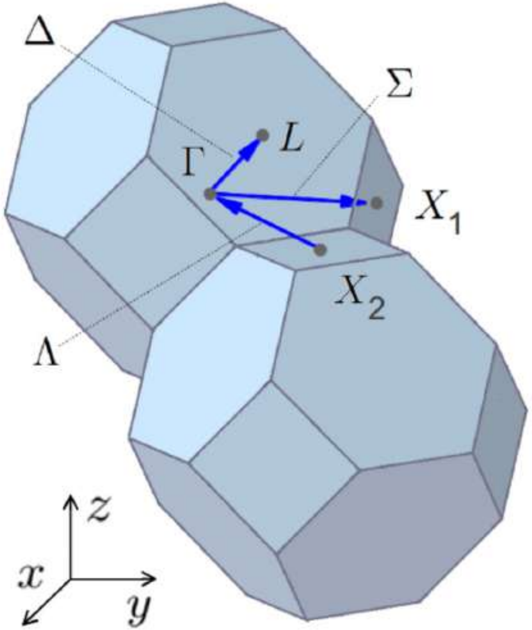
$$\frac{\partial^2 U}{\partial R_{I\alpha}^2} \simeq -\frac{F_{I\alpha}(R_{I\alpha}^0 + u) - F_{I\alpha}(R_{I\alpha}^0 - u)}{2u}$$

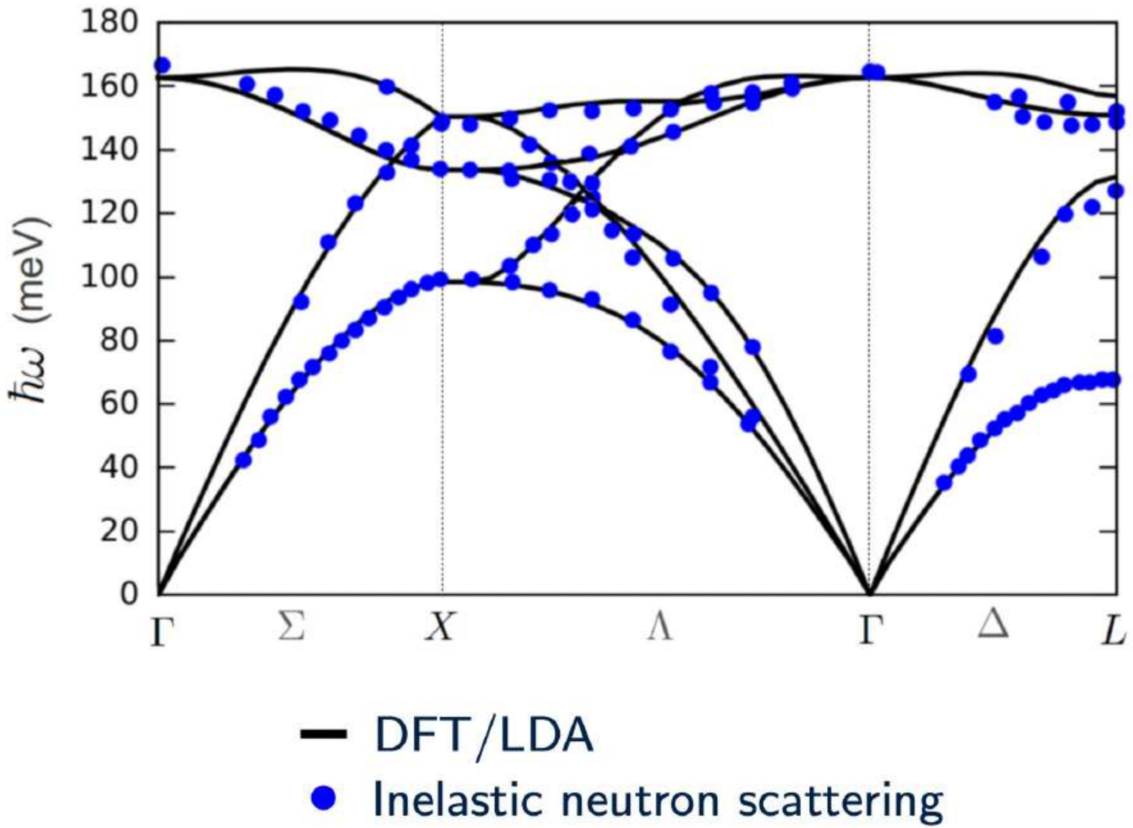
2) Density-functional perturbation theory (DFPT)

The method of choice for crystals

see Baroni et al, Rev. Mod. Phys. 73, 515 (2001)

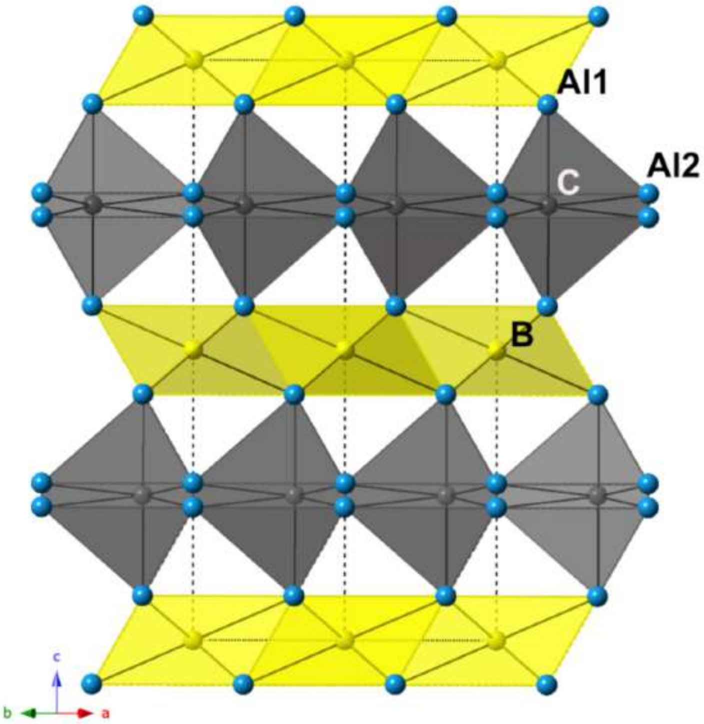
Phonons dispersions relations

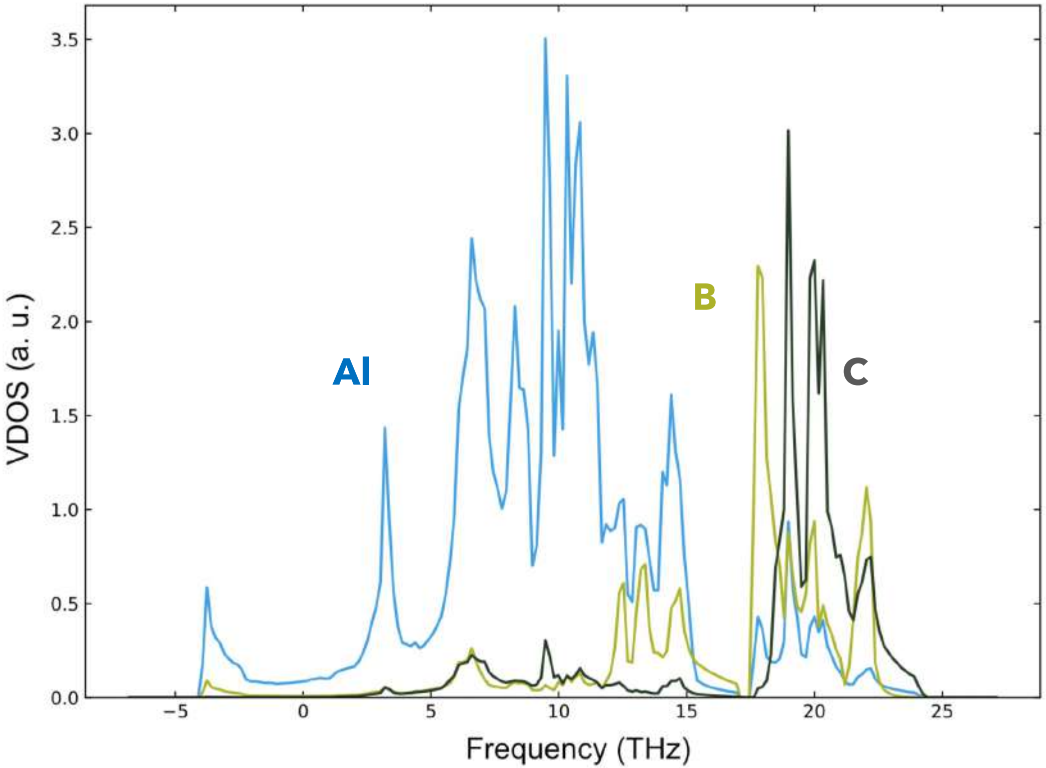




Negative frequencies

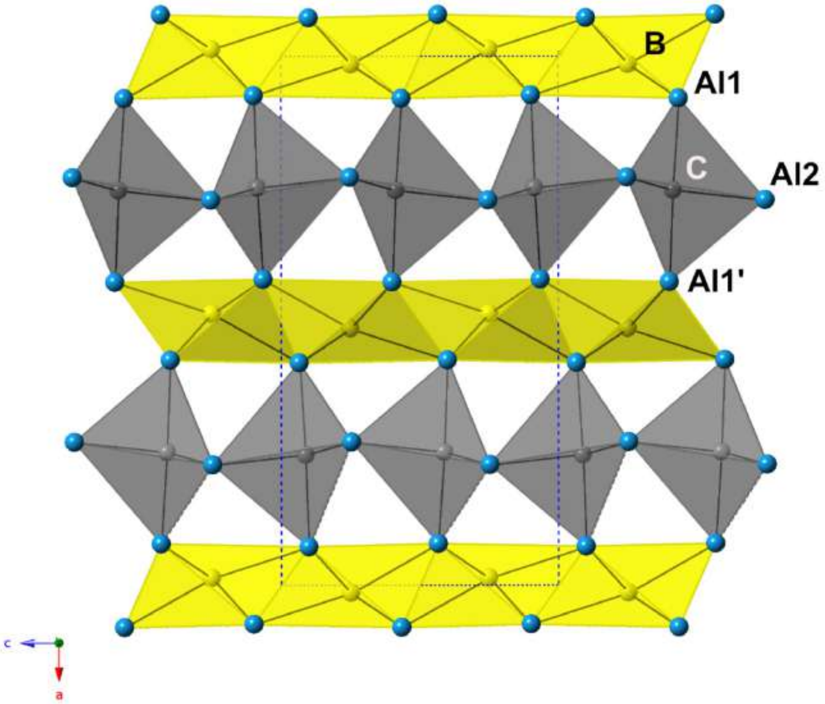
Al_3BC

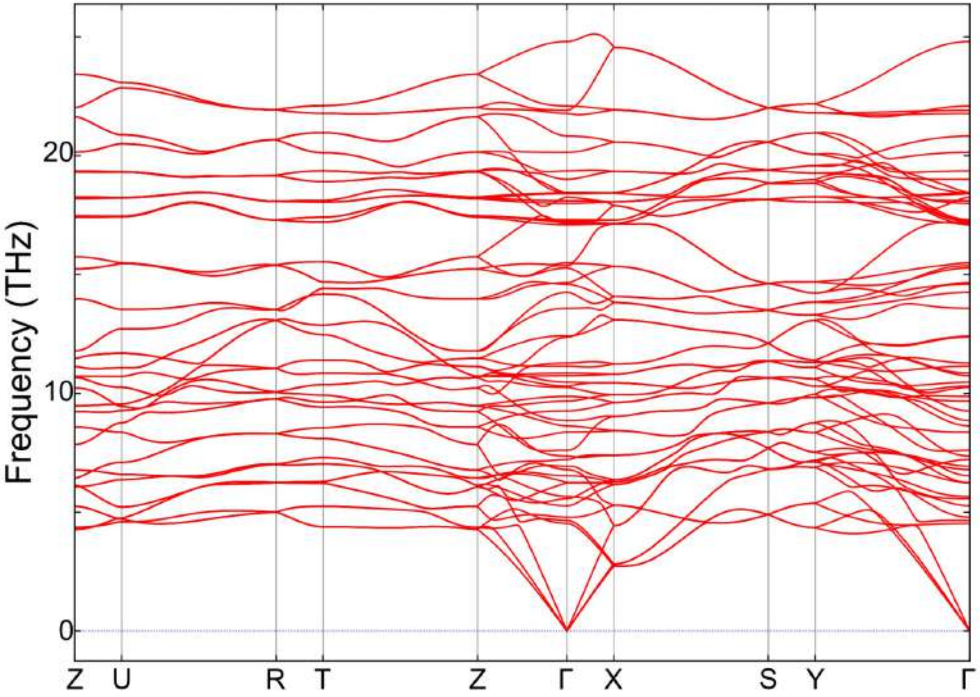




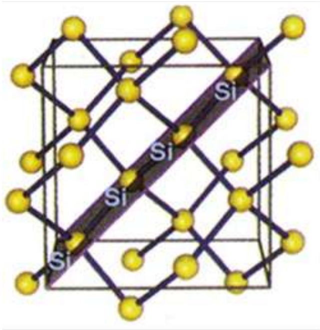
Negative frequencies

Al_3BC

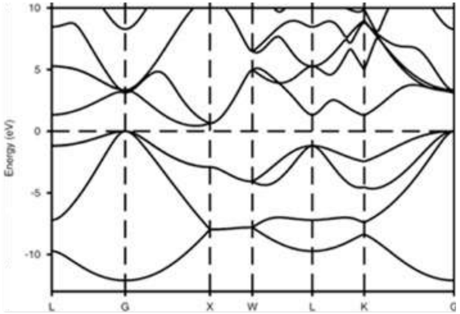




How Theory Can Help?



Structural
model

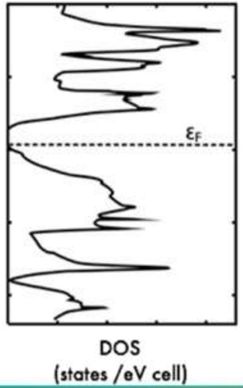


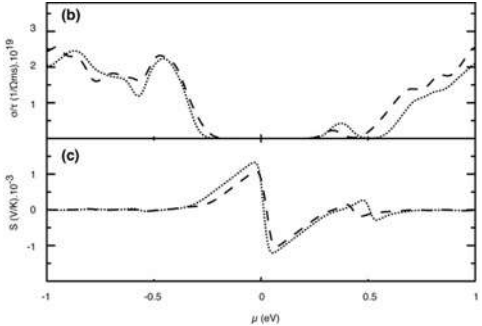
Electronic
Structure

Predicting

Transport
Properties

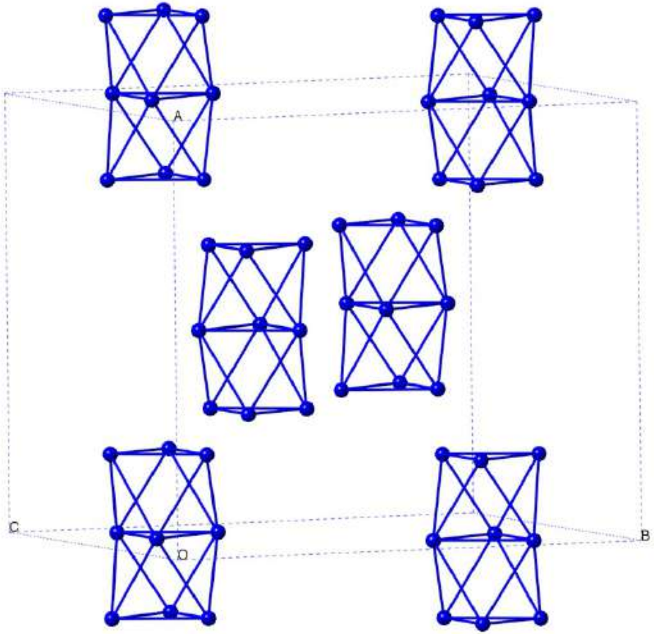
Understanding





Structural models

$Ag_4Mo_9Se_{11}$



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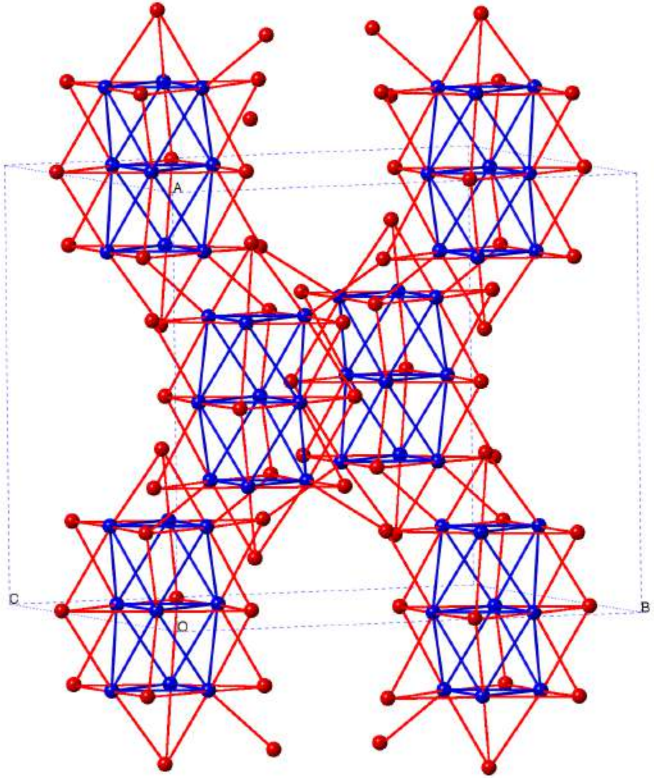

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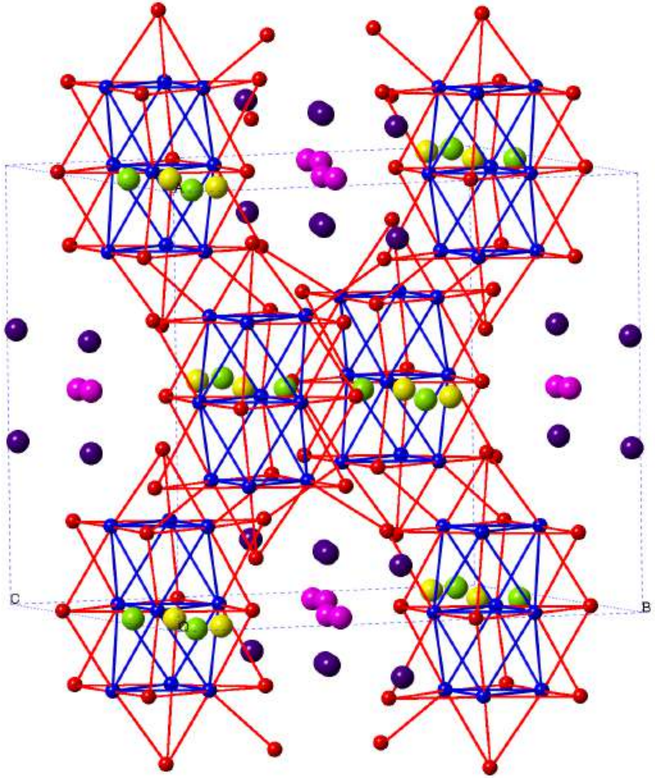
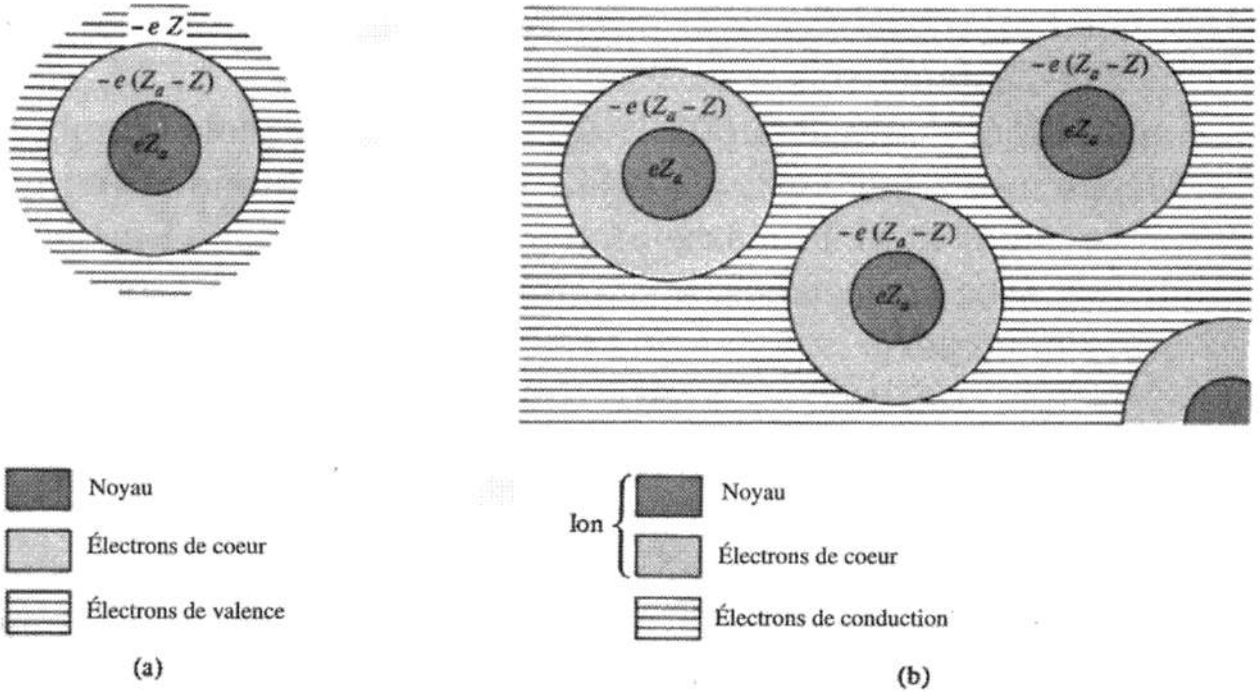


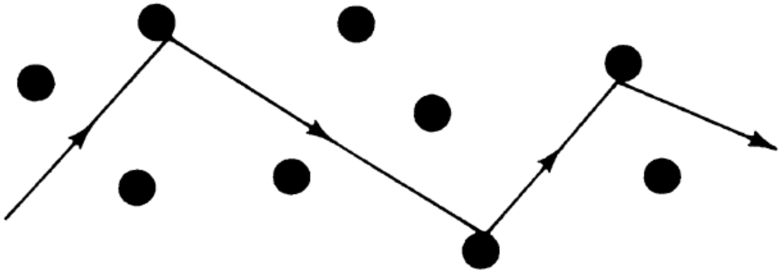
- 8 Ag_1 ●
- 4 Ag_2 ●
- 4 Ag_3 ●
- 8 Ag_4 ●

Drude theory of metals



➡ Valence electrons move freely: electron gas model

Drude theory of metals



Trajectory of conduction electron diffused by ions according to Drude

- porteurs de charge positive **immobiles** (// Born-Oppenheimer)
- approximation des **électrons indépendants**
- approximation des **électrons libres**
- les collisions sont des évènements **instantanés** ⇔ négligence des forces à longue portée
- probabilité qu'un électron subisse une collision dans l'intervalle de temps dt est égal à dt/τ avec τ appelé temps de **collision**, temps de **vol moyen** ou temps de **relaxation**.
- équilibre thermique des électrons atteint uniquement par le biais des collisions

Drude theory of metals

Thermal conductivity of metals

➡ Wiedemann-Franz law

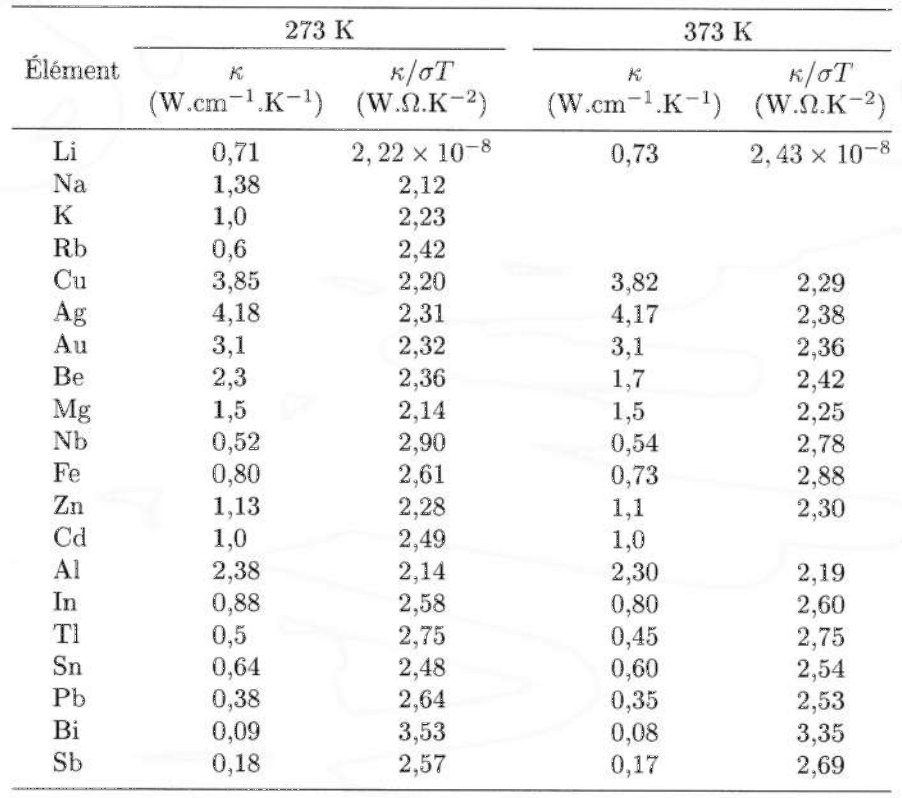
$$\frac{\kappa}{\sigma T} = cste$$

Lorenz number

κ : thermal conductivity

σ: electrical conductivity

T : temperature



Élément	273 K		373 K	
	κ (W.cm^{-1}.K^{-1})	$\kappa/\sigma T$ (W.Ω.K^{-2})	κ (W.cm^{-1}.K^{-1})	$\kappa/\sigma T$ (W.Ω.K^{-2})
Li	0,71	$2,22 \times 10^{-8}$	0,73	$2,43 \times 10^{-8}$
Na	1,38	2,12		
K	1,0	2,23		
Rb	0,6	2,42		
Cu	3,85	2,20	3,82	2,29
Ag	4,18	2,31	4,17	2,38
Au	3,1	2,32	3,1	2,36
Be	2,3	2,36	1,7	2,42
Mg	1,5	2,14	1,5	2,25
Nb	0,52	2,90	0,54	2,78
Fe	0,80	2,61	0,73	2,88
Zn	1,13	2,28	1,1	2,30
Cd	1,0	2,49	1,0	
Al	2,38	2,14	2,30	2,19
In	0,88	2,58	0,80	2,60
Tl	0,5	2,75	0,45	2,75
Sn	0,64	2,48	0,60	2,54
Pb	0,38	2,64	0,35	2,53
Bi	0,09	3,53	0,08	3,35
Sb	0,18	2,57	0,17	2,69

Source : G. W. C. Kaye et T. H. Laby, *Table of Physical and Chemical Constants*, Longmans Green, London, 1966.

Modeling Transport Properties: The Semi-Classical Approach

group velocity:

$$\vec{v}_{\vec{k}} = \frac{1}{\hbar}\frac{\partial \varepsilon_{\vec{k}}}{\partial \vec{k}}$$

transport distribution:

$$\Xi(\varepsilon) = \sum_{\vec{k}} \vec{v}_{\vec{k}} \vec{v}_{\vec{k}} \tau_{\vec{k}}$$

relaxation time

Seebeck coefficient:

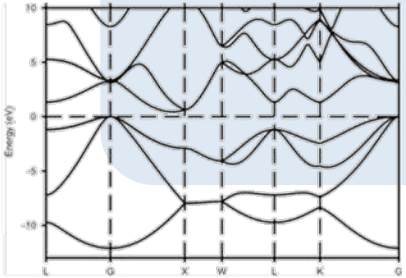
$$\alpha = \frac{ek_B}{\sigma}\int d\varepsilon\left(-\frac{\partial f_0}{\partial \varepsilon}\right)\Xi(\varepsilon)\,\frac{\varepsilon-\mu}{k_BT}$$

electrical conductivity:

$$\sigma = e^2\int d\varepsilon\left(-\frac{\partial f_0}{\partial \varepsilon}\right)\Xi(\varepsilon)$$

electronic thermal conductivity:

$$\kappa_e = k_B^2T\int d\varepsilon\left(-\frac{\partial f_0}{\partial \varepsilon}\right)\Xi(\varepsilon)\left[\frac{\varepsilon-\mu}{k_BT}\right]^2$$

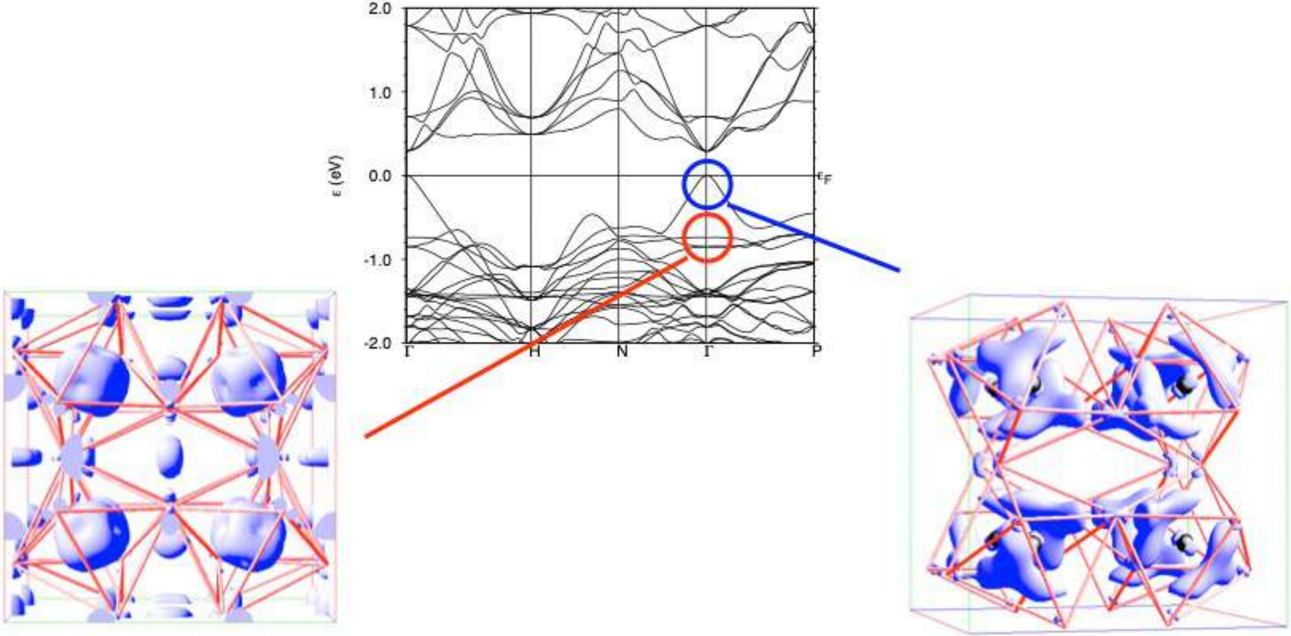


BoltzTraP software

G.K.H. Madsen, D.J. Singh *Comput. Phys. Commun.* **67** 175 (2006)

Wave packet velocity

Velocity of a wave packet: $\mathbf{v}_{n\mathbf{k}} = \frac{1}{\hbar}\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial \mathbf{k}}$



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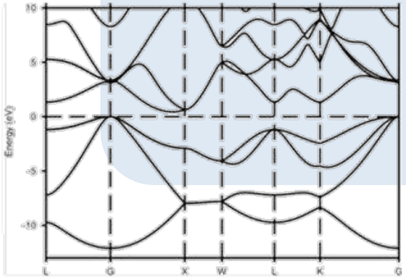

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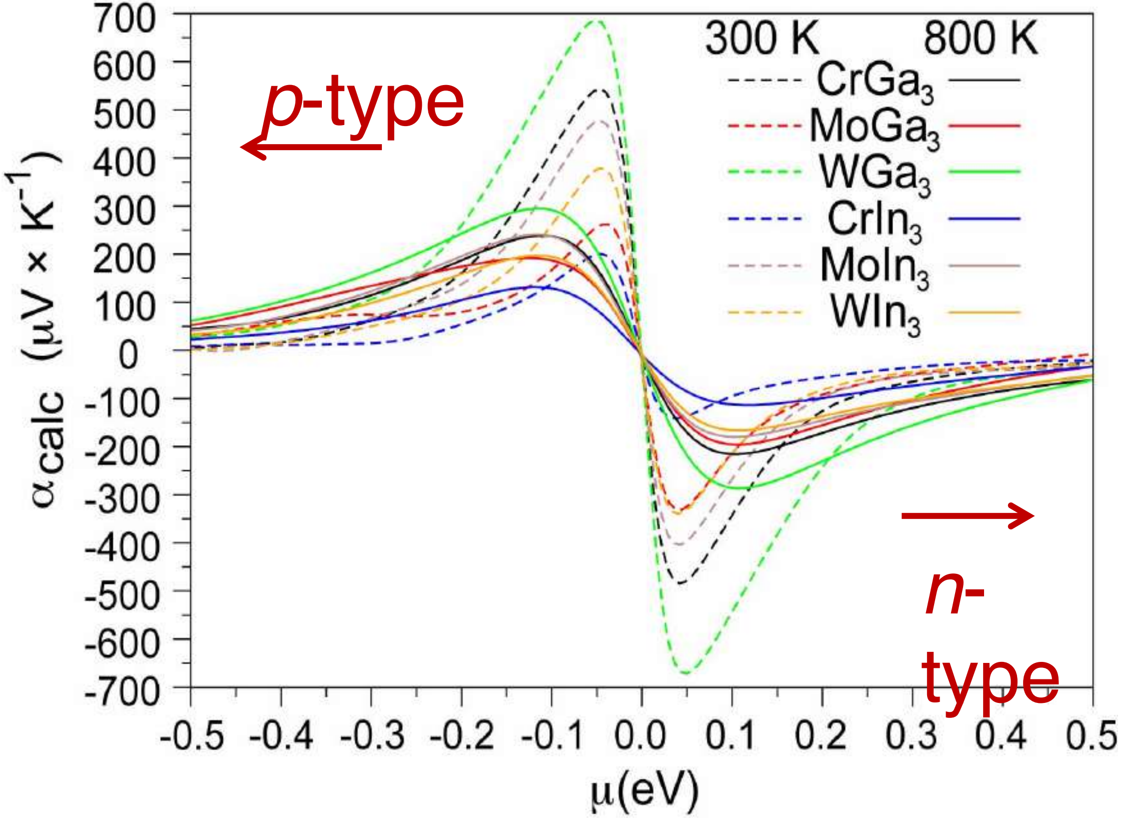
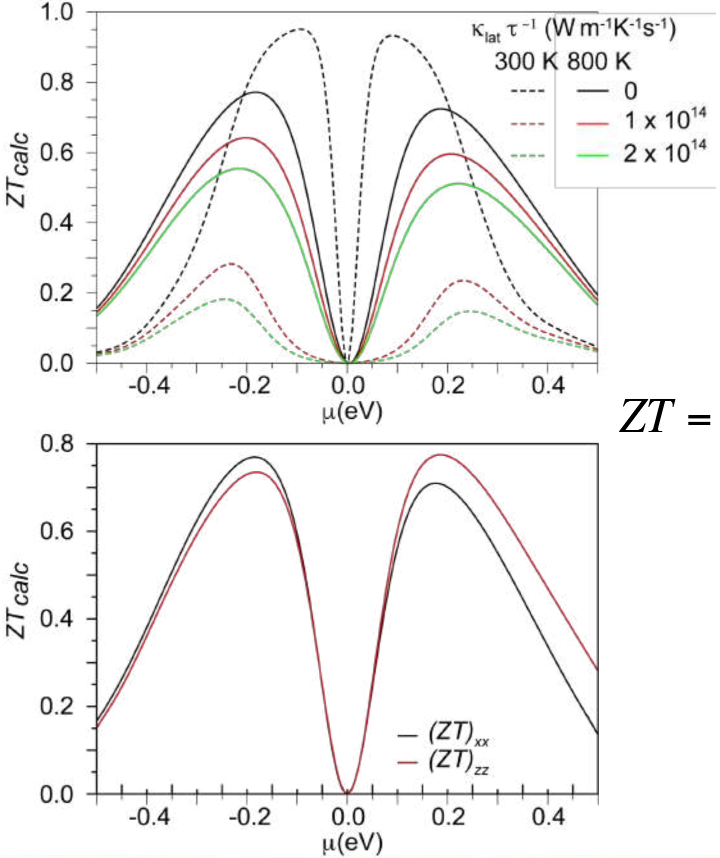
Electrical transport properties

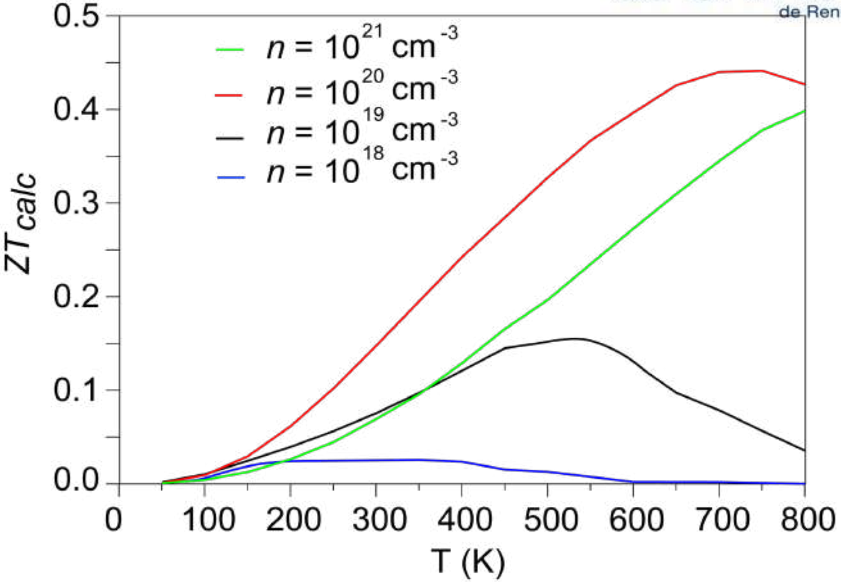


Inorg. Chem. 56, 4229 (2017)

Electrical transport properties



$$ZT = \frac{\alpha^2 \dfrac{\sigma}{\tau}}{\dfrac{\kappa_e}{\tau} + \boxed{\dfrac{\kappa_{lat}}{\tau}}} T$$



Set at $\frac{\kappa_{lat}}{\tau} = 2 \times 10^{14}$ W/(mKs)

Inorg. Chem. 56, 4229 (2017)

Main codes

https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software