Introduction To Density Functional Theory (DFT)

Speaker: Dr. Christophe A. Adessi

Institut Lumière Matière (ILM)
"Light & Matter Institute"

Université Claude Bernard Lyon 1 (UCBL1)

email : christophe.adessi@univ-lyon1.fr

Outlines

- Empirical vs ab initio calculations
- The many-body issue
- Hartree-Fock
- Density Functional Theory (DFT)
  - The energy a functional of the density
  - Variational principle for the density
  - The Kohn-Sham approach and the "eigenvalues"
  - The Local Density Approximation (LDA)
  - Generalized Gradient Approximatiom (GGA)
  - Self-consistency
- Pseudopotentials
- Cell and atomic structure optimization
- Application: Phonon calculation using DFT

Empirical vs ab initio calculations

Empirical approaches:

- Interaction between two atoms described by an explicit function of their positions (ex: Lennard-Jones, 1922): $V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$ where σ and ϵ are adjusted to reproduce experimental interatomic distances, vibrational frequencies, etc.

- Semi-empirical description of the hamiltonian for the electronic problem (tight-binding, Hückel, etc.)

Question: can the same parameters describe diamond, graphite, nanotubes and fullerenes? In the case of inaccessible systems (earth center, new materials, etc.) which parameters do we use?

First principle approaches:

The aim is to calculate structural, dynamical, electronic response properties without any adjustable parameters using basic physical quantities (mass, charge ...) and fundamental equations.

First principle for electrons: $H\,\Psi = E\Psi$

$$H = -\frac{\hbar^2}{2m}\sum_i^N \nabla_i^2 - \underbrace{\frac{e^2}{4\pi\epsilon_0}\sum_i^N\sum_I^{ions}\frac{Z_I}{|R_I - r_i|}}_{e^- - Ions} + \underbrace{\frac{e^2}{4\pi\epsilon_0}\sum_{j\neq i}^N\frac{1}{|r_j - r_i|}}_{e^- - e^-} \tag{1}$$

Born-Oppenheimer approximations, $M \gg m$: We separate the ions dynamic from electrons.

We assume the nuclei are fixed and we compute the electronic wave function. The nuclei motion is dissociated from the electronic wave function.

- $\Psi_0(r_1\,, ..., r_N)$ is antisymmetric with respect to electron interchange.
- $|\Psi_0(r_1\,, ..., r_N)|^2 dr_1..dr_N$ probability of finding electron i in $[r_i, r_i + dr_i]$
- $\rho(r) = \sum_i \langle \Psi_0 | \delta(r - r_i) | \Psi_0 \rangle$ charge density
- Ground state energy: $E_0 = \iiint \Psi_0^*(r_1\,, ..., r_N)\, H\, \Psi_0(r_1\,, ..., r_N) dr_1 ... dr_N$

Problem: We don't know Ψ_0. We could use variational principle. Howerver calculating E_0 would require $(ngrid)^{3N} \simeq 10^{30}$ operations!

The Hartree Fock Approximation

Variational approach with exact Hamiltonian but approximate wave function $i.e.$ a single Slater determinant (Pauli principle):

$$\begin{aligned}\Psi(r_1\,,...,r_N) &= \frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(r_1) & \cdots & \phi_N(r_1)\\ \vdots & \ddots & \vdots\\ \phi_1(r_N) & \cdots & \phi_N(r_N)\end{vmatrix} \\ &= \frac{1}{\sqrt{N}}\sum_P(-1)^{\epsilon(P)}\phi_{P(1)}(r_1)...\phi_{P(N)}(r_N)\end{aligned} \tag{2}$$

$$\text{Ground State Energy: } E_0^{HF} = -\frac{\hbar^2}{2m}\sum_i^N\langle\phi_i|\nabla_i^2|\phi_i\rangle + \sum_{i,j}(J_{i,j}-K_{i,j}) \tag{3}$$

$$J_{i,j} = \int drdr'\frac{|\phi_i(r)|^2|\phi_j(r')|^2}{|r-r'|} \text{ and } K_{i,j} = \int drdr'\frac{\phi_i^*(r)\phi_j(r)\phi_i^*(r')\phi_j(r')}{|r-r'|} \tag{4}$$

where $J_{i,j}$ and $K_{i,j}$ are the classic Coulomb (or Hartree) potential and the quantum exchange (Fock) term. However, it misses a key quantity **the correlation**. The instantaneous correlations between the electronic motions are not taken into account. This leads to nonzero probabilities of finding two electrons occupying simultaneously the same point of the space: $E_{HF} > E_{exp}$

The Density Functional Theory (DFT)

The central idea is that the ground-state energy is a functional of the charge density: $E[\Psi] \rightarrow E[\rho]$

Hohenberg & Kohn (nobel prize 1998)

Theorem 1: For a given $\rho(r)$, there exists only one external potential $V_{ext}(r)$ that can realize $\rho(r)$. The proof comes from *reducio ad absurbum*.

Reminder: $V_{ext}(r_i) = -\frac{e^2}{4\pi\epsilon_0} \sum_{I}^{ions} \frac{Z_I}{|R_I - r_i|}$

E is therefore a functional of ρ:

$$\begin{cases} E[\rho] &= \int d^3r\, V_{ext}(r)\rho(r) + F_{HK}[\rho] \\ F_{HK}[\rho] &= \underbrace{T[\rho]}_{kinetic} + \underbrace{V[\rho]}_{e-e} \end{cases} \quad (5)$$

Problem: F_{HK} is a universal functional of ρ. However, we do not know F_{HK}.
There are numerous (unsatisfactory) approaches to find F_{HK} (Thomas, Fermi, Slater, Dirac ...)
Theorem 2: Given a test density ρ^{test} then $E[\rho^{test}] \geq E_{GS}$.
This implies that it is possible to find by minimization $\rho(r)$ which gives the Ground State energy E_{GS}.

The Kohn and Sham (KS) approach

The most successful approach is to come back to an "exact" expression for the kinetic energy T by re-introducing **one-body orbitals** $\{\Phi_i(r)\}$.

$$T_0 = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int dr \Phi_i^*(r)\nabla^2\Phi_i(r) \text{ and } \rho(r) = \sum_{i=1}^{N} f_i|\Phi_i(r)|^2 \tag{6}$$

To do that, KS introduce a fictitious equivalent system of non-interacting electrons under the action of an effective external potential V^{eff} generating the same density $\rho(r)$ that the real system.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V^{eff}(r)\right]\Phi_i = \epsilon_i\Phi_i\,, \quad V^{eff}(r) = V^{ions}(r) + V^{H}(r) + \underbrace{\frac{\partial E_{XC}[\rho]}{\partial\rho(r)}}_{Ex.-Corr.} \tag{7}$$

where $E_{XC}[\rho] = T[\rho] - T_0[\rho] + V[\rho] - J[\rho]$. Determining E_{XC} have less detrimental effects than a direct approximation of $T[\rho]$.

Remark: the exchange-correlation energy contains some correction to the kinetic energy, not solely the deviation $(V[\rho] - J[\rho])$ from the electron-electron interaction to the classical Hartree term.

The Local Density Approximation

$$\begin{aligned} E_{XC}[\rho] &= \int dr\, \rho(r)\epsilon_{XC}(r)\,, \\ V_{XC}^{\mathsf{LDA}}(r) &= \frac{\partial E_{XC}[\rho]}{\partial \rho} \\ &= \epsilon_{XC} + \rho\frac{\partial \epsilon_{XC}}{\partial \rho} \end{aligned} \tag{8}$$

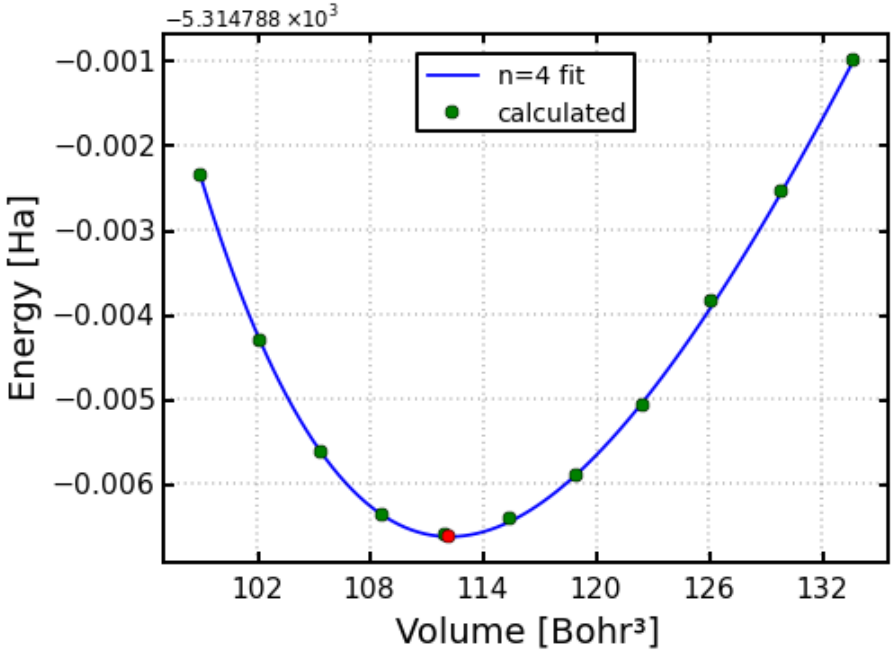
It assumes that the exchange-correlation energy per electron ϵ_{XC} for an electron located in r only depends on the local value of the electronic density $\rho(r)$. It is only rigorous for homogeneous gas. Surprisingly, LDA gives rather accurate results even for solid with very inhomogeneous density.

For weakly correlated materials, such as semiconductors and simple metals, the LDA accurately describes structural and vibrational properties.

Famous parametrization:

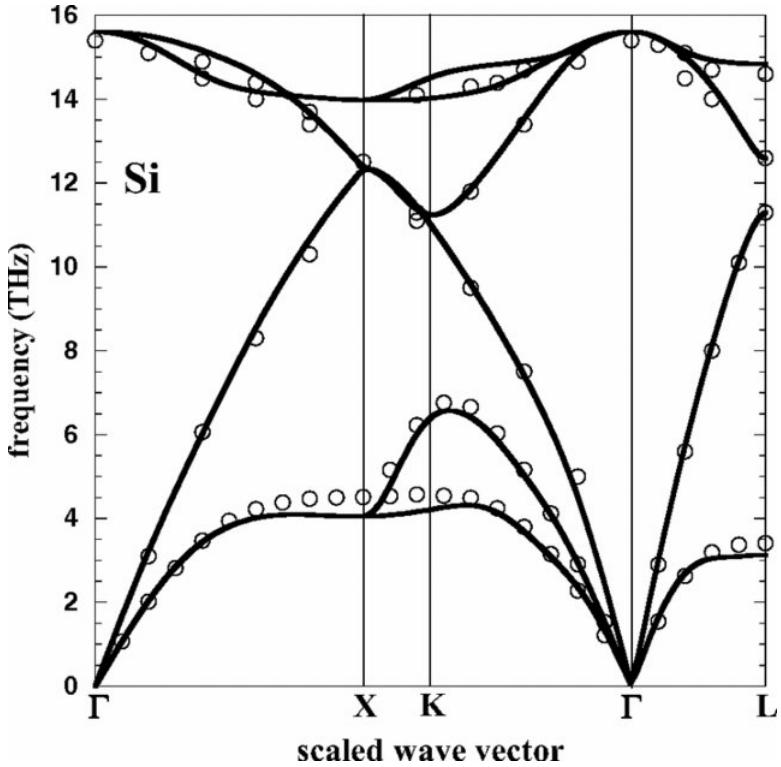
- PZ: Perdew-Zunger, PRB 23, 5048 (1981) Obtained from Quantum Monte Carlo calculation on homogeneous electron gas done by Ceperley-Alder, PRL 45,566 (1980)

- PW: Perdew-Wang, PRB 45, 13244 (1992)



http://exciting.wikidot.com/beryllium-volume-optimization-for-cubic-systems

Cell optimization for Silver (Ag) and comparison withe the experimental cell volume.



L. Lindsay *et al.* PRB 87.165201, 2013

Phonon dispersion for Si and comparison with experimental frequencies.

Generalized Gradient Approximation

To go beyond the locality of LDA, one step is to introduce "gradient corrections:

$$V_{XC}^{GGA}[\rho, s] \text{ with } s = \frac{\nabla \rho}{k_F \rho}. \tag{9}$$

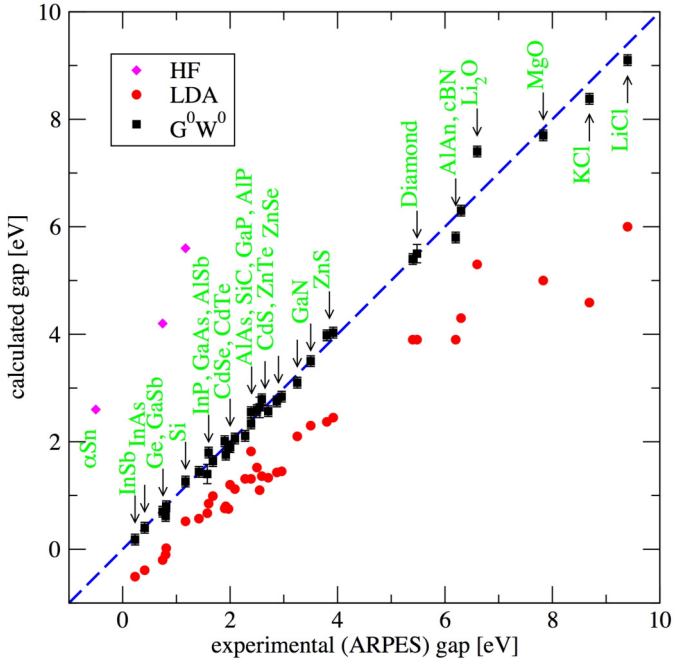
Famous parametrization:

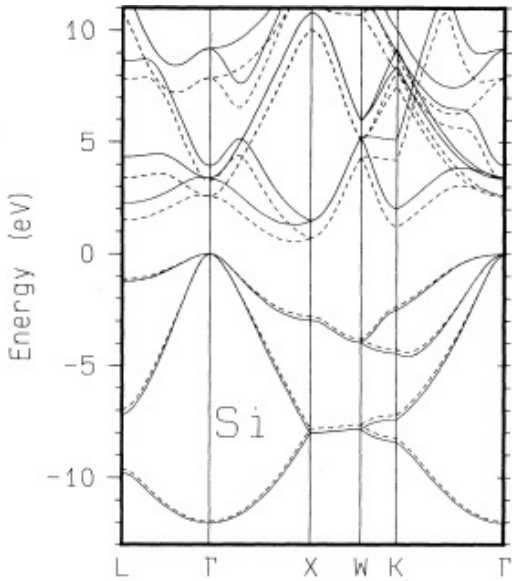
- PW91: Perdew, Wang PRB45, 13244 (1992)

- PBE: Perdew, Burke, Ernzerhof, PRL 77, 3865 (1996)

Rule of thumb: LDA tends to underestimate bond lengths, and overestimate binding energies and bulk modulus. The GGA functionals do ... the contrary!

The band gap issue: The band gap of standard semiconductors and insulators. DFT calculations using the LDA XC potential underestimate the band-gap and similar results are obtained with GGA XC.





M. Rohlfing, *et al.* Phys. Rev. B 48, 17791 (1993)

The Self Consistent Field cycle

DFT gives the ground state energy of a system based on an effective potential.

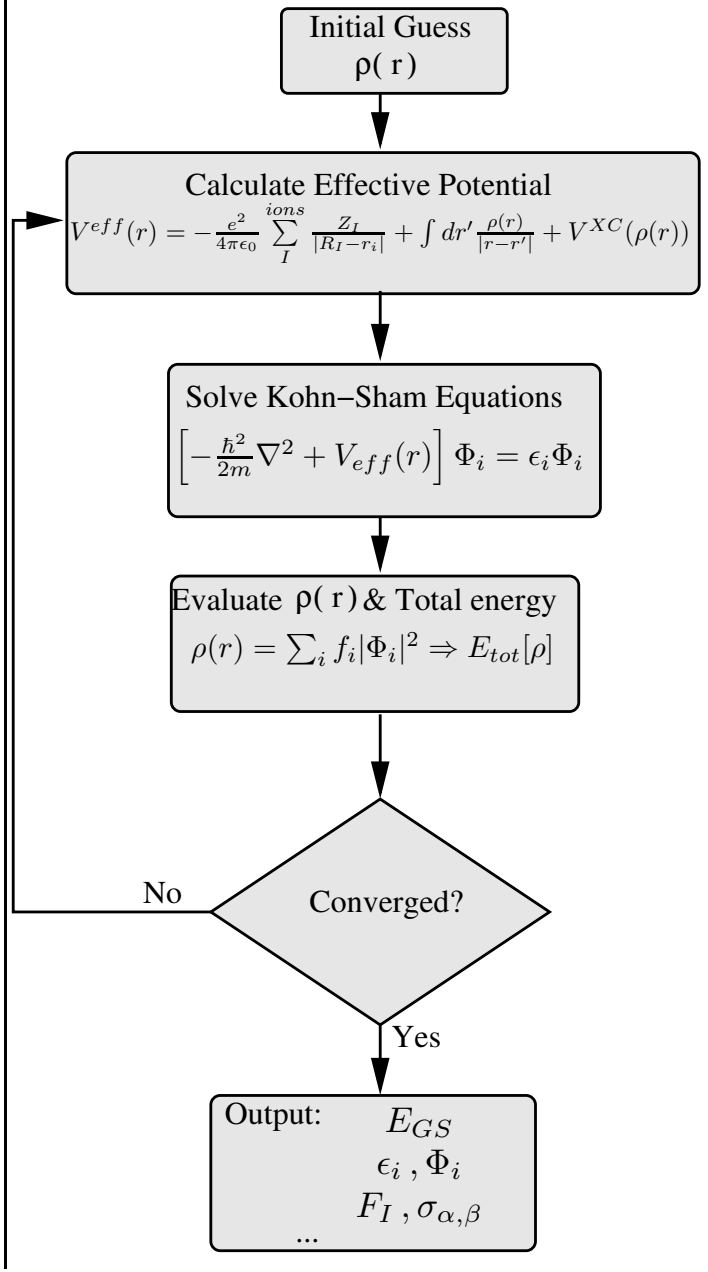
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V^{eff}(r)\right]\Phi_i = \epsilon_i \Phi_i \tag{10}$$

$$\begin{aligned} V^{eff}(r) &= -\frac{e^2}{4\pi\epsilon_0}\sum_{I}^{ions}\frac{Z_I}{|R_I - r_i|} \\ &\quad + \int dr' \frac{\rho(r)}{|r-r'|} + V^{XC}(\rho(r)) \end{aligned} \tag{11}$$

$$\rho = \sum_{i=1}^{N} f_i |\Phi_i|^2$$

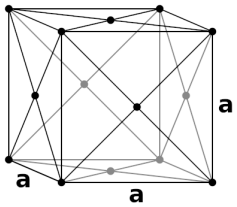
We need ρ to compute V^{eff}, to solve the KS equation and obtain the eigenvalues ϵ_i and eigenvectors Φ_i which gives ρ!

The initial guess for ρ is usually atomic ground states configuration.
A mixing is mandatory during the SCF cycle:
$\rho_{new} = x.\rho_{old} + (1-x)\rho_n$

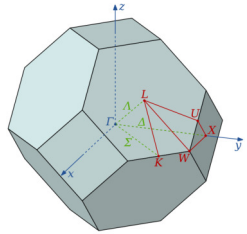


Solving the KS equation for solid

For a periodic solid (characterised by its primitive cell), Φ must fullfill the Block's Theorem:



$$\Phi(r) = e^{ik.r}.u(r) \qquad (12)$$



where the wave vector k lies within the First Brillouin Zone and $u(r)$ a periodic function. It is straightforward to expand the periodic function $u(r)$ using Fourier series:

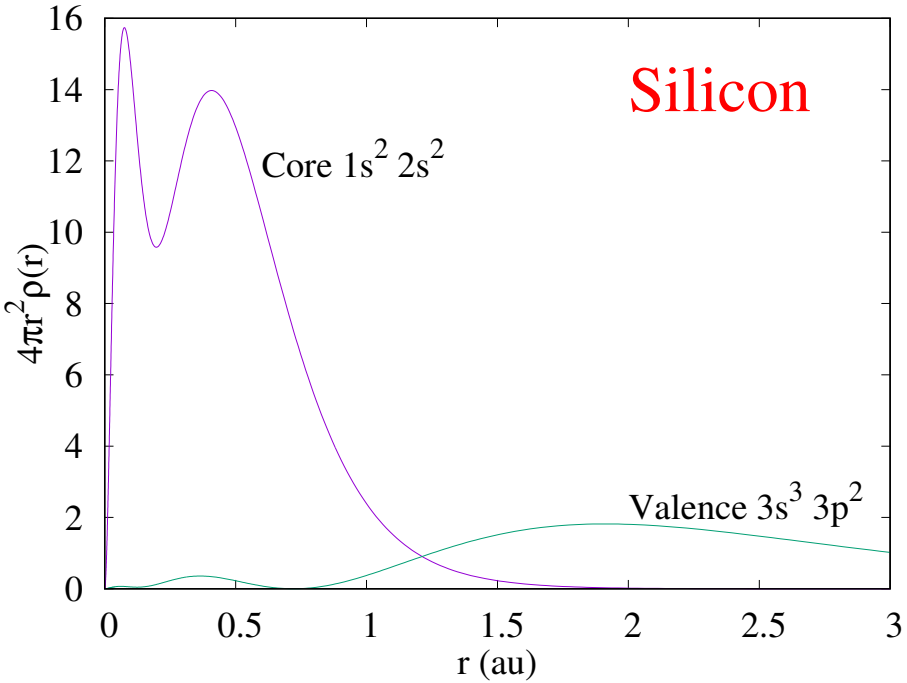
$$u(r) = \frac{1}{\sqrt{\Omega}} \sum_G c_G \, e^{iG.r} \quad \Longleftrightarrow \quad \Phi(r) = \frac{1}{\sqrt{\Omega}} \sum_G c_G \, e^{i(k+G).r} \qquad (13)$$

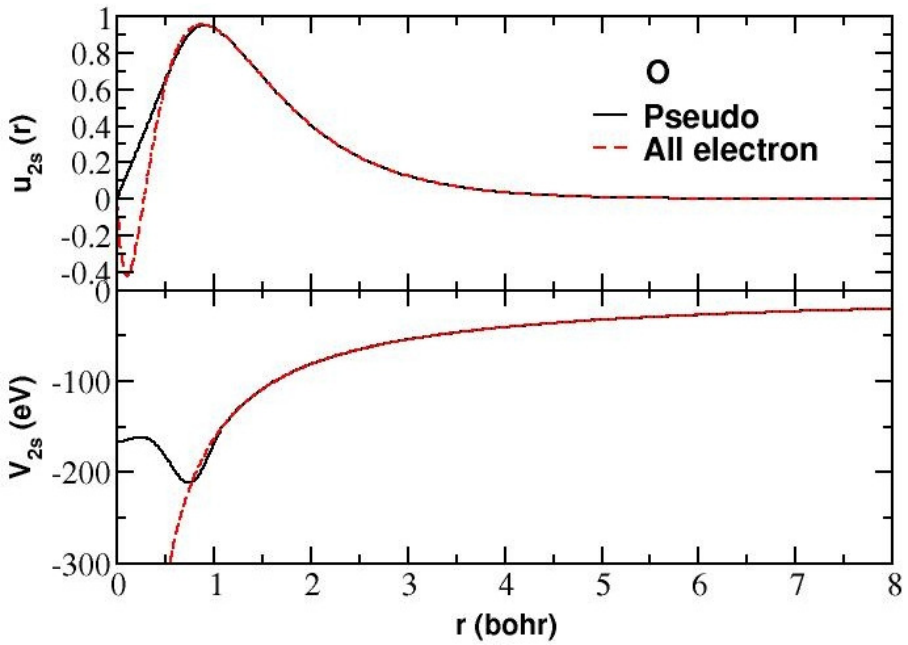
Remark: This expansion requires to define a Cut Off: $\frac{\hbar^2}{2m} G_{Max}^2 \leq E_{cut}$

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\Phi(r) + V^{eff}(r)\Phi(r) = \epsilon\Phi(r) \Leftrightarrow \left[\frac{\hbar^2}{2m}(k+G)^2 - \epsilon\right] C_G + \sum_{G'} U_{G-G'}.C_{G'} = 0 \qquad (14)$$

- The KS equation becomes an eigenvalue problem easely solved numerically.
- The KS equation It must be solved for some given sampling of the FBZ: Monkhosrt k points sampling.

Dealing with core electrons





Core electrons are highly localized at very depth energies and thus may be considered as chemically inert.

Rapid variation of the density close to the core ⇒ increase the plane wave cut-off.

We replace the effects of core electrons by an effective potential:
The Pseudopotential.
The requirement is that the pseudo wave-functions must be identical to the all-electron wave functions.

Famous Pseudopotentials:

- The norm conserving pseudo potential. Fullfill the norm conservation of the charge inside a given radius.

- The ultra soft pseudopotential. Release norm conservation to obtain smoother wave function using a core augmentation charge.

Remarks:
The pseudo divide into a local and non local term:

$$V_{PS} = V_{loc}(r) + \sum_{lm} \delta V_l(r) Y_{lm}(\theta', \phi') Y_l m(\theta, \phi) \tag{15}$$

Due to the non locality of the XC (overlap of core and valence electrons) it may be required to add non-linear core corrections.

The pseudo is usually defining, for the SCF cycle, the XC functionnal.

Forces and Structure Optimization

Reminder: Born Oppenheimer approximation: We separate Hamiltonian into a nulcear and electronic part.

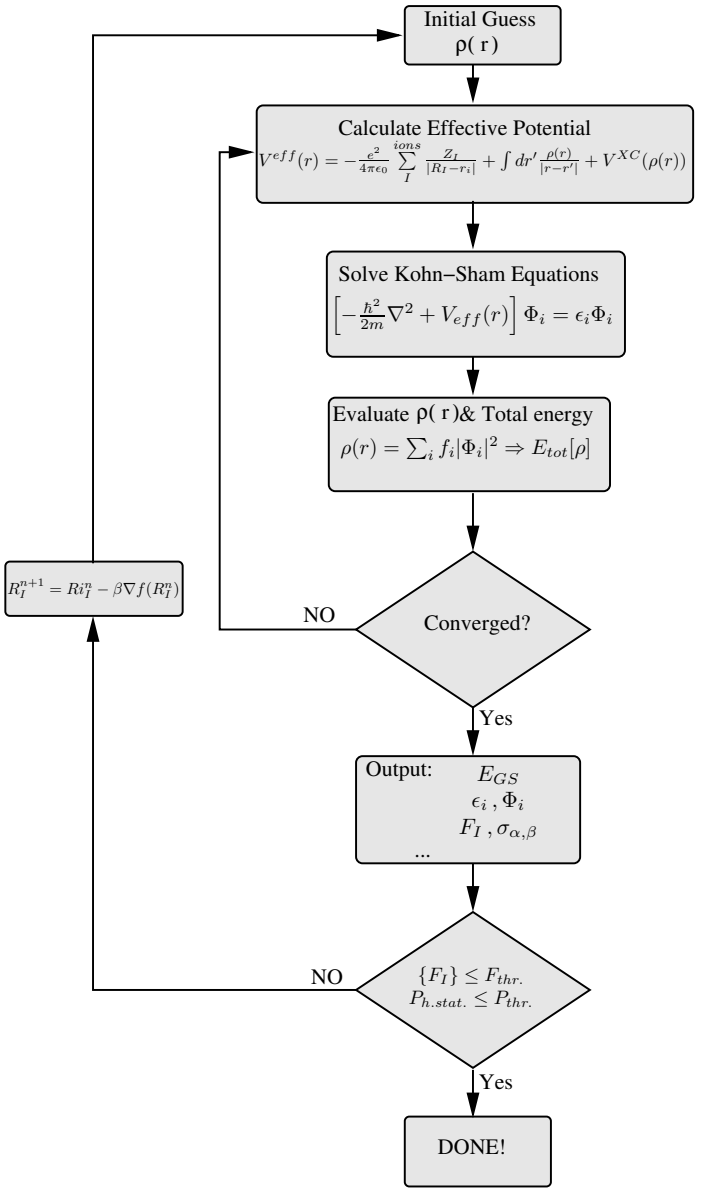
From Ground State energy we may extract forces on atoms (Hellmann-Feynman theorem):$F_I = -\frac{\partial E}{\partial R_I}$

Remark: If ϕ is not an exact eigenstate (no satisfactory convergence) may get big errors in forces!

We need a procedure to optimize the attomic structure and/or the unit cell $\Rightarrow$ minimization of the forces and/or the stress.

Famous Methods:

- SD: Steepest Descent.
- CG: Conjugated Gradient.
- BFGS: Quasi-Newton algorithm (Broyden, Fletcher, Goldfarb, Shanno)
- FIRE: Fast Inertial Relaxation Engine Euler integration scheme
- Carr-Parrinelo: Molecular Dynamics



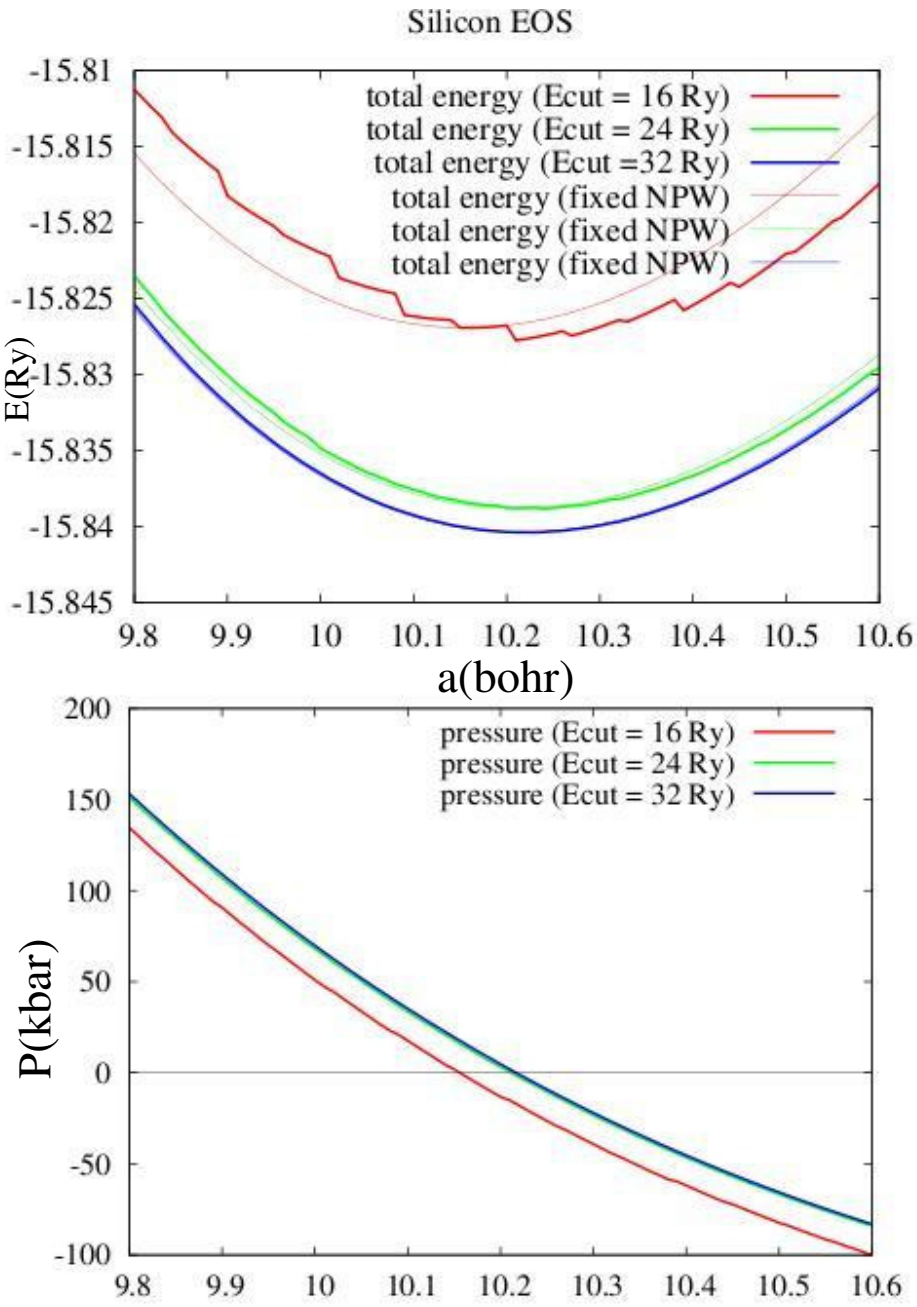
Remark:

- Structural optimization may be trapped in a local minimum. It cannot overcome potential barriers.
- An optimization under strain ($\epsilon_{\alpha\beta}$) may be done.

The stress is defined as $\sigma_{\alpha\beta} = -\frac{1}{\Omega}\frac{\partial E}{\partial \epsilon_{\alpha\beta}}$.

Hydrostatic Pressure: $P = -\frac{1}{3}Tr(\sigma)$
Bulk Modulus (B_0) using phenomenological Murnaghan equation of state:

$$
\begin{aligned}
P(V) &= \frac{B_0}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'} - 1\right] \\
P(V) &= -\frac{\partial E}{\partial V} \\
E(V) &= E(V_0) + \frac{B_O.V}{B_O'}\left[\frac{V_O/V)^{B_0'}}{B_0'-1} + 1\right] \\
&\quad -\frac{B_0.V_0}{B_0'-1}
\end{aligned}
\tag{16}
$$



Phonon calculations

Phonons frequencies ω and eigenvectors u can be determined under the harmonic approximation using the secular equation:

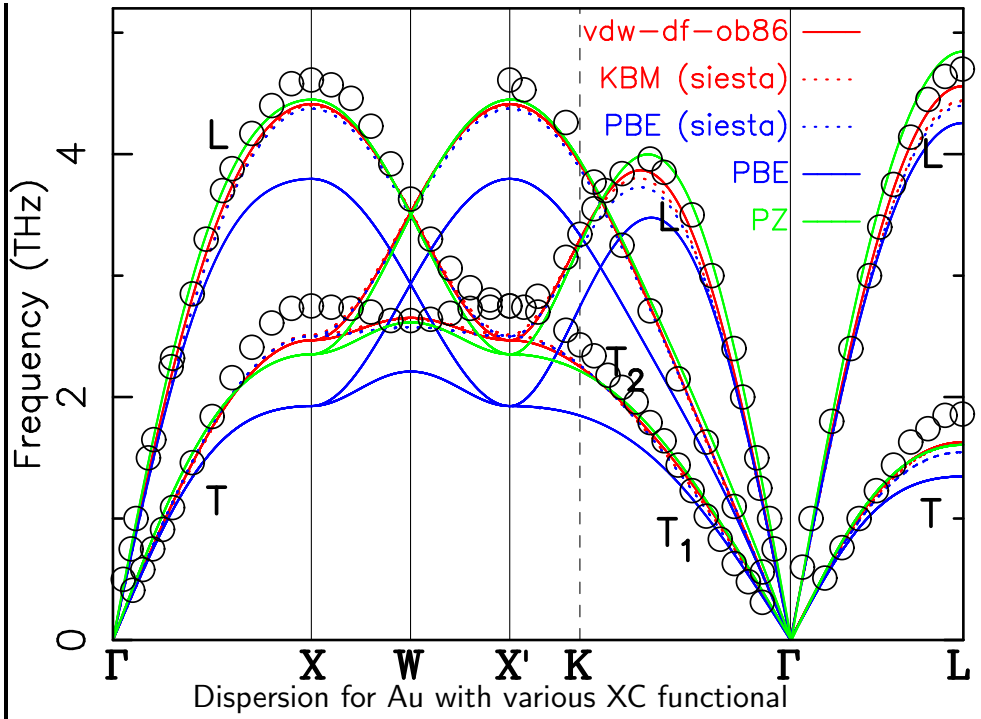
$$\sum_{j,\beta} D_{i,j,\alpha,\beta}(q)\, u_{j,\beta}(q) = \omega^2\, u_{i,\alpha}(q)\,,$$

$$D_{i,j,\alpha,\beta}(q) = \frac{1}{\sqrt{M_i M_j}} \sum_R \underbrace{\frac{\partial^2 E}{\partial u_{i,\alpha} \partial u_{R(j),\beta}}}_{C_{i,\alpha,j,\beta}} e^{iq.R}\,.$$

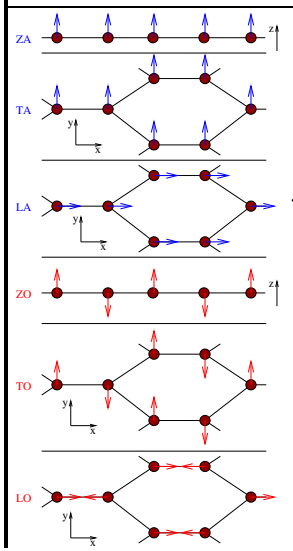
$D_{i,j,\alpha,\beta}(q)$ is the Dynamical matrix.
$C_{i,\alpha,j,\beta}$ are the Inter Atomic Force Constants.

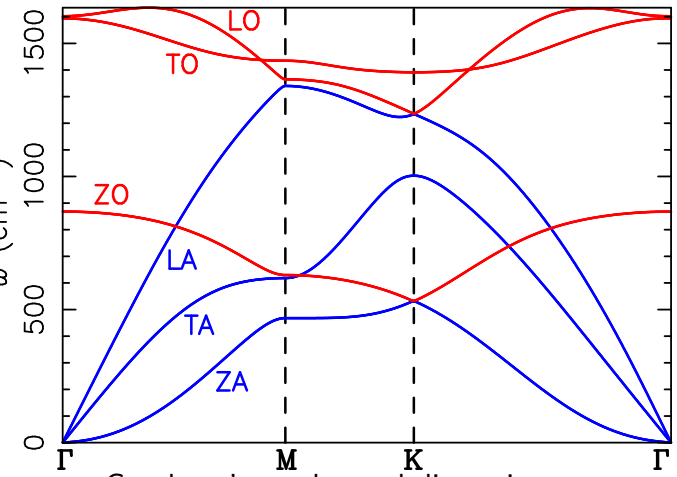
Remarks:

- IFC must satisfy translational invariance (or acoustic sum rule) : $\sum_{j\neq i} C_{i,\alpha,j,\beta} = C_{i,\alpha,i,\beta}$
- Imaginary modes ($\omega^2 < 0$) corresponds to unstable (or stressed) system.
- For polar materials, a macroscopic electric field appears as a consequence of the long-range character of the Coulomb interaction. A non-analytical term must be added.



Dispersion for Au with various XC functional





Graphene's modes and dispersion

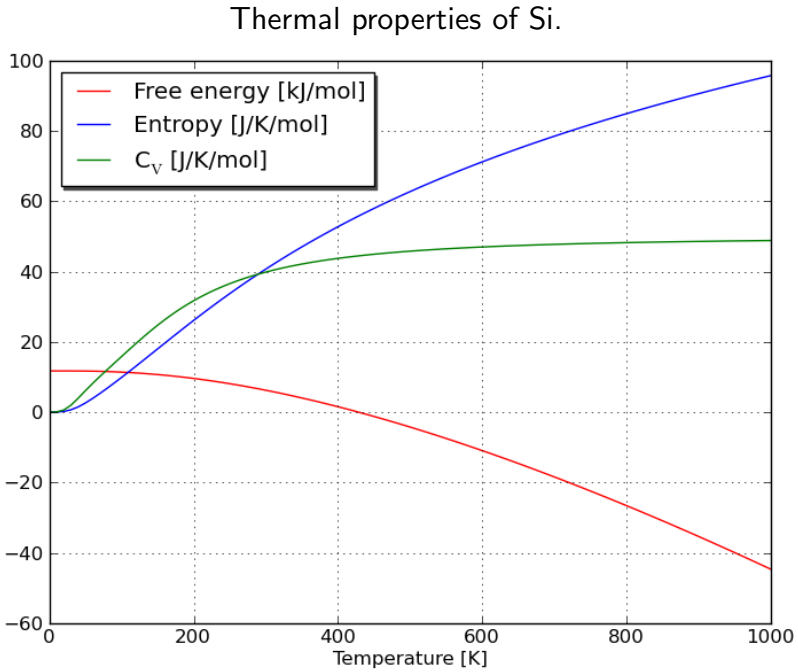
Computing the IFC:

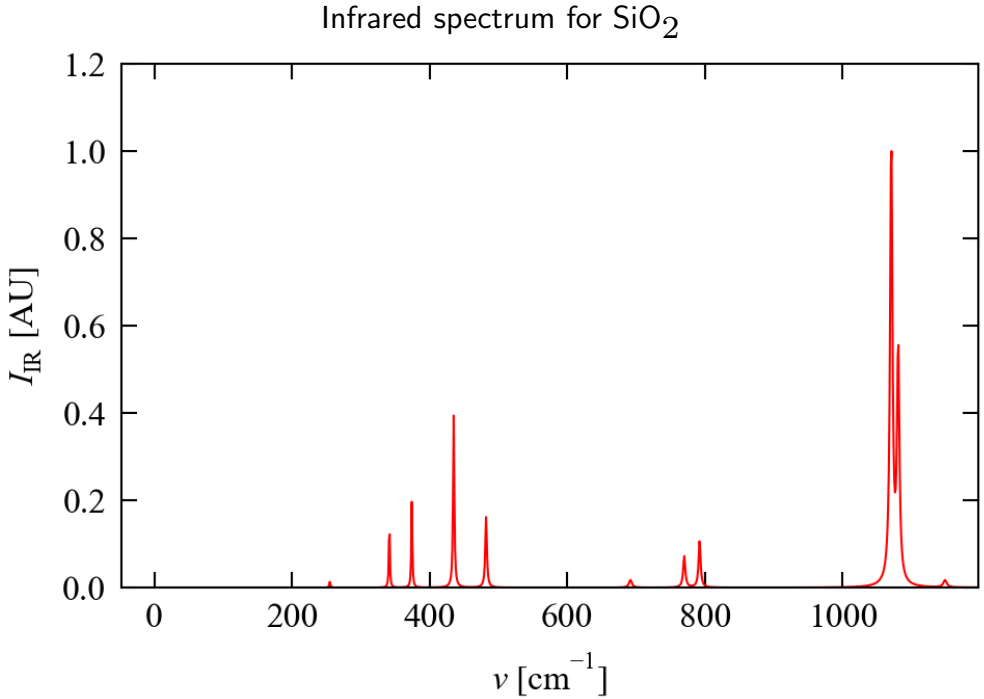
- The finite displacement method:
  - Direct calculation of the Forces $F_{i,\alpha}$.
  - From $F_{i,\alpha}$,the IFC are computed by finite difference using a small displacement δ $C_{i,\alpha,j,\beta} = -\frac{\partial F_{i,\alpha}(u)}{\partial u_{j,\beta}} \simeq \frac{F_{i,\alpha}(u+\delta) - F_{i,\alpha}(u-\delta)}{2\delta}$
  - Require a supercell (multiple of the unit cell)
  - PHONOPY: https://phonopy.github.io/phonopy/
- From density perturbation theory by means of linear response: $\frac{\partial \rho}{\partial u_{i,\alpha}}$.
  - Gives direct access to $D_{i,j,\alpha,\beta}(q)$
  - Must perform FFT^{-1} to obtain the IFC

For both methods, a large number of q points or supercell is mandatory.
Si Bulk: $(n_{q1} = 4, n_{q2} = 4, n_{q3} = 4)$ or supercell $(4 \times 4 \times 4)$

Remark: The harmonic approximation do not allow to have access to phonon lifetime $i.e.$ the thermal conductivity needs anharmonic terms $C^{an}_{i,\alpha,j,\beta,k,\gamma}$ (PHONO3PY, ShengBTE).

Physical properties from harmonic phonon calculations:





Specific Heat: $C_V = \left(\frac{\partial E}{\partial T}\right)_V$
Free Energy: $F = -k_B T \ln Z$

Group Velocity: $v = \nabla_q \omega(q)$
Gruneisen parameter: $\gamma = -\frac{V}{\omega}\frac{\partial \omega}{\partial V}$

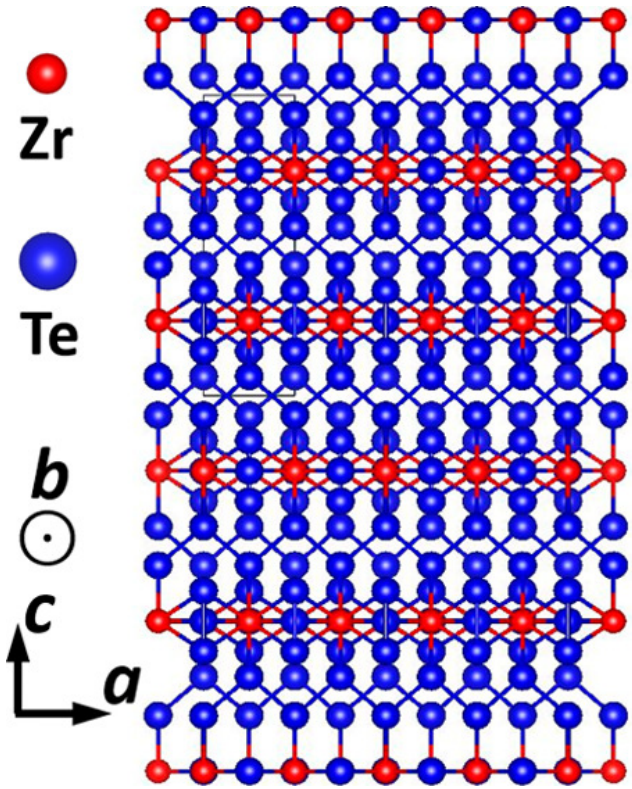
Physical properties from anharmonic phonon calculations:

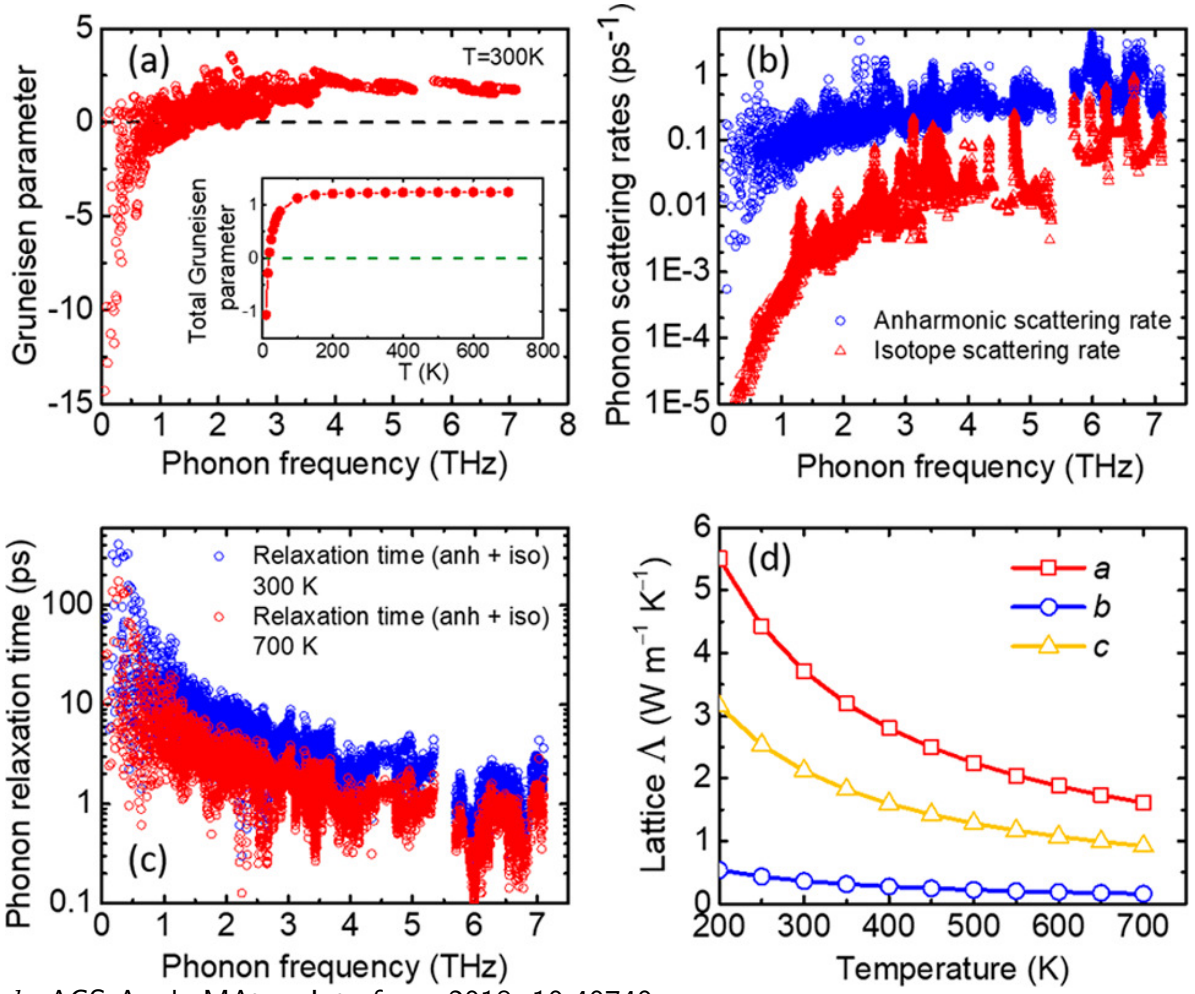
Thermal conductivity tensor using Boltzmann transport equation:

$$\kappa_{\alpha,\beta} = \frac{1}{V}\sum_q \left(\frac{\partial n_{be}}{\partial T}\right) \hbar\omega(q) v_q^\alpha v_q^\beta \tau(q) \qquad (17)$$

n_{be} is the Bose-Einstein distribution, v_i the group velocity and τ_i the lifetime.

Gruneisen parameter, scatering rates, lifetine and thermal conductivity for $ZrTe_5$:





Jie Zhu *et al.*, ACS Appl. MAter. Interfaces 2018, 10,40740

Thank you
For your attention!