Introduction to the Theory of Lattice Vibrations and their Ab Initio Calculation

Lecture 1: Electrons and Ions in Solids

Ion Errea

Dept. Applied Physics, University of the Basque Country (UPV/EHU),
San Sebastian, Spain

Centro de Fśica de Materiales (CSIC-UPV/EHU), San Sebastian, Spain

Donostia International Physics Center,
San Sebastian, Spain

University of Science and Technology Beijing

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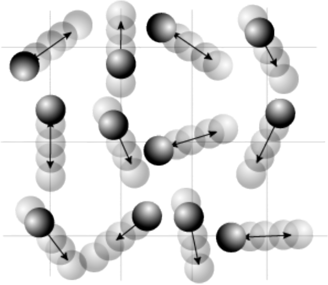

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Universidad del País Vasco
Euskal Herriko Unibertsitatea

Materialen Fisika Zentroa
Materials Physics Center
Centro de Física de Materiales

Donostia International Physics Center

Outline

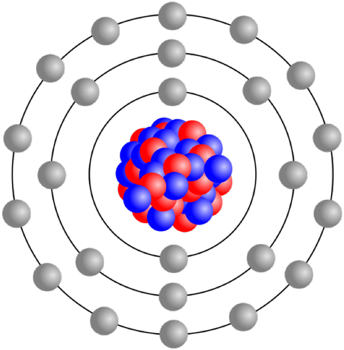
1. The atomic structure of solids
    - Bravais lattices
    - The reciprocal lattice
    - X-ray diffraction
2. Intrinsic ionic quantum fluctuations
3. The system full Hamiltonian
    - The Born-Oppenheimer approximation
4. The electronic problem
    - Single particle Hamiltonians
    - Density-functional theory
    - Pseudopotentials
    - Bloch's theorem
    - Numerical details of DFT calculations
5. Exercises

The atom

"If we were to name the most powerful assumption of all, which leads one on and on in an attempt to understand life, it is that all things are made of atoms, and that everything that living things do can be understood in terms of the jigglings and wigglings of atoms"

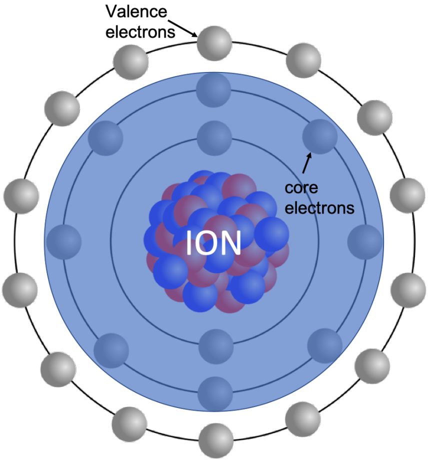
Richard P. Feynman

- Atoms are the unit of matter
- Atoms bind together and form all forms of matter
- Consists of a very small nucleus formed by neutrons and protons that has all the mass of the atom and orbiting electrons around it
- Electrons obey quantum mechanics

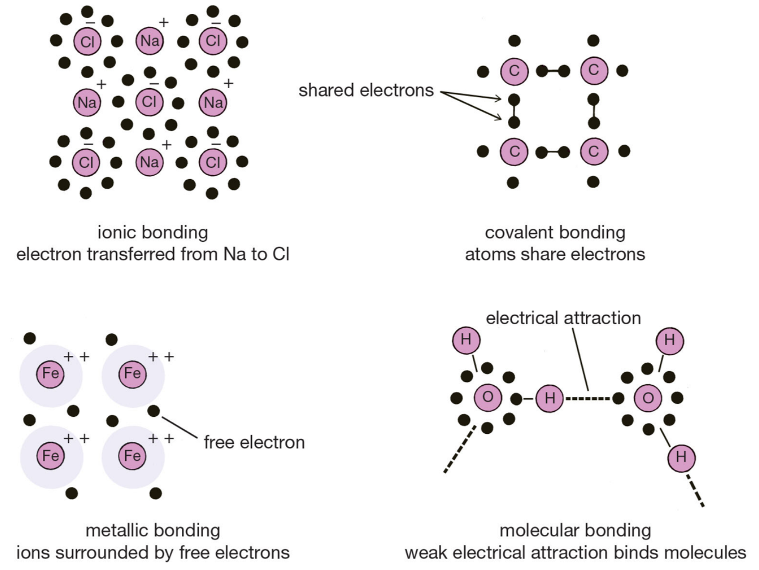


Valence electrons and ions

- Core electrons do not play any role in the bonding of atoms
- Core electrons and the nucleus form the ions
- The bonding of atoms is due to the interaction between valence electrons and ions
- The units for the study of matter are thus (valence) electrons and ions



Bonding types



ionic bonding
electron transferred from Na to Cl

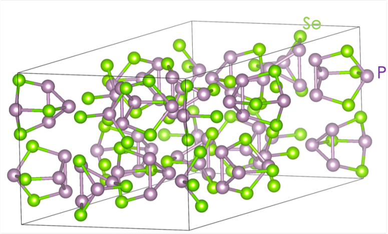
covalent bonding
atoms share electrons

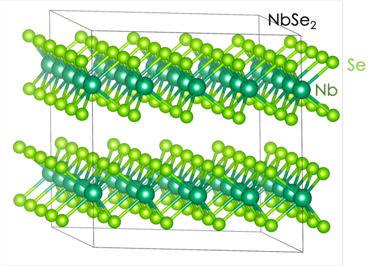
metallic bonding
ions surrounded by free electrons

molecular bonding
weak electrical attraction binds molecules

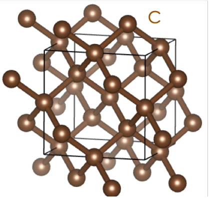
Different type of compounds

P_4Se_3

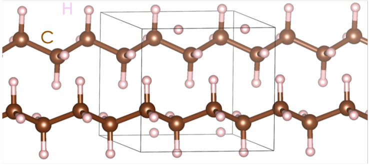




Diamond

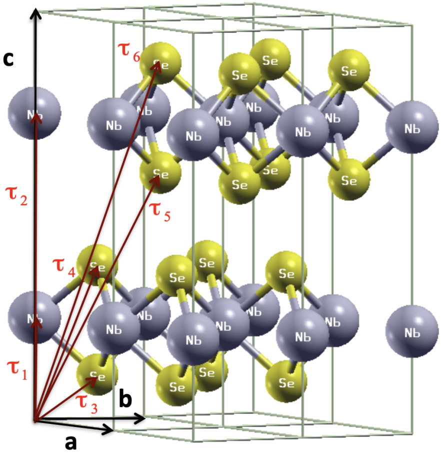


Polymers



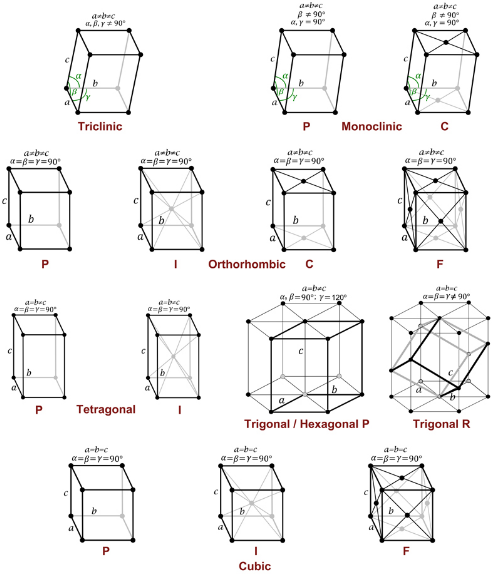
The crystal structure of solids

- The ions in a crystalline solid are formed by the periodic repetition of a given unit, the unit cell
- The type of unit cells are 14 and are called Bravais lattices
- The ionic positions are:
  $\boldsymbol{R}_i(\boldsymbol{T}) = \boldsymbol{\tau}_i + \boldsymbol{T}$
  where $\boldsymbol{\tau}_i$ is the position vector of atom i in the unit cell and $\boldsymbol{T}$ is a translation vector
- The translation vectors can be written as:
  $\boldsymbol{T} = n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c}$
  where n_1, n_2, and n_3 are integer numbers; and $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ are the lattice vectors that form the unit cell



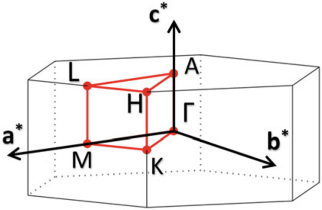
Bravais lattices

- Depending on the length of the lattice vectors and the angles between them there are 14 different Bravais lattices
- The angles between the vectors are defined as:
  $\alpha = \widehat{\boldsymbol{bc}}$
  $\beta = \widehat{\boldsymbol{ac}}$
  $\gamma = \widehat{\boldsymbol{ab}}$
- Some Bravais lattices have some centering. These are called the conventional unit cells. In these cases there is a smaller unit cell that can be chosen, which is called the primitive unit cell.



The reciprocal lattice

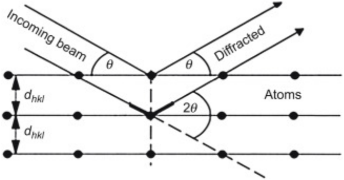
- Is the Fourier transform of the Bravais lattice, which forms a new lattice, the reciprocal lattice
- It is useful to define Fourier transformed objects
- The reciprocal lattice vectors are calculated as:
  $a^* = \frac{\boldsymbol{b}\times\boldsymbol{c}}{\boldsymbol{a}\cdot(\boldsymbol{b}\times\boldsymbol{c})}$
  $b^* = \frac{\boldsymbol{b}\times\boldsymbol{c}}{\boldsymbol{a}\cdot(\boldsymbol{c}\times\boldsymbol{a})}$
  $c^* = \frac{\boldsymbol{b}\times\boldsymbol{c}}{\boldsymbol{a}\cdot(\boldsymbol{a}\times\boldsymbol{b})}$
- Any reciprocal lattice vector is given by:
  $\boldsymbol{G} = n_1\boldsymbol{a}^* + n_2\boldsymbol{b}^* + n_3\boldsymbol{c}^*$
  where n_1, n_2, and n_3 are integer numbers.
- The first Brillouin zone is the unit cell of the reciprocal lattice in which the points that form it are closer to one $\boldsymbol{G}$.



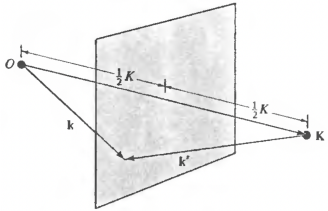
BZ of the hexagonal lattice

X-ray diffraction

- X-ray diffraction can be useful to detect the ionic positions in crystals
- There is constructive interference between reflected x-rays by different atoms only if (Bragg's law)
  $n\lambda = 2d_{hkl}\sin\theta$,
  where λ is the wavelength of the x-ray beam, θ is the angle of incidence of the beam with respect to the plane (h,k,l) and d_{hkl} is the interatomic distance in the plane
- An equivalent condition is the one given by von Laue:
  $\boldsymbol{G} = \boldsymbol{k}' - \boldsymbol{k}$,
  where $\boldsymbol{k}$ is the wave vector of the incident beam, and $\boldsymbol{k}'$ the one of the scattered beam

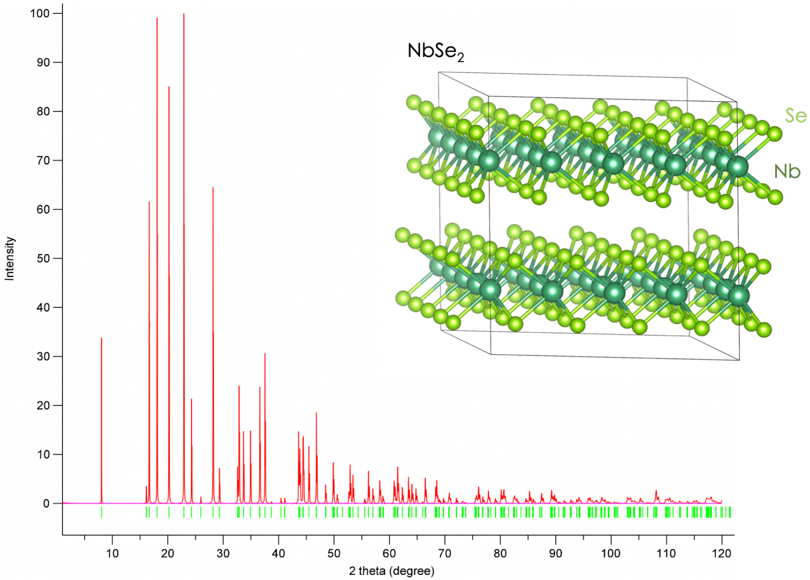


Bragg condition



Von Laue condition

X-ray diffraction



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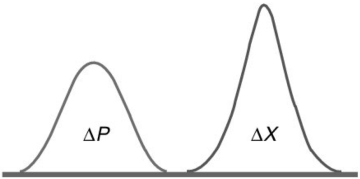
Are ions static at the lattice sites?

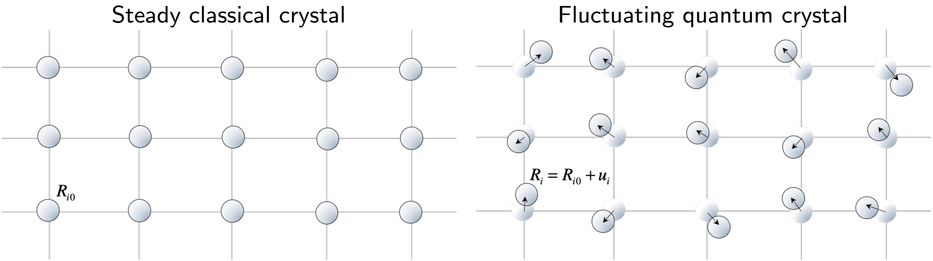
Heisengberg's uncertainty principle



$$\Delta x \Delta p \sim \hbar \qquad \text{or} \qquad \Delta x \Delta v \sim \frac{\hbar}{m}$$

- Position and momentum (or velocity) cannot be determined at the same time for a quantum particles
- The effect is larger for lighter particles
- As the positions and the velocities cannot be determined exactly, quantum particles must fluctuate, in other words, must be described by a quantum wave function, not a single point in space

Ionic quantum fluctuations

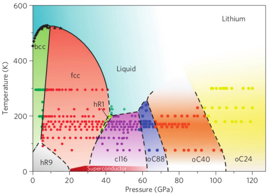


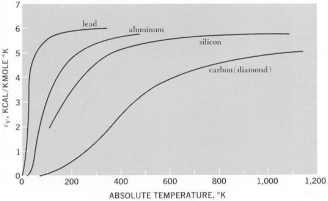
- Ions are never at the Bravais lattice sites, they fluctuate around them even at 0 K
- Bravais lattice sites identified by x-ray are the average position of ions
- The ionic fluctuations have an impact on the properties of solids
- The amplitude of the fluctuations increases with temperature until the crystal melts, and the average ionic positions are no longer arranged in a Bravais lattice
- The fluctuations are often called vibrations

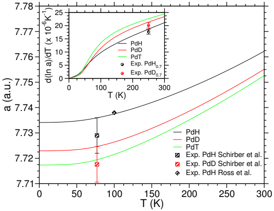
Physical relevance of ionic vibrations

Ionic vibrations determine many physical properties:

- Thermodynamical properties:
    - The temperature dependence of the Helmholtz free energy $F(V,T)$:
      $\hbar\omega_{vib} \sim 10meV \rightarrow T_{vib} = \frac{\hbar\omega_{vib}}{k_B} \sim 100K$
      $\hbar\omega_{ele} \sim 1eV \rightarrow T_{ele} = \frac{\hbar\omega_{vib}}{k_B} \sim 10000K$
    - Phase diagrams, specific heats, thermal expansion . . .

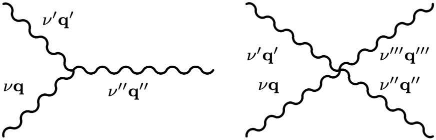




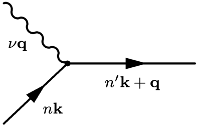


Physical relevance of ionic vibrations

- Transport properties:
  - Superconductivity (electron-phonon interaction)
  - Electrical conductivity (electron-phonon interaction)
  - Thermal conductivity (electron-phonon and phonon-phonon interactions)



phonon-phonon interaction



electron-phonon interaction

Outline

The theory of everything in a solid

- A solid is formed by a set of electrons and ions interacting via Coulomb interaction
- The properties of a solid can be fully determined, in principle, by solving the Schrödinger equation:

$$
\begin{aligned}
H|\Psi_A\rangle &= E_A|\Psi_A\rangle \\
H &= T_e + T_i + V_{e-e} + V_{e-i} + V_{i-i},
\end{aligned}
$$

- The terms contributing to the Hamiltonian (written in atomic units, $\boldsymbol{r}_i$ position of electron i, $\boldsymbol{R}_I$ position of ion I, M_I mass of ion I, Z_I charge of ion I):

Electron kinetic energy:	$T_e = \sum_i \frac{\boldsymbol{p}_i^2}{2}$
Ionic kinetic energy:	$T_i = \sum_I \frac{\boldsymbol{P}_I^2}{2M_I}$
Electron-electron interaction:	$V_{e-e} = \frac{1}{2}\sum_{ij} \frac{1}{\lvert\boldsymbol{r}_i - \boldsymbol{r}_j\rvert}$
Electron-ion interaction:	$V_{e-i} = -\sum_{iI} \frac{Z_I}{\lvert\boldsymbol{r}_i - \boldsymbol{R}_I\rvert}$
Ion-ion interaction:	$V_{i-i} = \frac{1}{2}\sum_{IJ} \frac{Z_I Z_J}{\lvert\boldsymbol{R}_I - \boldsymbol{R}_J\rvert}$

- We will neglect spin degrees of freedom

The Born-Oppenheimer (BO) approximation

- Electrons are lighter (faster) than ions
- The BO approximation assumes that for any ionic configuration $\boldsymbol{R}$ electrons are at the ground state of the electronic problem, so that ions always see electrons at the ground state
- $\boldsymbol{R}$ represents all ionic positions
- We assume that we can write the total wave function as a product of ionic ($|\Psi^i_\beta\rangle$) and electronic wave functions ($|\Psi^e_\alpha(\boldsymbol{R})\rangle$), the latter parametrized by the ionic positions:

$$|\Psi_A\rangle = |\Psi^e_\alpha(\boldsymbol{R})\rangle|\Psi^i_\beta\rangle$$

- We first solve the electronic part of the Hamiltonian with fixed ions at arbitrary positions $\boldsymbol{R}$:

$$\begin{aligned} H_e(\boldsymbol{R}) &= T_e + V_{e-e} + V_{e-i}(\boldsymbol{R}) + V_{i-i}(\boldsymbol{R}) \\ H_e(\boldsymbol{R})|\Psi^e_\alpha(\boldsymbol{R})\rangle &= E^e_\alpha(\boldsymbol{R})|\Psi^e_\alpha(\boldsymbol{R})\rangle \end{aligned}$$

The Born-Oppenheimer (BO) approximation

- After solving the electronic Hamiltonian we plug the solution into the total Hamiltonian:

$$\begin{aligned}
H\left[|\Psi^e_\alpha(\boldsymbol{R})\rangle|\Psi^i_\beta\rangle\right] &= T_i\left[|\Psi^e_\alpha(\boldsymbol{R})\rangle|\Psi^i_\beta\rangle\right] + H_e\left[|\Psi^e_\alpha(\boldsymbol{R})\rangle|\Psi^i_\beta\rangle\right] \\
&= \sum_I \frac{\boldsymbol{P}_I^2}{2M_I}\left[|\Psi^e_\alpha(\boldsymbol{R})\rangle|\Psi^i_\beta\rangle\right] + E^e_\alpha(\boldsymbol{R})|\Psi^e_\alpha(\boldsymbol{R})\rangle|\Psi^i_\beta\rangle \\
&= \sum_I |\Psi^i_\beta\rangle\left[\frac{\boldsymbol{P}_I^2}{2M_I}|\Psi^e_\alpha(\boldsymbol{R})\rangle\right] + \sum_I |\Psi^e_\alpha(\boldsymbol{R})\rangle\left[\frac{\boldsymbol{P}_I^2}{2M_I}|\Psi^i_\beta\rangle\right] \\
&+ \sum_I \left[\boldsymbol{P}_I|\Psi^i_\beta\rangle\right]\left[\frac{\boldsymbol{P}_I}{M_I}|\Psi^e_\alpha(\boldsymbol{R})\rangle\right] + E^e_\alpha(\boldsymbol{R})|\Psi^e_\alpha(\boldsymbol{R})\rangle|\Psi^i_\beta\rangle
\end{aligned}$$

- Projecting out the electronic wave function we obtain the Hamiltonian that we are supposed to solve to get the ionic motion

$$\begin{aligned}
\langle\Psi^e_{\alpha'}(\boldsymbol{R})|H\left[|\Psi^e_\alpha(\boldsymbol{R})\rangle|\Psi^i_\beta\rangle\right] &= \left[T_i + E_\alpha(\boldsymbol{R})\right]|\Psi^i_\beta\rangle\delta_{\alpha\alpha'} \\
&+ \sum_I \frac{1}{M_I}\langle\Psi^e_{\alpha'}(\boldsymbol{R})|\boldsymbol{P}_I|\Psi^e_\alpha(\boldsymbol{R})\rangle\boldsymbol{P}_I + \sum_I\langle\Psi^e_{\alpha'}(\boldsymbol{R})|\frac{\boldsymbol{P}_I^2}{2M_I}|\Psi^e_\alpha(\boldsymbol{R})\rangle
\end{aligned}$$

The Born-Oppenheimer (BO) approximation

- So far there is no approximation assumed, just a parametrization of the total wave function
- The following approximations are usually assumed:
    - **Adiabatic approximation:** ionic motion does not excite the electronic system from its ground state

$$E_\alpha(\boldsymbol{R}) \rightarrow E_0(\boldsymbol{R})$$

    - **Born-Oppenheimer approximation:** the coupling terms between the ionic and electronic motions can be neglected

$$\Delta H_{\alpha\alpha'} = \sum_I \frac{1}{M_I} \langle \Psi^e_{\alpha'}(\boldsymbol{R}) | \boldsymbol{P}_I | \Psi^e_\alpha(\boldsymbol{R}) \rangle \boldsymbol{P}_I + \sum_I \langle \Psi^e_{\alpha'}(\boldsymbol{R}) | \frac{\boldsymbol{P}_I^2}{2M_I} | \Psi^e_\alpha(\boldsymbol{R}) \rangle \rightarrow 0$$

- Within the Born-Oppenheimer adiabatic approximation the ionic problem is

$$H_i | \Psi^i_\beta \rangle = \left[T_i + V(\boldsymbol{R}) \right] | \Psi^i_\beta \rangle = E_\beta | \Psi^i_\beta \rangle$$

where we have defined the Born-Oppenheimer potential $V(\boldsymbol{R})$ as the ground state energy of the electronic problem for the ionic configuration $\boldsymbol{R}$

$$V(\boldsymbol{R}) = E_0(\boldsymbol{R})$$

The Born-Oppenheimer (BO) approximation

In a nutshell:

- Solve the electronic part of the Hamiltonian:

$$\begin{aligned} H_e(\boldsymbol{R}) &= T_e + V_{e-e} + V_{e-i}(\boldsymbol{R}) + V_{i-i}(\boldsymbol{R}) \\ H_e(\boldsymbol{R})|\Psi^e_\alpha(\boldsymbol{R})\rangle &= E^e_\alpha(\boldsymbol{R})|\Psi^e_\alpha(\boldsymbol{R})\rangle \end{aligned}$$

- Define the Born-Oppenheimer potential from the ground state of the solution:

$$V(\boldsymbol{R}) = E_0(\boldsymbol{R})$$

- Solve the ionic problem:

$$H_i|\Psi^i_\beta\rangle = \left[T_i + V(\boldsymbol{R})\right]|\Psi^i_\beta\rangle = E_\beta|\Psi^i_\beta\rangle$$

The Born-Oppenheimer (BO) approximation and the free energy

- Solving the ionic problem allows to calculate the free energy and perform thermodynamic calculations
- The free energy can be calculated as:

$$F = U - TS = \langle H \rangle_\rho - k_B T \langle \ln \rho \rangle_\rho = -k_B T \ln Z = -k_B T \ln \left(\sum_\beta e^{-\frac{E_\beta}{k_B T}} \right)$$

- Notation:
  Quantum statistical averages: $\langle O \rangle_\rho = \mathrm{tr}(\rho O)$
  The density matrix: $\rho = e^{-\frac{H}{k_B T}} / Z$
  The partition function: $Z = \mathrm{tr}(e^{-\frac{H}{k_B T}})$
- In this approach only ionic states contribute to the free energy

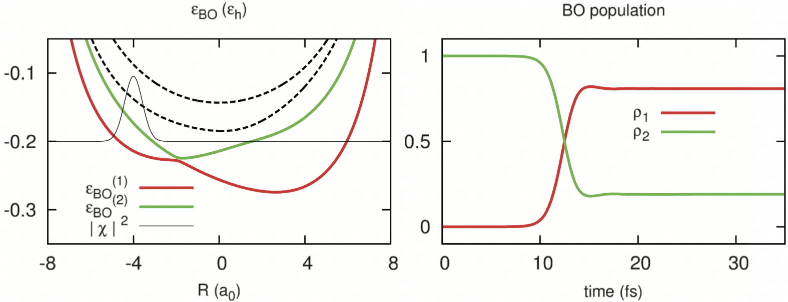
Are ions and electrons independent of each other in the adiabatic Born-Oppenheimer approximation?

How can we interpret the $\Delta H_{\alpha\alpha'}$ term neglected?

$$\Delta H_{\alpha\alpha'} = \sum_I \frac{1}{M_I} \langle \Psi^e_{\alpha'}(\boldsymbol{R}) | \boldsymbol{P}_I | \Psi^e_{\alpha}(\boldsymbol{R}) \rangle \boldsymbol{P}_I + \sum_I \langle \Psi^e_{\alpha'}(\boldsymbol{R}) | \frac{\boldsymbol{P}_I^2}{2M_I} | \Psi^e_{\alpha}(\boldsymbol{R}) \rangle$$

Beyond the Born-Oppenheimer approximation

- The electron-phonon interaction is a non-adiabatic correction
- More sophisticated approaches not fully developed yet



F. Agostini, A. Abedi and E. K. U. Gross, J. Chem. Phys. 141, 214101 (2014)

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The electronic problem

- Before attempting to solve the ionic problem, the electronic problem must be solved:

$$\begin{aligned} H_e(\boldsymbol{R}) &= T_e + V_{e-e} + V_{e-i}(\boldsymbol{R}) + V_{i-i}(\boldsymbol{R}) \\ H_e(\boldsymbol{R})|\Psi^e_\alpha(\boldsymbol{R})\rangle &= E^e_\alpha(\boldsymbol{R})|\Psi^e_\alpha(\boldsymbol{R})\rangle \end{aligned}$$

where,

$$\begin{aligned} T_e &= \sum_i \frac{\boldsymbol{p}_i^2}{2} \\ V_{e-e} &= \frac{1}{2}\sum_{ij} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \\ V_{e-i} &= -\sum_{iI} \frac{Z_I}{|\boldsymbol{r}_i - \boldsymbol{R}_I|} \\ V_{i-i} &= \frac{1}{2}\sum_{IJ} \frac{Z_I Z_J}{|\boldsymbol{R}_I - \boldsymbol{R}_J|} \end{aligned}$$

- The presence of the two-body V_{e-e} term makes the problem not-separable into single-body Hamiltonians

Single body Hamiltonians

- Let's assume the Hamiltonian of the many-body electron system is separable (forget about the parametric dependence on $\boldsymbol{R}$)

$$H_e(\boldsymbol{r}) = \sum_i H(\boldsymbol{r}_i) = \sum_i \left[\frac{\boldsymbol{p}_i^2}{2} + V(\boldsymbol{r}_i) \right]$$

- Then it is enough to solve the single-particle Hamiltonian

$$\left[\frac{\boldsymbol{p}_i^2}{2} + V(\boldsymbol{r}_i) \right] \psi_{\alpha_i}(\boldsymbol{r}_i) = E_{\alpha_i} \psi_{\alpha_i}(\boldsymbol{r}_i)$$

- Considering that electrons are fermions and the total wave function must be asymmetric, the total electronic wave function is a Slater determinant for the system with N_e electrons

$$\Psi^e_{\alpha_1,\cdots,\alpha_{N_e}}(\mathrm{r}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \psi_{\alpha_1}(\mathrm{r}_1) & \cdots & \psi_{\alpha_1}(\mathrm{r}_{N_e}) \\ \vdots & \vdots & \vdots \\ \psi_{\alpha_{N_e}}(\mathrm{r}_1) & \cdots & \psi_{\alpha_{N_e}}(\mathrm{r}_{N_e}) \end{vmatrix}$$

- The total electronic energy is

$$E_\alpha = \sum_i^{N_e} E_{\alpha_i}$$

Density-functional theory (DFT)

- The magic of DFT is that, thanks to the Hohenberg-Kohn theorems, the many-body electronic Hamiltonian can be rewritten as a separable Hamiltonian with Kohn-Sham equations:

$$H_e(\boldsymbol{r}) = \sum_i H_{KS}(\boldsymbol{r}_i) = \sum_i \left[\frac{\boldsymbol{p}_i^2}{2} + V_{KS}(\boldsymbol{r}_i) \right]$$

- Then it is enough to solve the the single-particle Kohn-Sham Hamiltonian

$$\left[\frac{\boldsymbol{p}_i^2}{2} + V_{KS}(\boldsymbol{r}_i) \right] \psi_{\alpha_i}(\boldsymbol{r}_i) = E_{\alpha_i} \psi_{\alpha_i}(\boldsymbol{r}_i)$$

Density-functional theory (DFT)

- The Kohn-Sham potential is

  $$V_{KS}(\boldsymbol{r}_i) = V_{e-i}(\boldsymbol{r}_i) + V_H(\boldsymbol{r}_i) + V_{xc}(\boldsymbol{r}_i)$$

  where

  - The electron-ion potential is $V_{e-i}(\boldsymbol{r}_i) = -\sum_I \frac{Z_I}{|\boldsymbol{r}_i - \boldsymbol{R}_I|}$
  - The Hartree potential is $V_H(\boldsymbol{r}_i) = \int d\boldsymbol{r}_j \frac{n(\boldsymbol{r}_j)}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$
    with $n(\boldsymbol{r}_j)$ the ground state electronic density at point $\boldsymbol{r}_j$
  - The exchange-correlation potential $V_{xc}(\boldsymbol{r}_i)$ is unknown
- Note that we have forgot about the E_{i-i} term, but this is just a constant energy for the electronic problem that does not affect anything.
- The problem of DFT is that despite being exact we need to approximate V_{xc}: LDA, GGA, etc. (the zoo of functionals)

DFT variational principle

- The ground state total energy in DFT is a functional of the density n

$$E_0^e = T_e[n] + E_H[n] + E_{e-i}[n] + E_{xc}[n]$$

  where

  - The kinetic energy functional is $T_e[n]$
  - The Hartree energy is $E_H[n] = \frac{1}{2}\int d\boldsymbol{r}_i d\boldsymbol{r}_j \frac{n(\boldsymbol{r}_i)n(\boldsymbol{r}_j)}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$
  - The energy of the electron ion interaction is $E_{e-i}[n] = \int d\boldsymbol{r}_i n(\boldsymbol{r}_i) V_{e-i}(\boldsymbol{r}_i)$
  - The exchange-correlation energy is unknown $E_{xc}[n]$

- If the ground state density is written in terms of single particle wave functions,

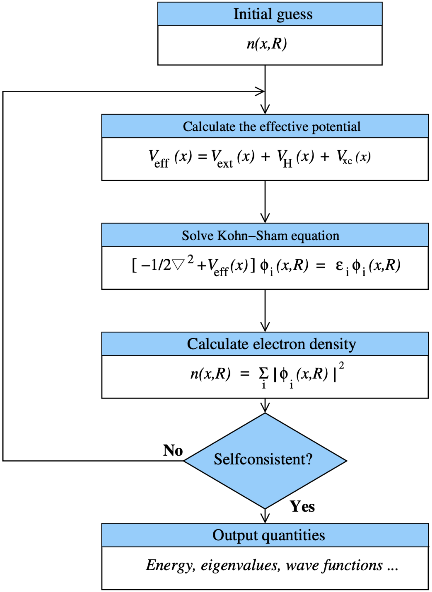
$$n(\boldsymbol{r}_i) = \sum_j^{N_e} |\phi_{\alpha_j}(\boldsymbol{r}_i)|^2,$$

  KS equations are obtained variationally deriving the energy

- Once the KS equations are solved and the density calculated the total ground state energy is

$$E_0^e = \sum_i^{N_e} E_{\alpha_i} - E_H[n] + E_{xc}[n] - \int d\boldsymbol{r}_i n(\boldsymbol{r}_i) V_{xc}(\boldsymbol{r}_i)$$

The DFT self-consistent loop



Initial guess

$n(x,R)$

Calculate the effective potential

$V_{\mathrm{eff}}(x) = V_{\mathrm{ext}}(x) + V_{\mathrm{H}}(x) + V_{\mathrm{xc}}(x)$

Solve Kohn–Sham equation

$[-1/2\nabla^2 + V_{\mathrm{eff}}(x)]\,\phi_i(x,R) = \varepsilon_i\,\phi_i(x,R)$

Calculate electron density

$n(x,R) = \sum_i |\phi_i(x,R)|^2$

Selfconsistent?

No

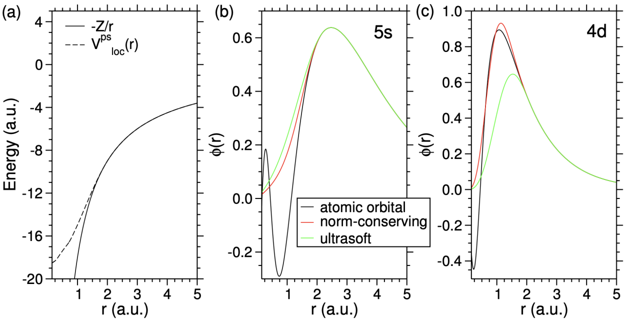
Yes

Output quantities

Energy, eigenvalues, wave functions ...

The pseudopotential approximation

- In order to remove core electrons from the calculation only valence electrons are usually solved in DFT making use of pseudopotentials
- Atomic orbitals obtained with the pseudopotential match the full electron orbitals obtained with the real core beyond a cutoff radius
- Different types of pseudopotentials: norm-conserving, ultrasoft, PAW
- We need to carefully choose the number of valence electrons included
- Example for Pd (Kr4d^{10}):



Lattice periodicity and Bloch's theorem

- Due to the Bravais lattice periodicity of the electron-ion potential, the KS potential is lattice-periodic:

$$V_{KS}(\boldsymbol{r} + \boldsymbol{T}) = V_{KS}(\boldsymbol{r})$$

- This implies that KS states are Bloch states:

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = u_{n\boldsymbol{k}}(\boldsymbol{r})e^{i\boldsymbol{k}\cdot\boldsymbol{r}},$$

  where $u_{n\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{T}) = u_{n\boldsymbol{k}}(\boldsymbol{r})$ is the periodic part of the wave function, and that consequently

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{T}) = \psi_{n\boldsymbol{k}}(\boldsymbol{r})e^{i\boldsymbol{k}\cdot\boldsymbol{T}}$$

- Consequences of Bloch's theorem
  - Bloch states are diagonal (up to a reciprocal lattice vector) so that the wave number $\boldsymbol{k}$ is a good quantum number and the KS equations need to be solved independently for each $\boldsymbol{k}$

$$\langle \psi_{n'\boldsymbol{k}'} | H_{KS} | \psi_{n\boldsymbol{k}} \rangle \propto \delta_{\boldsymbol{k}-\boldsymbol{k}',\boldsymbol{G}}$$

  - For each $\boldsymbol{k}$ we need to solve the KS equation and we will get different energies $E_{n\boldsymbol{k}}$. These form the band structure

Bloch's theorem and Born-Von Karman boundary conditions

- In order to remove the effect of the boundaries of the crystal, it is common to assume Born-Von Karman periodic boundary conditions:

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}+N_a\boldsymbol{a}) = \psi_{n\boldsymbol{k}}(\boldsymbol{r}+N_b\boldsymbol{b}) = \psi_{n\boldsymbol{k}}(\boldsymbol{r}+N_c\boldsymbol{c})\psi_{n\boldsymbol{k}}(\boldsymbol{r})$$

  where N_a, N_b, and N_c are the total number of cells along each lattice direction
- If we apply to this Bloch's theorem, we obtain that $e^{iN_a\boldsymbol{k}\cdot\boldsymbol{a}} = e^{iN_b\boldsymbol{k}\cdot\boldsymbol{b}} = e^{iN_c\boldsymbol{k}\cdot\boldsymbol{c}} = 1$
- This implies that

$$\boldsymbol{k} = \frac{2\pi n_a}{N_a}\boldsymbol{a}^* + \frac{2\pi n_b}{N_b}\boldsymbol{b}^* + \frac{2\pi n_c}{N_c}\boldsymbol{c}^*$$

  with $n_x \in [0, N_x - 1]$ are the allowed wave vectors for the KS states
- It is enough to take the $\boldsymbol{k}$ in the first BZ (or any primitive unit cell of the reciprocal lattice vectors) because $\psi_{n\boldsymbol{k}}(\boldsymbol{r})$ and $\psi_{n\boldsymbol{k}+\boldsymbol{G}}(\boldsymbol{r})$ are eigenfunctions of the translational operator $\hat{\boldsymbol{T}}$ with the same eigenvalue:

$$\hat{\boldsymbol{T}}\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \psi_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{T}) = e^{i\boldsymbol{k}\cdot\boldsymbol{T}}\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{T}}\psi_{n\boldsymbol{k}}(\boldsymbol{r}),$$

- Thus KS states are periodic in reciprocal space:

$$\psi_{n\boldsymbol{k}+\boldsymbol{G}}(\boldsymbol{r}) = \psi_{n\boldsymbol{k}}(\boldsymbol{r}) \qquad E_{n\boldsymbol{k}+\boldsymbol{G}} = E_{n\boldsymbol{k}}$$

The plane-wave basis

- In order to solve the KS states for each $\boldsymbol{k}$ point in the BZ, a basis needs to be chosen
- Plane waves are the most standard choice:

  $$\langle \boldsymbol{r} | \boldsymbol{q} \rangle = \frac{1}{\sqrt{\Omega}} e^{i\boldsymbol{q}+\cdot\boldsymbol{r}}$$

  where Ω is the total volume of the crystal
- Due to translational symmetry only reciprocal lattice vectors contribute to the expansion:

  $$|\psi_{n\boldsymbol{k}}\rangle = \sum_{\boldsymbol{G}} c_{n\boldsymbol{k}+\boldsymbol{G}} |\boldsymbol{k}+\boldsymbol{G}\rangle$$

- The matrix to be diagonalized to get the band energies at $\boldsymbol{k}$ is

  $$\langle \boldsymbol{k}+\boldsymbol{G} | H_{KS} | \boldsymbol{k}+\boldsymbol{G}' \rangle = \frac{1}{2} |\boldsymbol{k}+\boldsymbol{G}|^2 \delta_{\boldsymbol{G},\boldsymbol{G}'} + V_{KS}(\boldsymbol{G}-\boldsymbol{G}')$$

  where $V_{KS}(\boldsymbol{q})$ is the Fourier transform of the KS potential
- The reciprocal lattice vectors are infinite and needs to be cut for practical calculations: the cutoff energy:

  $$\frac{1}{2} |\boldsymbol{k}+\boldsymbol{G}|^2 < E_{cut}$$

The $\boldsymbol{k}$-point grid

- Once the KS equations are solved we can construct the density energy and the energy

$$
\begin{aligned}
n(\boldsymbol{r}) &= \sum_{n\boldsymbol{k}} f_{n\boldsymbol{k}} |\psi_{n\boldsymbol{k}}(\boldsymbol{r})|^2 \\
E_0^e &= \sum_{n\boldsymbol{k}} f_{n\boldsymbol{k}} E_{n\boldsymbol{k}} - E_H[n] + E_{xc}[n] - \int d\boldsymbol{r}_i n(\boldsymbol{r}_i) V_{xc}(\boldsymbol{r}_i)
\end{aligned}
$$

- In the ground state electrons start occupying one state each (doubly degenerate because of spin) till the Fermi energy E_F. This is determined by the Fermi-Dirac occupation:

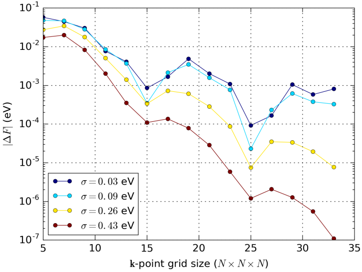
$$f_{n\boldsymbol{k}} = \frac{1}{e^{\beta(E_{n\boldsymbol{k}} - E_F)} + 1}$$

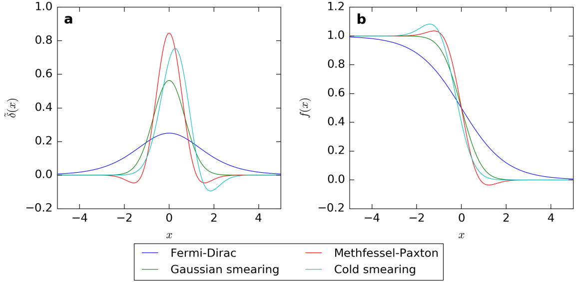
  with $\beta = 1/(k_B T)$

- In principle the sum over $\boldsymbol{k}$ points should be over all the first BZ. This is impossible and the calculation is usually limited to a regular (Monkhorst-Pack) grid

Smearing in metals

- In metals sometimes it is difficult to converge the Fermi level in terms of the ***k***-point grid and smearing techniques are used to speed up the convergence





`https://docs.quantumatk.com/index.html`

Exercises

1. Why is not the DFT energy ground state energy equal to $\sum_{n\boldsymbol{k}} f_{nk} |\psi_{n\boldsymbol{k}}|^2$?
2. Show that due to Bloch's theorem and lattice periodicity the KS Hamiltonian is diagonal in the wave number $\boldsymbol{k}$:

$$\langle \psi_{n'\boldsymbol{k}'} | H_{KS} | \psi_{n\boldsymbol{k}} \rangle \propto \delta_{\boldsymbol{k}-\boldsymbol{k}',\boldsymbol{G}}$$

3. Show that in the plane wave expansion of the KS states only reciprocal lattice vectors contribute and that for a given $\boldsymbol{k}$ point the equation to be solved is

$$\langle \boldsymbol{k} + \boldsymbol{G} | H_{KS} | \boldsymbol{k} + \boldsymbol{G}' \rangle = \frac{1}{2} |\boldsymbol{k} + \boldsymbol{G}|^2 \delta_{\boldsymbol{G},\boldsymbol{G}'} + V_{KS}(\boldsymbol{G} - \boldsymbol{G}')$$