NEUTRONS FOR SOCIETY

Introduction to Lattice Vibrations and Density Functional Theory

Elisa Rebolini
Institut Laue Langevin, Grenoble, France, rebolini@ill.fr

March 19th 2026

The theory of everything

- A system is formed by a set of N electrons and M nuclei (ions) interacting via Coulomb interaction

- The properties of a solid can be fully determined, in principle, by solving the (time independent) Schrödinger equation:

$$\hat{H}^{\text{tot}}|\Psi^{\text{tot}}\rangle = E^{\text{tot}}|\Psi^{\text{tot}}\rangle$$

- The terms contributing to the Hamiltonian (written in atomic units, $\mathbf{r}_i$ position of electron i, $\mathbf{R}_A$ position of ion A, m_A mass of ion A, Z_A charge of ion A):
  - Electron kinetic operator: $\hat{T}_e$
  - Nuclear kinetic operator: $\hat{T}_n$
  - Electron-electron interaction: $\hat{W}_{ee}$
  - Electron-nuclei interaction: $\hat{V}_{ne}$
  - Ion-ion interaction: $\hat{V}_{nn}$

The Born-Oppenheimer (BO) Approximation

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

$$|\Psi^{\text{tot}}\rangle = |\Psi^e(\{\mathbf{R}\})\rangle \cdot |\Psi^n\rangle$$

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

$$\hat{H}^e(\{\mathbf{R}\}) = \hat{T}_e + \hat{W}_{ee} + \hat{V}_{ne}(\{\mathbf{R}\}) + \hat{V}_{nn}(\{\mathbf{R}\})$$
$$\hat{H}^e(\{\mathbf{R}\})\,|\Psi^e(\{\mathbf{R}\})\rangle = E^e(\{\mathbf{R}\})\,|\Psi^e(\{\mathbf{R}\})\rangle$$

The Born-Oppenheimer (BO) Approximation

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

$$\begin{aligned}\hat{H}^{\text{tot}} \left|\Psi^e(\{\mathbf{R}\})\right\rangle \left|\Psi^n\right\rangle &= \hat{T}^n|\Psi^e(\{\mathbf{R}\})\rangle \left|\Psi^n\right\rangle + \hat{H}^e(\{\mathbf{R}\})|\Psi^e(\{\mathbf{R}\})\rangle \left|\Psi^n\right\rangle \\ &= \hat{T}^n|\Psi^e(\{\mathbf{R}\})\rangle \left|\Psi^n\right\rangle + E^e(\{\mathbf{R}\})|\Psi^e(\{\mathbf{R}\})\rangle \left|\Psi^n\right\rangle\end{aligned}$$

- We perform the **adiabatic** approximation (ionic motion does not excite the electronic system from its ground state) and **BO approximation** (the coupling terms between the ionic and electronic motions can be neglected)
- The nuclear problem is then:

$$\hat{H}^n|\Psi^n\rangle = \left[\hat{T}^n + \hat{V}(\mathbf{R})\right] \left|\Psi^n\right\rangle$$

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

$$V(\mathbf{R}) = E_0^e(\mathbf{R})$$

Outline

Definition of the Problem

Hypotheses

- Let's assume that we can solve the electronic problem to obtain $V(\mathbf{R})$ (second part of this lecture)
- And that we know the equilibrium geometry of the system, i.e. the ionic positions $\mathbf{R}_0$ that correspond to the minimum of $V(\mathbf{R})$.

Nuclear problem

We want to find the eigenfunctions $|\Psi^n\rangle$ of the Hamiltonian

$$\hat{H} = \hat{T}^n + \hat{V}(\mathbf{R}) = \sum_A \frac{1}{2m_A}\hat{\nabla}_A^2 + \hat{V}(\mathbf{R})$$

around the equilibrium position $\mathbf{R}_0$.

In order to simplify the resolution, we will first solve the classical equations of motion to identify the eigenmodes and their frequencies.

We will then move to the quantum formulation by transforming the displacement and momentum into their quantum counterparts.

Motivation and Useful References

Motivation

- Determination of the equilibrium geometry
- Dynamics of the system
- Neutron Observables

Useful Books

- N.W. Ashcroft and N. D. Mermin, *Solid State Physics*, Saunders Collage Publishing, 1976.
- C. Kittel, *Introduction to Solid State Physics*, John Wiley Sons, (2004).
- H. Schober, S. Rols, *Les excitations dans la matière condensée : vibrations et phonons*, JDN 10 3-136 (2010) (in French)

Expansion of the potential – Force Constants

Ionic displacements from the equilibrium positions are usually small compared to the interionic distance. The displacement vector of all ions is given by

$$\mathbf{u} = \sum_{A=1}^{M} \sum_{\alpha=x,y,z} u_{A\alpha} |A\alpha\rangle = \sum_{a=1}^{3M} u_a |a\rangle$$

where for the x component (similarly for y and z), $u_{A,x} = X_A - X_{A,0}$.

Taylor Expansion around the Equilibrium

The BO potential $V(\mathbf{R})$ can be Taylor-expanded around $\mathbf{R}_0$ as

$$V(\mathbf{R}) = V(\mathbf{R}_0) + V^{(2)}(\mathbf{R}) + V^{(3)}(\mathbf{R}) + V^{(4)}(\mathbf{R}) + \cdots,$$

$$V^{(n)}(\mathbf{R}) = \frac{1}{n!} \sum_{a_1 \ldots a_n = 1}^{3M} \Phi^{(n)}_{a_1 \ldots a_n} u_{a_1} \cdots u_{a_n}$$

The n-th order force-constants are given by

$$\Phi^{(n)}_{a_1 \ldots a_n} = \left. \frac{\partial^n V(\mathbf{R})}{\partial R_{a_1} \ldots \partial R_{a_n}} \right|_{\mathbf{R}=\mathbf{R}_0} = \left. \frac{\partial^n V(\mathbf{R})}{\partial u_{a_1} \ldots \partial u_{a_n}} \right|_{\mathbf{u}=0}$$

The first non-trivial approximation we can do to the vibrational problem is to assume the harmonic approximation. We assume that atoms oscillate around the $\mathbf{R}_0$ positions (classical approximation) and oscillate around them.

Harmonic Approximation

The potential is truncated at second order

$$V(\mathbf{R}) = V(\mathbf{R}_0) + V^{(2)}(\mathbf{R}) = V_0 + \frac{1}{2} \sum_{a_1, a_2 = 1}^{3M} \Phi^{(2)}_{a_1 a_2} u_{a_1} u_{a_2}$$

Classical treatment: Newton Equations

The Newton equations to be solved for the motion of the ions are

$$m_a \frac{d^2 u_a(t)}{dt^2} = - \left. \frac{\partial V(R)}{\partial u_a} \right|_{u=0} = - \sum_{b=1}^{3M} \Phi^{(2)}_{ab} u_b(t).$$

Mass weighted displacement

To simplify this set of coupled equations we introduce the $3M$ mass-weighted displacement vector

$$\bar{\mathbf{u}}(t) = \left(\sqrt{m_1}\mathbf{u}_{A_1}(t), \sqrt{m_2}\mathbf{u}_{A_2}(t), ..., \sqrt{m_M}\mathbf{u}_{A_M}(t)\right)$$

which can be written in the Cartesian basis as

$$\bar{\mathbf{u}}(t) = \sum_{A=1}^{M} \sum_{\alpha=x,y,z} \bar{u}_{A,\alpha}(t)|A\alpha\rangle = \sum_{a=1}^{3M} \bar{u}_a(t)|a\rangle$$

Newton Equations

The Newton equations rewrite as

$$\frac{d^2\bar{u}_a(t)}{dt^2} = -\sum_{b=1}^{3M} \frac{\Phi^{(2)}_{ab}}{\sqrt{m_a m_b}} \bar{u}_b(t) = -\sum_{b=1}^{3M} D_{ab}\bar{u}_b(t),$$

where $\mathbf{D}$ is the dynamical matrix defined by its elements in the Cartesian basis

$$D_{ab} = \frac{\Phi^{(2)}_{ab}}{\sqrt{m_a m_b}}$$

Newton Equations

$$\frac{d^2\bar{u}_a(t)}{dt^2} = -\sum_{b=1}^{3M} D_{ab}\bar{u}_b(t),$$

has solutions of the form

$$\bar{u}_a(t) = e_a \exp(-i\omega t)$$

where $\mathbf{e} = \sum_a e_a|a\rangle$ is a $3M$ polarization vector that determines how each atom is moving.

When plugged in the Newton Equations, it becomes

$$-\omega^2 e_a \exp(-i\omega t) = -\sum_{b=1}^{3M} D_{ab} e_b \exp(-i\omega t)$$

Eigenproblem for the Dynamical Matrix

The Newton Equations can be written in matrix form as

$$\mathbf{D}\mathbf{e}_\mu = \omega_\mu^2 \mathbf{e}_\mu$$

Eigenmodes of the Dynamical Matrix

The $3M$ eigenvalues of the dynamical matrix will determine the ω_μ frequencies of the ionic oscillations and the displacements of the ions will be determined by the eigenvectors $|\mu\rangle = \mathbf{e}_\mu$ of the same matrix.

$$|\mu\rangle = \sum_{a=1}^{3M} e_\mu^a |a\rangle$$

The set of eigenvectors $|\mu\rangle$ constitute a new basis such that

$$\mathbf{D} = \sum_{\mu=1}^{3M} \omega_\mu^2 |\mu\rangle\langle\mu|$$

$$\bar{u}_a(t) = \sum_{\mu=1}^{3M} e_\mu^a Q_\mu \exp(-i\omega_\mu t)$$

where the Q_μ are the coefficients of the displacement in the normal mode basis

$$\bar{\mathbf{u}}(t) = \sum_{a=1}^{3M} \bar{u}_a(t)|a\rangle = \sum_{\mu=1}^{3M} Q_\mu \exp(-i\omega_\mu t)|\mu\rangle$$

Harmonic potential

The potential can be written as an independent sum of harmonic oscillators

$$V(\mathbf{R}) = \frac{1}{2} \sum_{a_1, a_2 = 1}^{3M} \Phi^{(2)}_{a_1 a_2} u_{a_1} u_{a_2} = \frac{1}{2} \sum_{a_1, a_2 = 1}^{3M} D_{a_1 a_2} \bar{u}_{a_1} \bar{u}_{a_2} = \frac{1}{2} \sum_{\mu} \omega_\mu^2 |Q_\mu|^2$$

Classical Solutions

- For each normal mode of frequency ω_μ, the atomic displacement is given by the matching eigenvector.
- All atoms share the same phase
- The solutions are stationary.

- We can now use the normal mode basis to formulate the quantum Harmonic Problem

Instead of solving the classical equations of motion, we need to solve the Schrödinger equation

$$\hat{H}^n|\Psi^n\rangle = \left[\hat{T}^n + V(\hat{\mathbf{R}})\right]|\Psi^n\rangle$$

The operator symbol has been included for the kinetic energy and the position operator.

Quantum Hamiltonian in the Harmonic Approximation

In the harmonic approximation the potential is truncated at second order:

$$\hat{H}^n = \sum_{A=1}^{M} \frac{\hat{p}_A^2}{2m_A} + \frac{1}{2}\sum_{AB} \Phi_{AB}^{(2)} \hat{u}_A \hat{u}_B = \sum_{A=1}^{M} \frac{\hat{\tilde{p}}_A^2}{2} + \frac{1}{2}\sum_{AB} D_{AB} \hat{\tilde{u}}_A \hat{\tilde{u}}_B$$

where $\hat{\mathbf{p}}$ and $\hat{\tilde{\mathbf{p}}}$ are the (mass-weighted) momentum operators and

$$\hat{\tilde{u}}_A = \sqrt{m_A}\hat{u}_A = \sqrt{m_A}\left(\hat{R}_A - R_{A0}\right)$$

define the (mass-weighted) displacement operators.

Transformation in the Normal mode basis

The diagonalisation of the dynamical matrix define the normal mode basis

$$\mathbf{D} = \sum_{\mu} \omega_{\mu}^2 |\mu\rangle\langle\mu| \qquad |\mu\rangle = \sum_{A\alpha} e_{\mu}^{A\alpha} |A\alpha\rangle$$

The position and momentum operators in normal basis are

$$\sqrt{m_A}\hat{u}_A = \sum_{\mu} e_{\mu}^{A} \hat{Q}_{\mu}$$

$$\frac{\hat{p}_A}{\sqrt{m_A}} = \sum_{\mu} e_{\mu}^{A} \hat{P}_{\mu}$$

where $\hat{Q}_{\mu}$ and $\hat{P}_{\mu}$ are the normal displacement and momentum operators.

Normal Mode Hamiltonian

The Hamiltonian becomes a sum of 3M independent single-particle harmonic oscillators

$$\hat{H}^n = \frac{1}{2} \sum_{\mu} \left(\hat{P}_{\mu}^2 + \omega_{\mu}^2 \hat{Q}_{\mu}^2 \right).$$

Bosonic ladder operator

For each single harmonic oscillator $\hat{h}_\mu = \frac{1}{2}\left(\hat{P_\mu}^2 + \omega_\mu^2 \hat{Q_\mu}^2\right)$, we transform the normal mode displacement and momentum operator to ladder operators

$$\hat{Q}_\mu = \sqrt{\frac{\hbar}{2\omega_\mu}}\left(\hat{b}_\mu + \hat{b}_\mu^\dagger\right) \qquad \hat{P}_\mu = -i\sqrt{\frac{\hbar\omega_\mu}{2}}\left(\hat{b}_\mu - \hat{b}_\mu^\dagger\right)$$

which satisfy the bosonic commutation relations $[\hat{b}_\mu, \hat{b}_\mu^\dagger] = 1$

Solution to a single quantum harmonic oscillator

The Hamiltonian rewrites as

$$\hat{h}_\mu = \hbar\omega_\mu\left(\hat{b}_\mu^\dagger \hat{b}_\mu + \frac{1}{2}\right)$$

its eigenvectors are the Fock states $|\psi_{n,\mu}\rangle$, $n \geq 0$ with eigenvalues

$$E_{\mu,n} = \hbar\omega_\mu\left(n + \frac{1}{2}\right)$$

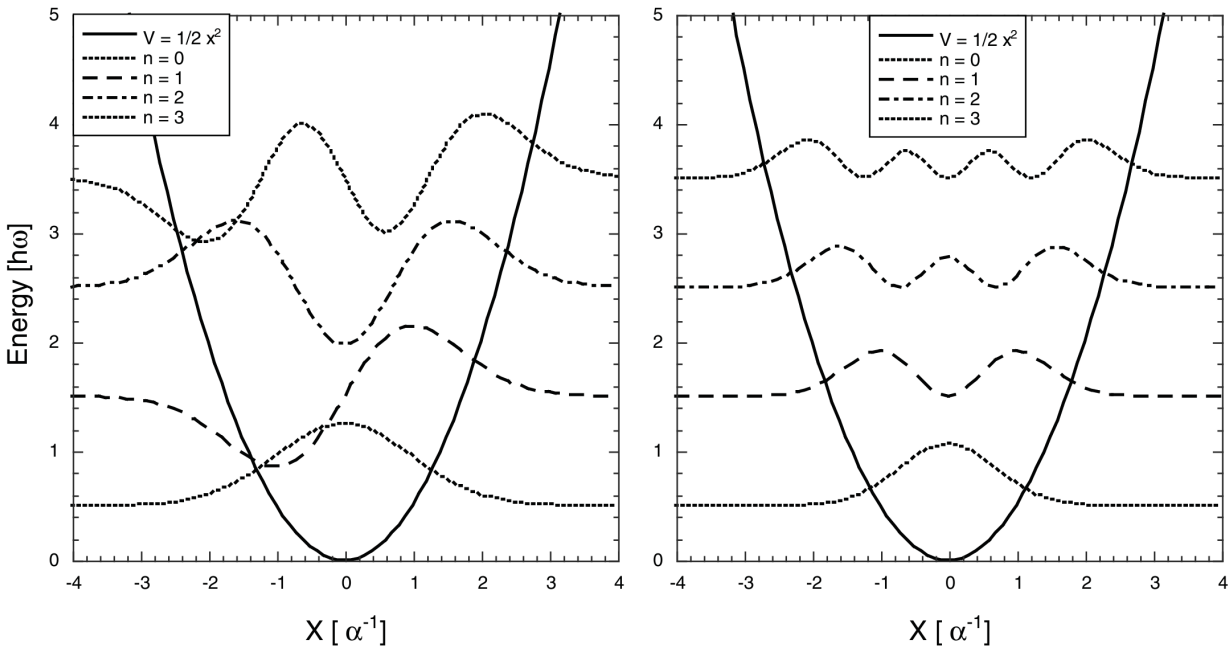
Quantum Solution to the Harmonic Problem

Eigenstates

The excited states can be expressed as a function of the normal modes as using

$$\psi_{n,\mu} = \frac{\alpha_\mu}{2^n n! \sqrt{\pi}} e^{-\frac{\omega_\mu Q_\mu^2}{2}} H_n(\sqrt{\omega_\mu} Q_\mu)$$

where the H_n are the usual Hermite polynomials but expressed as a function of the normal modes coordinates



Wave functions and their norms in a Harmonic well
Schober, Rols, (2010) https://doi.org/10.1051/sfn/2010001

What have we learned so far?

- Adiabatic and Born-Oppenheimer approximations
- Harmonic approximation of the nuclear potential
- Definition of the force constants and the dynamical matrix
- Definition of the normal mode basis
- Classical and quantum solutions of the harmonic problems for a general system

Outline

Periodicity in real space

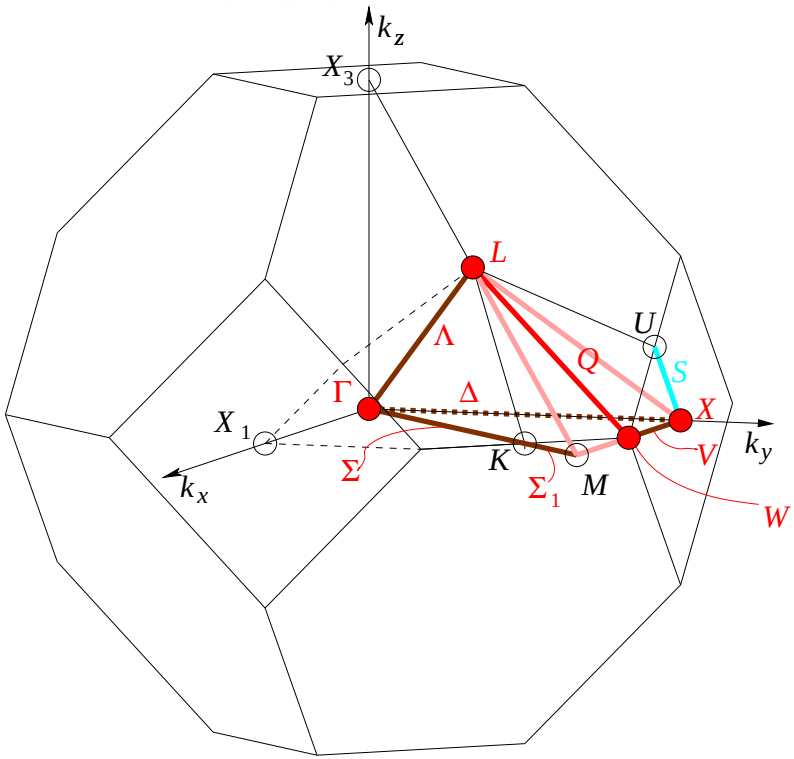
The ions in a crystalline solid are formed by the periodic repetition of a given unit, the unit cell. The ionic positions are:

$$\mathbf{R}_A(\mathbf{L}) = \tau_A + \mathbf{L}$$

where τ_A is the position vector of atom A in the unit cell and $\mathbf{L}$ is a lattice vector

$$\mathbf{L} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$$

where n_1, n_2, and n_3 are integer numbers; and $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are the lattice vectors that form the unit cell



©bilbao crystallographic server
http://www.cryst.ehu.es

The reciprocal lattice

It is useful to use the Fourier transform of objects. The reciprocal lattice vectors are defined as

$$\mathbf{a}^* = \frac{\mathbf{b}\times\mathbf{c}}{V} \qquad \mathbf{b}^* = \frac{\mathbf{c}\times\mathbf{a}}{V} \qquad \mathbf{c}^* = \frac{\mathbf{a}\times\mathbf{b}}{V} \qquad V = \mathbf{a}.(\mathbf{b}\times\mathbf{c})$$

The first Brillouin zone is the unit cell of the reciprocal lattice in which the points that form it are closer to the origin.

In a periodic crystal, the total number of atoms M is decomposed into $M_{at} \times N_L$, the numbers of atoms per cell times the number of lattice cells.

Translational symmetry

Assuming that the harmonic force constants can only depend on the difference between two lattice vectors

$$\Phi^{(2)}_{\mathbf{L}_1 A_1 \alpha_1, \mathbf{L}_2 A_2 \alpha_2} = \Phi^{(2)}_{A_1 \alpha_1, A_2 \alpha_2}(\mathbf{L}_1 - \mathbf{L}_2)$$

Reciprocal representations

The force constant and dynamical matrices can be written in reciprocal space as

$$\Phi^{(2)}_{A_1 \alpha_1, A_2 \alpha_2}(\mathbf{q}) = \sum_{\mathbf{L}} \Phi^{(2)}_{A_1 \alpha_1, A_2 \alpha_2}(\mathbf{L}) e^{i\mathbf{q}\cdot\mathbf{L}}$$

and

$$D_{A_1 \alpha_1, A_2 \alpha_2}(\mathbf{q}) = \frac{\Phi^{(2)}_{A_1 \alpha_1, A_2 \alpha_2}(\mathbf{q})}{\sqrt{m_1 m_2}}$$

Transformation of the problem

Instead of solving a $3M$ dimensional eigenproblem in real space,

$$\mathbf{D}\mathbf{e}_\mu = \omega_\mu^2 \mathbf{e}_\mu$$

we solve N_L $3M_{at}$-dimensional problems in reciprocal space at each $\mathbf{q}$ point in the first BZ

$$\mathbf{D}(\mathbf{q})\mathbf{e}_\mu(\mathbf{q}) = \omega_\mu^2(\mathbf{q})\mathbf{e}_\mu(\mathbf{q})$$

Harmonic potential in Reciprocal Space

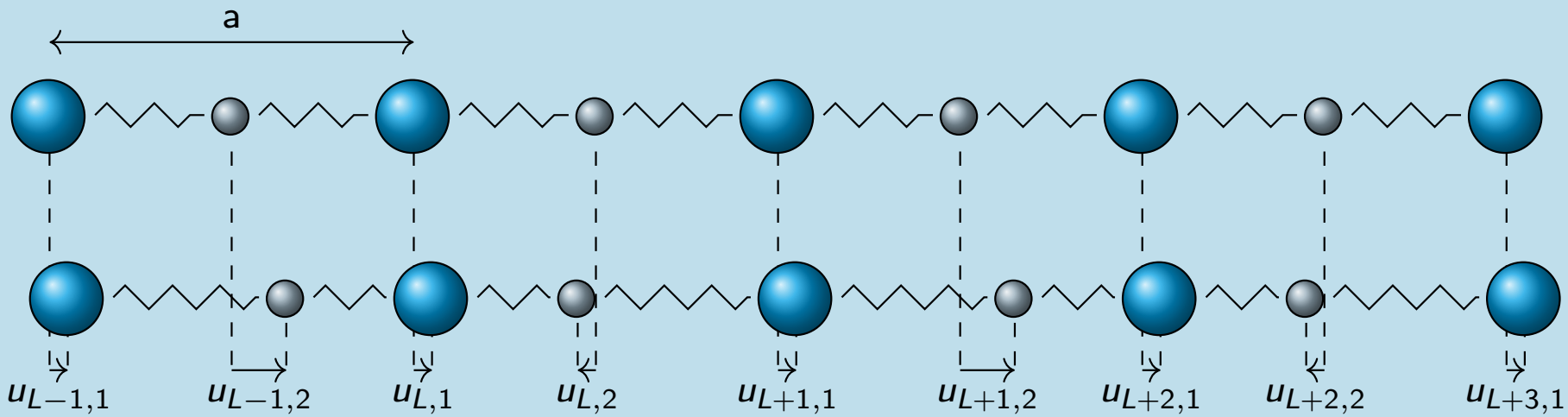
The Harmonic Potential can be written as a linear combination of the modes in $\mathbf{q}$ space

$$V(\mathbf{R}) = \frac{1}{2}\sum_{\mu\mathbf{q}} \omega_\mu^2(\mathbf{q})\,|Q_\mu(\mathbf{q})|^2$$

Ionic Displacements in a 1D crystal

Linear chain

For the sake of simplicity, let's consider a linear chain with two atoms of mass m_1 and m_2 per lattice cell. The lattice parameter is a and the force constant is Φ_{12}



Equations of Motion

The two coupled equations of motion are

$$m_1 \frac{d^2 u_{L,1}(t)}{dt^2} = \Phi_{12}[u_{L,2}(t) - u_{L,1}(t)] + \Phi_{12}[u_{L-1,2}(t) - u_{L,1}(t)]$$

$$m_2 \frac{d^2 u_{L,2}(t)}{dt^2} = \Phi_{12}[u_{L,1}(t) - u_{L,2}(t)] + \Phi_{12}[u_{L+1,1}(t) - u_{L,2}(t)]$$

Equations of Motion

The two coupled equations of motion are

$$m_1 \frac{d^2 u_{L,1}(t)}{dt^2} = \Phi_{12}[u_{L,2}(t) - u_{L,1}(t)] + \Phi_{12}[u_{L-1,2}(t) - u_{L,1}(t)]$$
$$m_2 \frac{d^2 u_{L,2}(t)}{dt^2} = \Phi_{12}[u_{L,1}(t) - u_{L,2}(t)] + \Phi_{12}[u_{L+1,1}(t) - u_{L,2}(t)]$$

which have solutions of the form

$$u_{L,1}(t) = u_1 e^{i(kLa-\omega(k)t)} \qquad u_{L,2}(t) = u_2 e^{i(kLa-\omega(k)t)}$$

From the Born von Karmann PBC, k can only takes discrete values

$$k = p\frac{2\pi}{N_L a},\ p = 0, \ldots N_L$$

The system of equations then becomes

$$-\omega^2(k) m_1 u_1 = -\Phi_{12}[2u_1 - u_2(1 + e^{-ika})]$$
$$-\omega^2(k) m_2 u_2 = -\Phi_{12}[2u_2 - u_1(1 + e^{ika})]$$

Matrix Formulation

With $e_1 = \sqrt{m_1}u_1$ and $e_2 = \sqrt{m_2}u_2$, one gets

$$\omega^2(k)e_1 = \frac{2\Phi_{12}}{m_1}e_1 - \frac{\Phi_{12}}{\sqrt{m_1 m_2}}(1 + e^{-ika})e_2$$

$$\omega^2(k)e_2 = -\frac{\Phi_{12}}{\sqrt{m_1 m_2}}(1 + e^{ika})e_1 + \frac{2\Phi_{12}}{m_2}e_2$$

which can be written in matrix form as

$$\omega(k)^2\mathbf{e}(k) = \mathbf{D}(k)\mathbf{e}(k)$$

where $\mathbf{D}(k)$ is the dynamical matrix in reciprocal space

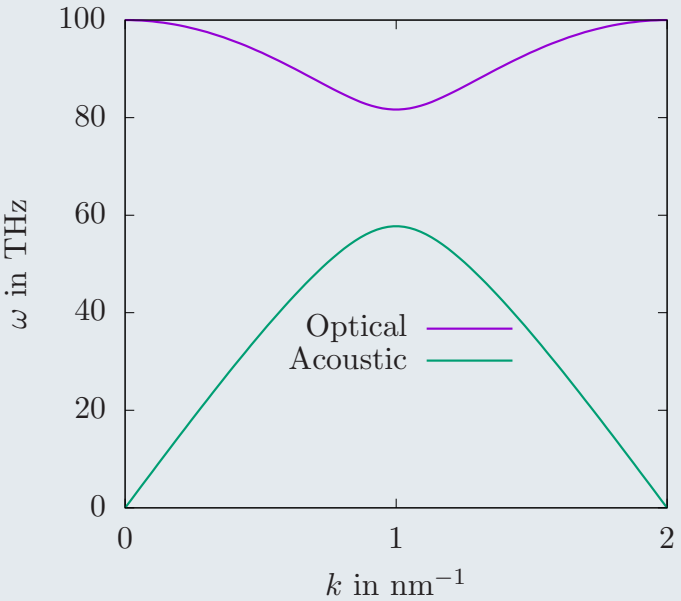
$$\mathbf{D}(k) = \begin{pmatrix} \frac{2\Phi_{12}}{m_1} & -\frac{\Phi_{12}}{\sqrt{m_1 m_2}}(1 + e^{-ika}) \\ -\frac{\Phi_{12}}{\sqrt{m_1 m_2}}(1 + e^{ika}) & \frac{2\Phi_{12}}{m_2} \end{pmatrix}$$

Eigenvalues of the Dynamical Matrix

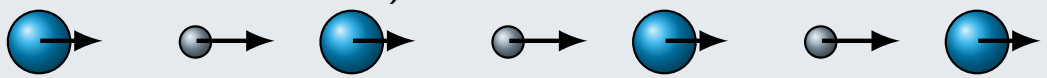
$$\omega_{\pm}^2(k) = \frac{\Phi_{12}}{m_1 m_2}\left(m_1 + m_2 \pm \sqrt{m_1^2 + m_2^2 + 2m_1 m_2 \cos(ka)}\right)$$

The curves $\omega_{\pm}^2(k)$ are the dispersion branches. For a 1D diatomic system, there are exactly 2 curves.

Optical and acoustic modes



- The acoustic mode has a zero frequency at the Gamma point, it is a translational mode where all ions move together. (In the 3D case there would be 3 acoustic branches)

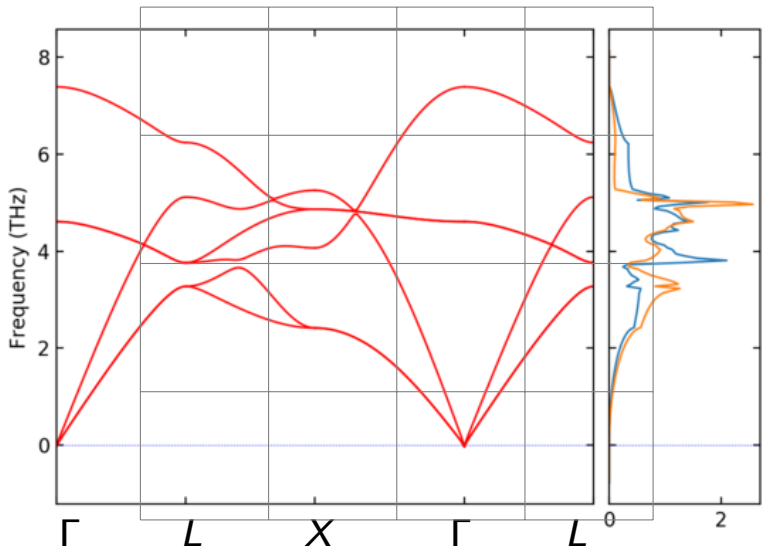


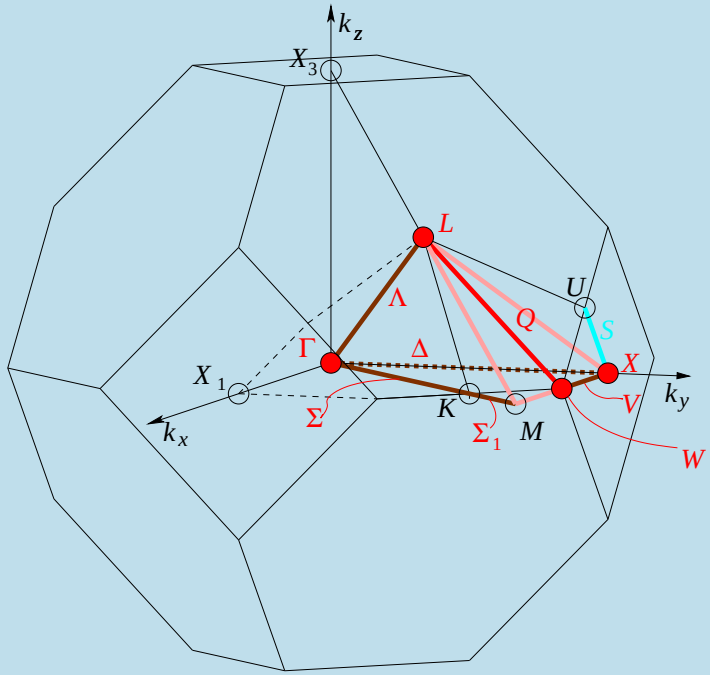
- All the other modes have a non-zero frequency and are called optic modes.

Phonon spectrum

- The $\omega(q)$ frequencies form the phonon spectrum.
- Usually plotted for q in the first Brillouin zone along high-symmetry lines
- The Phonon Density of States (PDOS) gives how many phonon modes are at a particular frequency

Example of NaCl





©bilbao crystallographic server
http://www.cryst.ehu.es

What have we learned so far?

- Definition of the Reciprocal space
- Transformation of the problem to reciprocal space
- Solution for a 1D diatomic chain
- Optical and Acoustic modes
- Phonon Spectrum and Phonon Density of States

Outline

1. Solve the electronic part of the Hamiltonian:

$$\hat{H}^e(\{\mathbf{R}\}) = \hat{T}_e + \hat{W}_{ee} + \hat{V}_{ne}(\{\mathbf{R}\}) + \hat{V}_{nn}(\{\mathbf{R}\})$$

$$\hat{H}^e(\{\mathbf{R}\})\,|\Psi^e(\{\mathbf{R}\})\rangle = E^e(\{\mathbf{R}\})\,|\Psi^e(\{\mathbf{R}\})\rangle$$

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

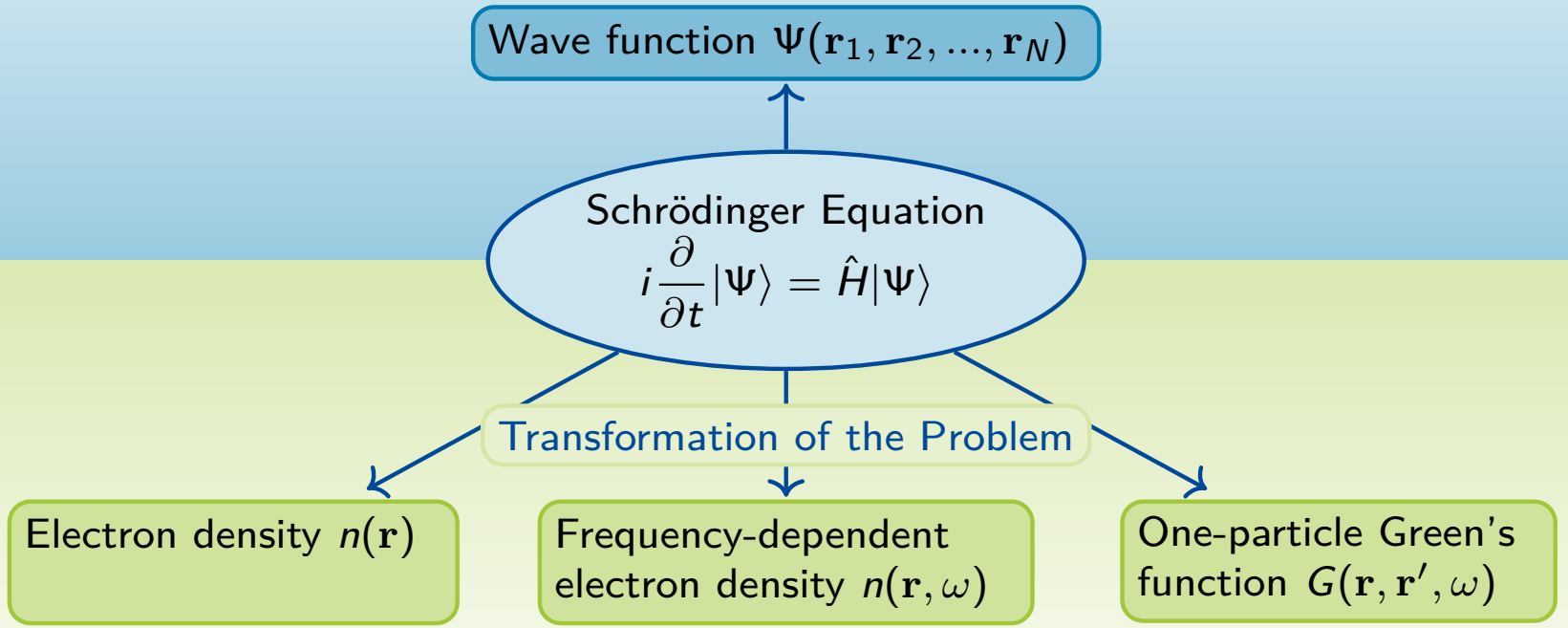
$$V(\mathbf{R}) = E_0^e(\mathbf{R})$$

3. Solve the ionic problem:

$$\hat{H}^n|\Psi^n\rangle = \left[\hat{T}^n + \hat{V}(\mathbf{R})\right]|\Psi^n\rangle$$

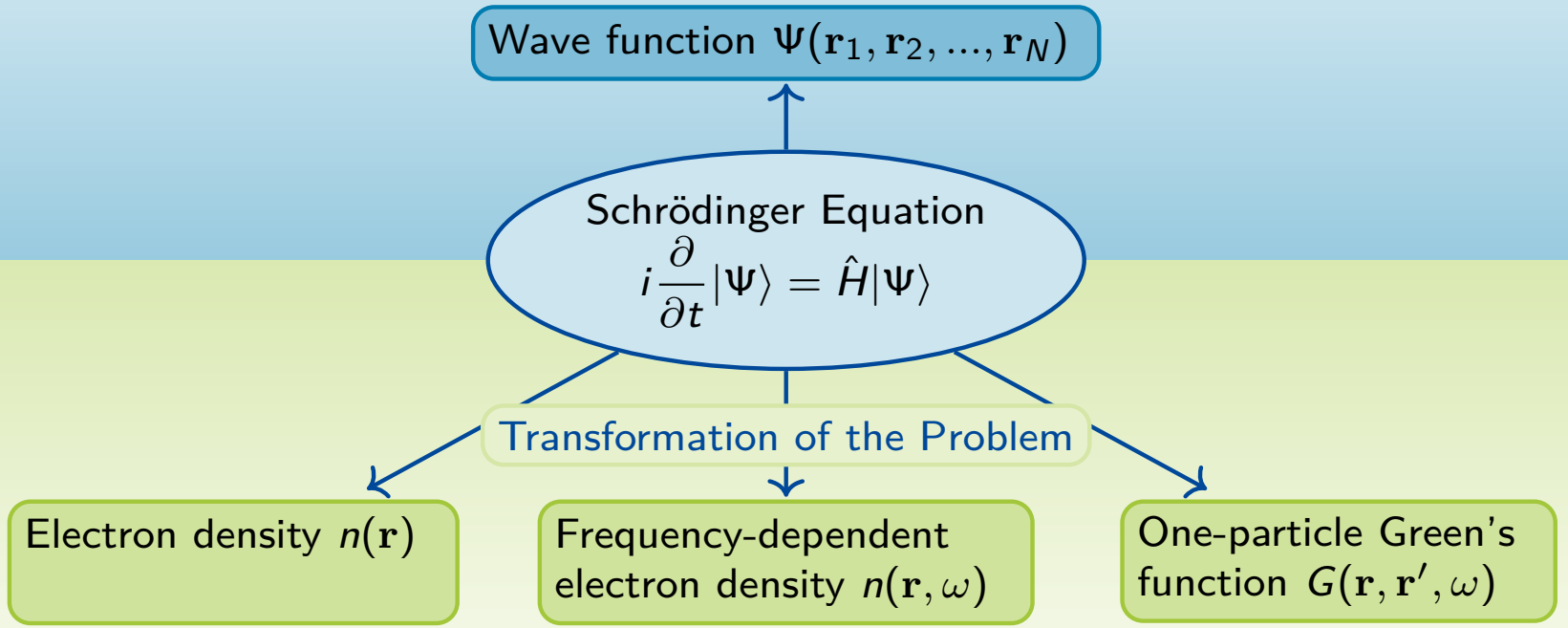
The BO potential is a complex many-body object that depends on $3M$ variables, where M is the total number of atoms in the system

Wave Function *vs* Density and Green's Function Methods



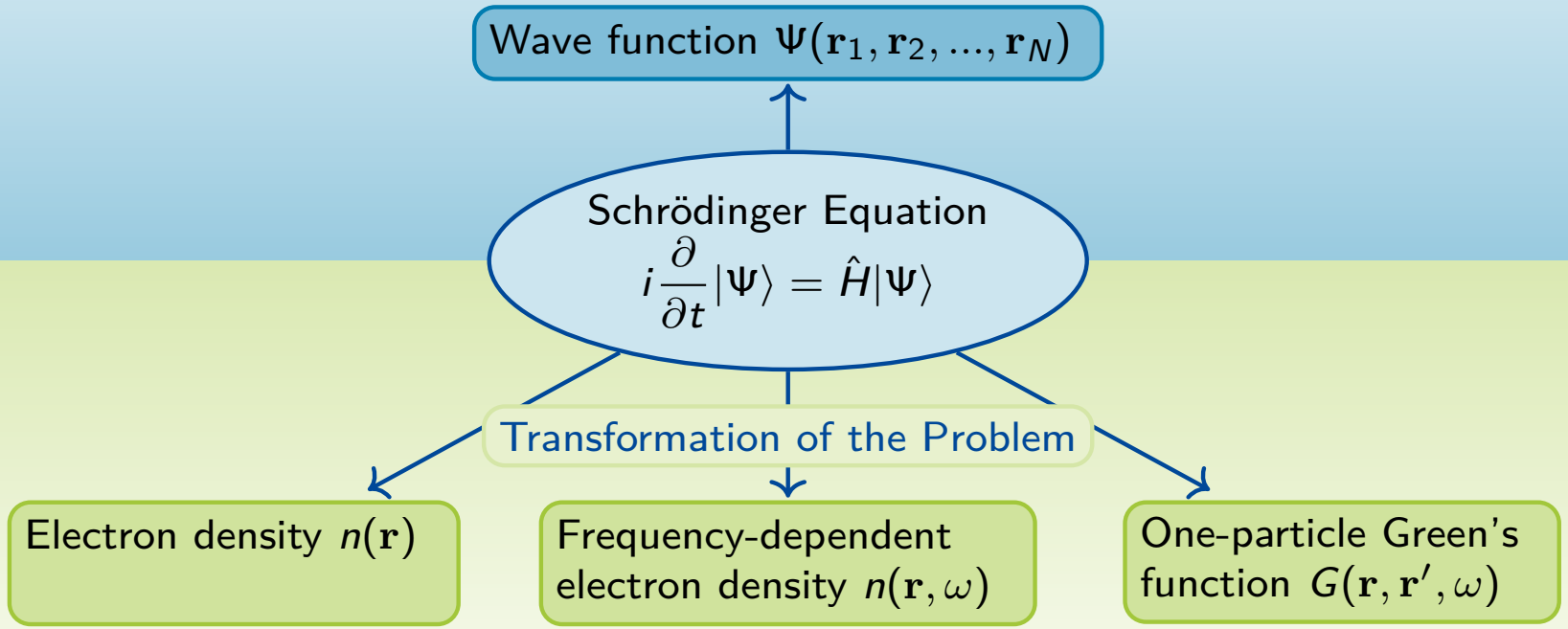
Wave Function *vs* Density and Green's Function Methods

- ☹ Complicated $3N$-dimensional object
- ☹ Expensive
- ☺ Systematic approach
- ☺ Clear how to compute properties



Wave Function *vs* Density and Green's Function Methods

- ☹ Complicated $3N$-dimensional object
- ☹ Expensive
- ☺ Systematic approach
- ☺ Clear how to compute properties



- ☺ Simpler object
- ☺ Cheaper
- ☹ No systematic approach (at least for n)
- ☹ Difficult to extract properties

Motivation for DFT

Density-functional theory (DFT) is:

- a **practical electronic-structure computational method**, widely used in quantum chemistry and condensed-matter physics;
- an **exact and elegant reformulation of the quantum many-body problem**, which has led to new ways of thinking in the field.

Useful Books

- R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, 1989.
- R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem*, Springer-Verlag, 1990.
- W. Koch and M. C. Holthausen, *A Chemist's Guide To Density Functional Theory*, Wiley-VCH, 2001.

Quantum many-electron problem

We consider an N-electron system in the Born-Oppenheimer and non-relativistic approximations

Electronic Hamiltonian

$$H[v] = -\frac{1}{2}\sum_{i=1}^{N}\nabla^2_{\mathbf{r}_i} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N} v(\mathbf{r}_i) \tag{1}$$

where v is the external potential. Usually it is taken as $v_{ne}(\mathbf{r}_i) = -\sum_A Z_A/|\mathbf{r}_i - \mathbf{R}_A|$, the nuclei-electron interaction potential.

Time-independent Schrödinger equation

Stationary states satisfy

$$H\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \tag{2}$$

where $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ is a wave function written with space-spin coordinates $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\sigma_i \in \{\uparrow, \downarrow\}$) which is antisymmetric with respect to the exchange of two space-spin coordinates; and E is the associated energy.

Second Quantization

Using Dirac notations (representation-independent formalism): $\hat{H}|\Psi_i\rangle = E|\Psi_i\rangle$ where $\hat{H} = \hat{T} + \hat{W}_{ee} + \hat{V}_{ne}$.

Expectation Value

The energy can be calculated as an expectation value

$$E = \langle \Psi | H[v] | \Psi \rangle$$

where Ψ is a normalized N-electron wave function (spanning the space $\mathcal{W}$).

Variational Principle

Given a system with a time-independent Hamiltonian H. If Ψ is a well-behaved wavefunction (trial wavefunction) of the system that satisfied the boundary conditions of the problem, then

$$\langle \Psi | H[v] | \Psi \rangle = E \geq E_0$$

where E_0 is the ground state energy of H ,i.e. lowest eigenvalue of H over the space $\mathcal{W}$.

Interpretation of the Wave Function

- The quantity $|\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N)|^2 \, d\mathbf{x}_1 d\mathbf{x}_2 \cdots \mathbf{x}_N$ is the probability of finding electron 1 in $d\mathbf{x}_1$, electron 2 in $d\mathbf{x}_2$, etc
- Integrating over the space-spin coordinates of electrons $2, 3, \cdot, N$, together with the spin coordinate of electron 1, gives

$$\left(\int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdot \mathbf{x}_N)|^2 \, ds_1 d\mathbf{x}_2 \cdots \mathbf{x}_N \right) d\mathbf{r}_1$$

which is the probability of finding electron 1 in volume element $d\mathbf{r}_1$, whilst the other electrons are anywhere.

Definition of the One-Electron Density

Multiplying by N gives the probability of finding any electron in $d\mathbf{r}_1$, namely the one-electron density

$$n(\mathbf{r}_1) = N \left(\int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdot \mathbf{x}_N)|^2 \, ds_1 d\mathbf{x}_2 \cdots \mathbf{x}_N \right)$$

Hohenberg P. and Kohn W., Phys. Rev. **136**, B864 (1964)

- Consider an electronic system with an arbitrary external local potential $v(r)$ (that binds N electrons).

- The corresponding ground-state wave function Ψ can be obtained by solving the Schrödinger equation, from which an associated ground-state density $n(\mathbf{r})$ can be deduced. Therefore, one has the mapping:

$$v(\mathbf{r}) \rightarrow n(\mathbf{r})$$

First HK Theorem – inverse mapping

The ground-state electron density $n(\mathbf{r})$ determines the external potential $v(\mathbf{r})$ up to an arbitrary real-value constant

$$n(\mathbf{r}) \rightarrow v(\mathbf{r}) + const.$$

The Bright Wilson observation

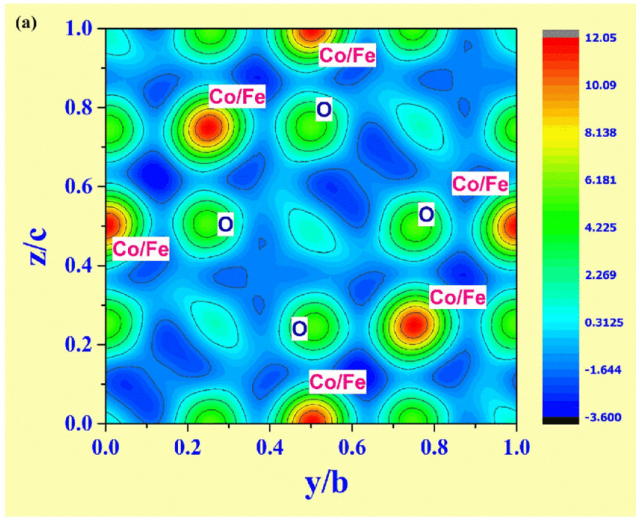
To know the Hamiltonian, we need to know the number of electrons and the external potential, ie the number of electrons, the nuclear charges, and their positions.

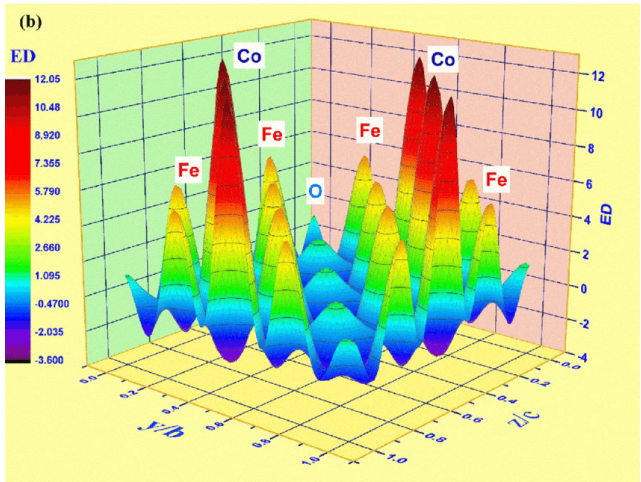
All of these can be determined from a knowledge of the density:

$$n(\mathbf{r})d\mathbf{r} = N \qquad \frac{\partial}{\partial r_A}\bar{n}(r_A)\Big|_{r_A=0} = 2Z_A\bar{n}(0)$$

where $\bar{n}$ is the spherical average of the density.

The cusps of the density tell us where the nuclei are. $n(\mathbf{r})$ therefore determines the Hamiltonian and hence everything about the system.





2D and 3D -Electron Density map in unit cell of $CoFe_2O_4$ nanoparticles, Dubey et al (2022)

Second HK Theorem – Universal Functional

For non degenerate ground-states, the ground-state wave function Ψ is a functional of n, denoted by $\Psi[n]$. Hohenberg and Kohn defined the universal density functional (system-independent)

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

and the total electronic energy functional

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

The Hohenberg-Kohn universal functional is only defined for N-electron densities n that are ground-state densities associated with some local potential, the so-called set of v-representable densities which we will denote by $\mathcal{A}$.

Variational Principle

Hohenberg and Kohn showed that we have a variational property giving the exact ground-state energy

$$E_0 = \min_{n \in \mathcal{A}} \{ F[n] + \int v_{ne}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \}.$$

The minimum is reached for an exact ground-state density $n_0(\mathbf{r})$ of the potential $v_{ne}(\mathbf{r})$

Levy-Lieb constrained-search formulation

Levy-Lieb functional

In 1979 Levy, and later in 1983 Lieb, proposed to redefine the universal density functional as

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

where $\Psi \to n$ means that the wave function Ψ is constrained to yield the fixed density n.

This so-called Levy-Lieb functional $F[n]$ does not require the existence of a local potential associated with the density.
It is an extension of the Hohenberg-Kohn functional: it is defined on the larger set of N-electron densities coming from a wave function $\Psi \in \mathcal{W}$, the so-called set of N-representable densities $\mathcal{D}$.

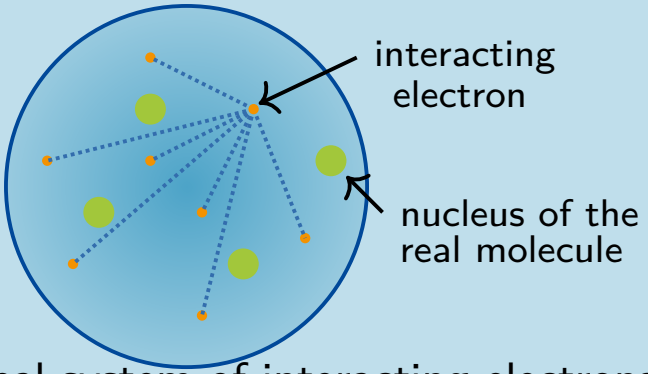
Variational Property

$$E = \min_{\Psi \in \mathcal{W}} \langle \Psi | \hat{T} + \hat{W}_{ee} + \hat{V}_{ne} | \Psi \rangle = \min_{n \in \mathcal{D}} \{ F[n] + \int v_{ne}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \}$$

Hence, in DFT, we replace $\min_\Psi$ by $\min_n$ which is a tremendous simplification!
However, $F[n] = T[n] + W_{ee}[n]$ is very difficult to approximate, in particular the kinetic energy part $T[n]$.

Kohn-Sham method: principle

Real System

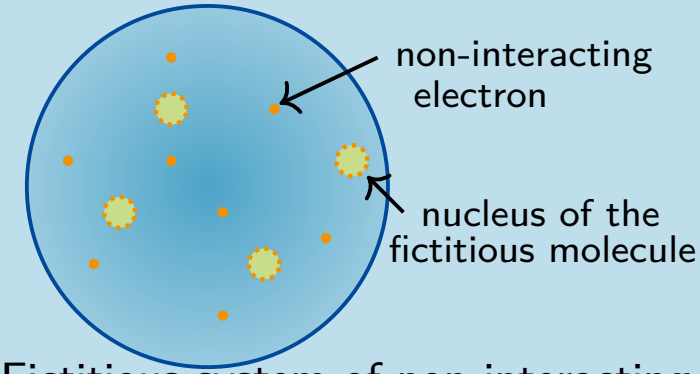


- Real system of interacting electrons
- Exact Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}$$

- Exact ground-state density n_0

Kohn-Sham System



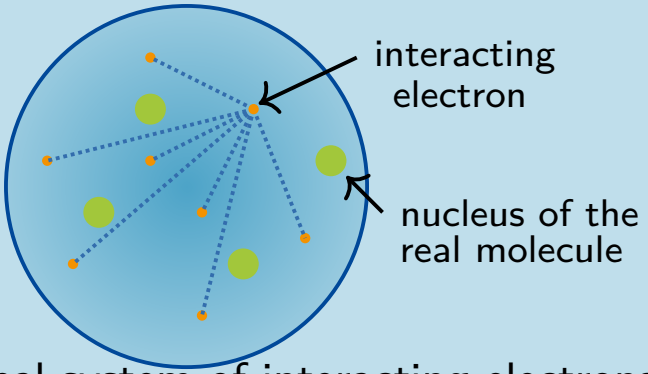
- Fictitious system of non-interacting electrons
- Kohn-Sham Hamiltonian

$$\hat{H}^{\text{KS}} = \hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{Hxc}}$$

- Exact density $n_0^{\text{KS}} = n_0$

Kohn-Sham method: principle

Real System

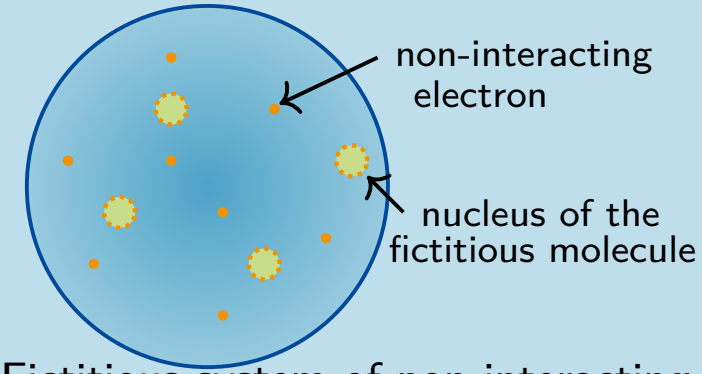


- Real system of interacting electrons
- Exact Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}$$

- Exact ground-state density n_0

Kohn-Sham System



- Fictitious system of non-interacting electrons
- Kohn-Sham Hamiltonian

$$\hat{H}^{\text{KS}} = \hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{Hxc}}$$

- Exact density $n_0^{\text{KS}} = n_0$

Ground-State Energy

Standard WF formalism

$$E_0 = \langle \Psi_0 | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi_0 \rangle$$

Ψ_0: multi-determinantal wave function corresponding to n_0

Kohn-Sham formalism

$$E_0 = \langle \Phi_0 | \hat{T} + \hat{V}_{\text{ne}} | \Phi_0 \rangle + E_{\text{Hxc}}[n_0]$$

Φ_0: mono-determinantal wave function corresponding to n_0

Kohn-Sham method: decomposition of the universal functional

KS decomposition of the universal functional

In 1965, Kohn and Sham proposed to decompose $F[n]$ as

$$F[n] = T_s[n] + E_{Hxc}[n]$$

Kinetic term

$T_s[n]$ is the non-interacting kinetic-energy functional:

$$T_s[n] = \min_{\substack{\Phi \in \mathcal{S} \\ \Phi \to n}} \langle \Phi | \hat{T} | \Phi \rangle = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle$$

where the minimization is done over single-determinant wave functions $\Phi \in \mathcal{S}$ yielding the fixed density n.

Electronic interaction term

The remaining functional $E_{Hxc}[n]$ is called the Hartree-exchange-correlation functional.
$E_{Hxc}[n]$ is decomposed as

$$E_{Hxc}[n] = E_H[n] + E_{xc}[n]$$

$T_s[n]$ is still defined over the entire set of N-representable densities $\mathcal{D}$ because any N-representable density can be obtained from a single-determinant wave function. Therefore, the Kohn-Sham decomposition does not introduce any approximation.

Ground-state Energy

The exact ground-state energy can the be expressed as

$$
\begin{aligned}
E_0 &= \min_{n\in\mathcal{D}} \left\{ F[n] + \int v_{ne}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\} \\
&= \min_{n\in\mathcal{D}} \left\{ \min_{\substack{\Phi\in\mathcal{S} \\ \Phi\to n}} \langle \Phi | \hat{T} | \Phi \rangle + E_{Hxc}[n] + v_{ne}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\} \\
&= \min_{\Phi\in\mathcal{S}} \left\{ \langle \Phi | \hat{T} + \hat{V}_{ne} | \Phi \rangle + E_{Hxc}[n_\Phi] \right\}
\end{aligned}
$$

and a minimizing single-determinant KS wave function gives an exact ground-state density $n_0(\mathbf{r})$.

Hence, in KS DFT, we replace $\min_\Psi$ by $\min_\Phi$ which is still a tremendous simplification! The advantage of KS DFT over pure DFT is that a major part of the kinetic energy is treated explicitly with the single-determinant wave function Φ.

The Hartree functional

$E_H[n]$ is the Hartree energy functional

$$E_H[n] = \frac{1}{2} \iint \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

representing the classical electrostatic repulsion energy for the charge distribution $n(\mathbf{r})$ and which is calculated exactly.

The Exchange-Correlation functional

$E_{xc}[n]$ is the exchange-correlation energy functional that remains to approximate. Assuming $\Phi[n]$ is unique, this functional is often decomposed as $E_{xc}[n] = E_x[n] + E_c[n]$ where $E_x[n]$ is the exchange energy functional

$$E_x[n] = \langle \Phi[n] | \hat{W}_{ee} | \Phi[n] \rangle - E_H[n]$$

and $E_c[n]$ is the correlation energy functional

$$Ec[n] = \langle \Psi[n] | \hat{T} + \hat{W}_{ee} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{W}_{ee} | \Phi[n] \rangle = T_c[n] + U_c[n]$$

containing a kinetic contribution $T_c[n] = \langle \Psi[n] | \hat{T} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} | \Phi[n] \rangle$ and a potential contribution $U_c[n] = \langle \Psi[n] | \hat{W}_{ee} | \Psi[n] \rangle - \langle \Phi[n] | \hat{W}_{ee} | \Phi[n] \rangle$.

Orbital minimization

The single determinant Φ is constructed from a set of N orthonormal occupied spin-orbitals $\psi_i(\mathbf{x}) = \varphi_i(\mathbf{r})\delta_{\sigma_i,\sigma}$. The total energy to be minimized is

$$E[\{\varphi_i\}] = \sum_{i=1}^{N} \int \varphi_i^*(\mathbf{r}) \left[-\frac{1}{2}\nabla^2 + v_{ne}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) d\mathbf{r} + E_{Hxc}[n]$$

and the density is $n(r) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$

Lagrangian method

For minimizing over the orbitals $\{\varphi_i\}$with the constraint of keeping the orbitals orthonormalized, we introduce the Lagrangian

$$\mathcal{L}[\{\varphi_i\}] = E[\{\varphi_i\}] - \sum_{i=1}^{N} \varepsilon_i \left(\int \varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r}) d\mathbf{r} - 1 \right)$$

where ε_i is the Lagrange multiplier associated with the normalization condition of $\varphi_i(\mathbf{r})$.

The Lagrangian must be stationary with respect to variations of the orbitals $\dfrac{\partial \mathcal{L}}{\partial \varphi_i^*(\mathbf{r})} = 0$

Kohn-Sham Equations

We find for the functional derivative of the Lagrangian

$$0 = \frac{\partial \mathcal{L}}{\partial \varphi_i^*(\mathbf{r})} = \left[-\frac{1}{2}\nabla^2 + v_{ne}(\mathbf{r})\right]\varphi_i(\mathbf{r}) + \frac{\partial E_{Hxc}[n]}{\partial \varphi_i^*(\mathbf{r})} - \varepsilon_i \varphi_i(\mathbf{r})$$

We calculate the term $\frac{\partial E_{Hxc}[n]}{\partial \varphi_i^*(\mathbf{r})}$ using the chain rule

$$\frac{\partial E_{Hxc}[n]}{\partial \varphi_i^*(\mathbf{r})} = \int \frac{\partial E_{Hxc}[n]}{\partial n(\mathbf{r}')}\frac{\partial n(\mathbf{r}')}{\partial \varphi_i^*(\mathbf{r})} d\mathbf{r}' = v_{Hxc}[n](\mathbf{r})\varphi_i(\mathbf{r})$$

where we have introduced the Hartree-exchange-correlation potential $v_{Hxc}[n](\mathbf{r}) = \frac{\partial E_{Hxc}[n]}{\partial n(\mathbf{r})}$ which is itself a functional of the density.

Kohn-Sham Equations

We arrive at the KS equations

$$\left[-\frac{1}{2}\nabla^2 + v_{ne}(\mathbf{r}) + v_{Hxc}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

The orbitals $\varphi_i(\mathbf{r})$ are called the KS orbitals and ε_i are the KS orbital energies.

Kohn-Sham Hamiltonian

The KS orbitals are eigenfunctions of the KS one-electron Hamiltonian

$$h_s = -\frac{1}{2}\nabla^2 + v_s(\mathbf{r})$$

where $v_s(\mathbf{r}) = v_{ne}(\mathbf{r}) + v_{Hxc}(\mathbf{r})$ is the KS potential.

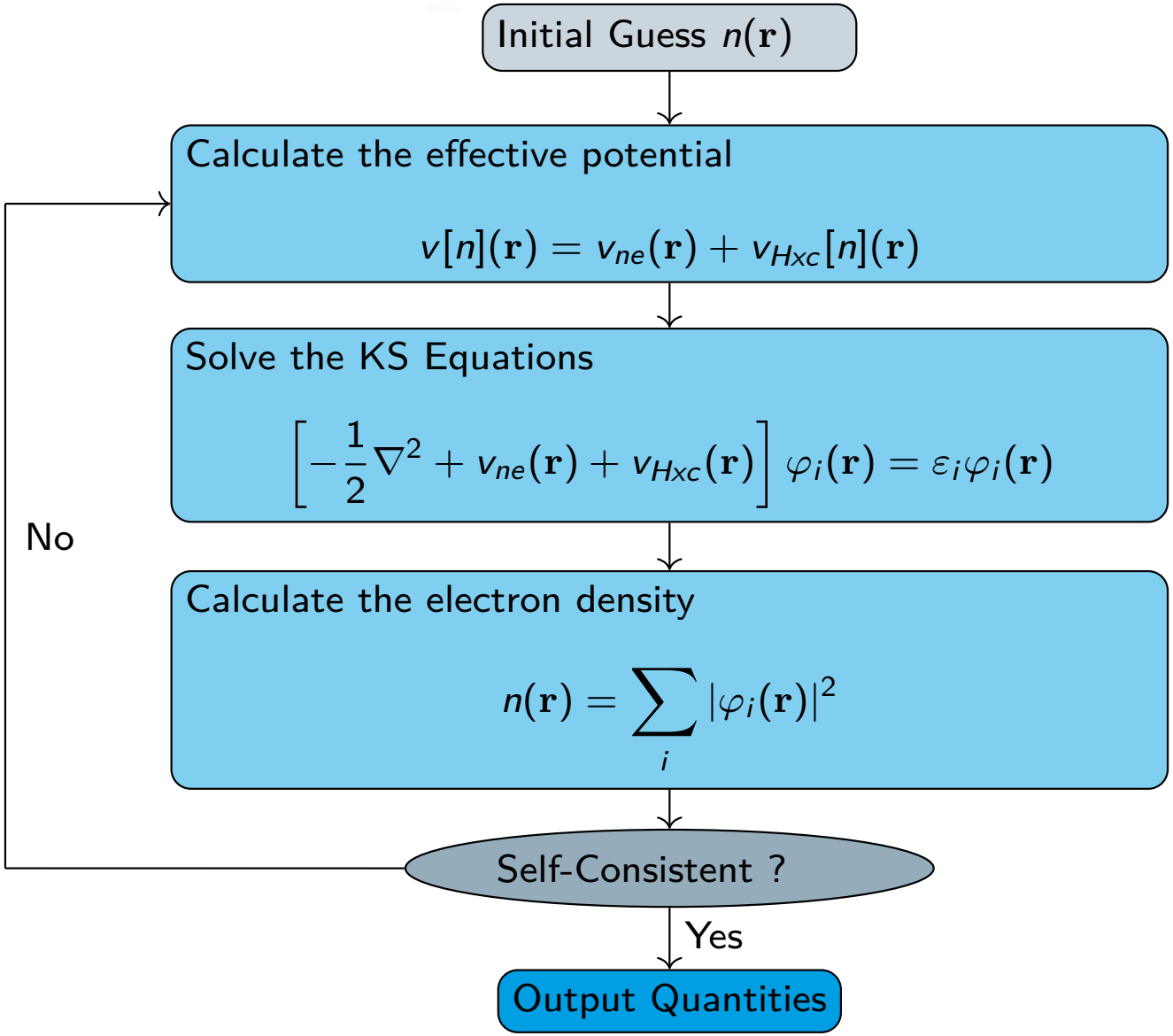
Mathematically, the KS equations are a set of coupled self-consistent equations since the potential $v_{Hxc}(\mathbf{r})$ depends on all the occupied orbitals $\{\varphi_i\}_{i=1,\dots N}$ through the density.

Physically, h_s defines the KS system which is a system of N non-interacting electrons in an effective external potential $v_s(\mathbf{r})$ ensuring that its ground-state density $n(\mathbf{r})$ is the same as the exact ground-state density $n_0(\mathbf{r})$ of the physical system of N interacting electrons.

The KS equations also defines virtual KS orbitals $\{\varphi_a\}_{a\geq N+1}$.

$h_s(\mathbf{r})$ is a self-adjoint operator and thus the set of KS orbitals can be chosen as orthonormal.

DFT Self-Consistent Loop



What have we learned so far?

- One-electron density
- Hohenberg-Kohn Theorems
  - Existence
  - Universal Functional
- Kohn-Sham Theory
  - Hartree-exchange-correlation functional
  - SCF resolution of Kohn-Sham Equations

Outline

Basis Set Expansion

We consider a basis of M atom-centered functions $\{\chi_\nu\}$, e.g. GTO basis functions. The orbitals are expanded as

$$\varphi_i(\mathbf{r}) = \sum_{\nu=1}^{M} C_{\nu i}\chi_\nu(\mathbf{r})$$

Inserting this expansion in the KS equations

$$h_s\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$$

and multiplying on the left by $\chi^*_\mu(\mathbf{r})$ and integrating over $\mathbf{r}$, we arrive at the familiar SCF generalized eigenvalue equation

$$\sum_{\nu=1}^{M} F_{\mu\nu}\,C_{\nu i} = \varepsilon_i \sum_{\nu=1}^{M} S_{\mu\nu}\,C_{\nu i}$$

where $F_{\mu\nu} = \int \chi^*_\mu(\mathbf{r})h_s\chi_\nu(\mathbf{r})d\mathbf{r}$ are the elements of the KS Fock matrix and $S_{\mu\nu} = \int \chi^*_\mu(\mathbf{r})\chi_\nu(\mathbf{r})d\mathbf{r}$ are the elements of the overlap matrix.

The Fock matrix is calculated as

$$F_{\mu\nu} = h_{\mu\nu} + J_{\mu\nu} + V_{xc,\mu\nu}$$

One-Electron Contribution

$h_{\mu\nu}$ are the one-electron integrals:

$$h_{\mu\nu} = \int \chi^*_\mu(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{ne}(\mathbf{r}) \right) \chi_\nu(\mathbf{r}) d\mathbf{r}$$

Hartree Contribution

$J_{\mu\nu}$ is the Hartree potential matrix:

$$J_{\mu\nu} = \int \chi^*_\mu(\mathbf{r}) v_H(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r} = \sum_{\lambda=1}^{M} \sum_{\gamma=1}^{M} P_{\gamma\lambda} (\chi_\mu \chi_\nu | \chi_\lambda \chi_\gamma)$$

where $(\chi_\mu \chi_\nu | \chi_\lambda \chi_\gamma) = \iint \frac{\chi^*_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1)\chi^*_\lambda(\mathbf{r}_2)\chi_\gamma(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$ are the two-electron integrals and $P_{\gamma\lambda} = \sum_{i=1}^{N} C_{\gamma i} C^*_{\lambda i}$ is the density matrix.

Exchange Correlation Contribution

$V_{xc,\mu\nu}$ is the exchange-correlation potential matrix:

$$V_{xc,\mu\nu} = \int \chi^*_\mu(\mathbf{r}) v_{xc}(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r}$$

The total electronic energy is calculated as

$$E = \sum_{\mu=1}^{M}\sum_{\nu=1}^{M} P_{\nu\mu} h_{\mu\nu} + \frac{1}{2}\sum_{\mu=1}^{M}\sum_{\nu=1}^{M} P_{\nu\mu} J_{\mu\nu} + E_{xc}$$

The density is calculated as

$$n(r) = \sum_{\lambda=1}^{M}\sum_{\gamma=1}^{M} P_{\gamma\lambda} \chi_\gamma(\mathbf{r}) \chi^*_\lambda(\mathbf{r})$$

Kohn-Sham Potential and orbitals

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

$$v^{KS}(\mathbf{r}+\mathbf{T}) = v^{KS}(\mathbf{r})$$

This implies that KS orbitals are Bloch states:

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

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

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

Consequences of Bloch Theorem

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

$$\langle\varphi_{n'\mathbf{k}'}|h_S|\varphi_{n\mathbf{k}}\rangle\delta_{\mathbf{k},\mathbf{k}'}\delta_{nn'}$$

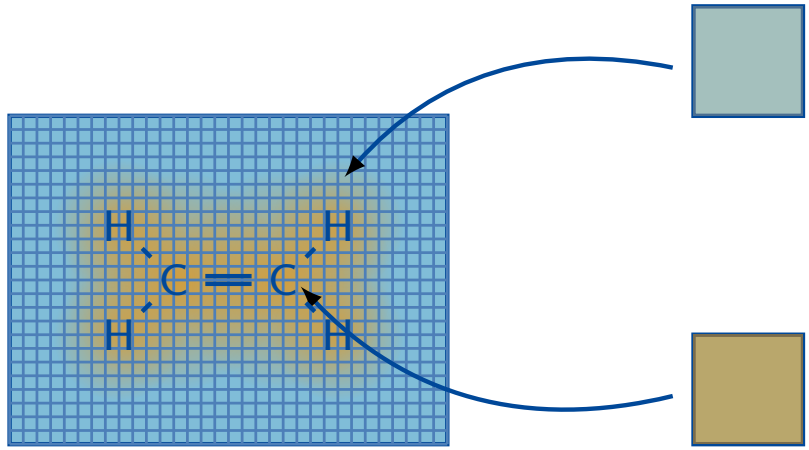
For each $\mathbf{k}$ we need to solve the KS equation and we will get different energies $E_{n\mathbf{k}}$. These form the band structure

Local Density Approximation (LDA)

In the local-density approximation (LDA), introduced by Kohn and Sham (1965), the exchange-correlation functional is approximated as

$$E_{xc}^{\mathrm{LDA}}[n] = \int n(\mathbf{r})\varepsilon_{xc}^{\mathrm{UEG}}(n(\mathbf{r}))d\mathbf{r}$$

where $\varepsilon_{xc}^{\mathrm{UEG}}(n)$ is the exchange-correlation energy per particle of the infinite uniform electron gas (UEG) with the density n.



The idea underlying the LDA is to divide the system onto a grid and to substitute the xc energy density on each volume element $d\mathbf{r}$ around the position $\mathbf{r}$ by the one calculated for a UEG of density $n(\mathbf{r})$.

The exchange energy per particle of the UEG can be calculated analytically For the correlation energy per particle of the UEG, there are some parametrized functions of n fitted to QMC data and imposing the high- and low-density expansions.

Gradient-Expansion Approximation

The next logical step beyond the LDA is the gradient-expansion approximation (GEA) which consists in a systematic expansion of Exc[n] in terms of the gradients of n(r). However this expansion is valid if the gradient is small which is not always the case and the GEA turns out to be a worse approximation than LDA

Generalized Gradient Approximation

The failure of the GEA lead to the development of generalized-gradient approximations (GGAs), started in the 1980s, of the generic form

$$E_{xc}^{\mathrm{GGA}}[n] = \int e_{xc}^{\mathrm{GGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}))d\mathbf{r}$$

The GGAs provide a big improvement over LDA for molecular systems. The GGAs are often called semilocal approximations, which means that they involve a single integral on $\mathbf{r}$ using "semilocal" information through $\nabla n(\mathbf{r})$.

Many GGA functionals have been proposed including BLYP, PW91 or PBE for the most widely used.

3-parameter Hybrid

In 1993, Becke proposed to mix Hartree-Fock (HF) exchange with GGA functionals in a three-parameter hybrid (3H) approximation

$$E_{xc}^{3H}[\Phi] = aE_x^{HF}[\Phi] + bE_x^{GGA}[n_\Phi] + (1-a-b)E_x^{LDA}[n_\Phi] + cE_c^{GGA}[n_\Phi] + (1-c)E_c^{LDA}[n_\Phi]$$

where a, b, and c are empirical parameters. Example: B3LYP (a = 0.20)

Adding a fraction a of HF exchange decreases the self-interaction error, which tends to favor too much delocalized electron densities. However, a too large a tends to increase the static-correlation error (stretched chemical bonds, transition metal elements, ...).

1-parameter hybrid

In 1996, Becke proposed a simpler one-parameter hybrid (1H) approximation

$$E_{xc}^{1H}[\Phi] = aE_x^{\mathrm{HF}}[\Phi] + (1a)E_x^{DFA}[n_\Phi] + E_c^{DFA}[n_\Phi]$$

where E_x^{DFA} and E_c^{DFA} can be any semilocal density-functional approximations (DFAs). The optimal a is often around 0.25. Example: PBE0 = HF/PBE hybrid with a = 0.25.

Hellmann-Feynman Theorem

$$\frac{dE_\lambda}{d\lambda} = \left\langle \Psi_\lambda \left| \frac{d\hat{H}_\lambda}{d\lambda} \right| \Psi_\lambda \right\rangle$$

where

- $\hat{H}_\lambda$ is a Hermitian operator depending upon a continuous parameter λ
- $|\Psi_\lambda\rangle$ is an eigenstate of the Hamiltonian, depending implicitly upon λ
- E_λ is the energy (eigenvalue) of the state $|\Psi_\lambda\rangle$

Hellmann-Feynman Forces

The most common application of the Hellmann–Feynman theorem is the calculation of intramolecular forces in molecules.

$$\hat{H}^e(\{\mathbf{R}\}) = \hat{T}_e + \hat{W}_{ee} + \hat{V}_{ne}(\{\mathbf{R}\}) + \hat{V}_{nn}(\{\mathbf{R}\})$$

The x-component of the force acting on a nucleus I is

$$F_{X_I} = -\frac{\partial E}{\partial X_I} = -\left\langle \Psi \left| \frac{\partial \hat{H}^e(\{\mathbf{R}\})}{\partial X_I} \right| \Psi \right\rangle$$

Differentiation of the Hamiltonian

$$\frac{\partial \hat{H}^e(\{\mathbf{R}\})}{\partial X_I} = \frac{\partial}{\partial X_I}\left(-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}\right)$$

$$= -Z_I \sum_{i=1}^{N}\frac{x_i - X_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} + Z_I \sum_{A\neq I} Z_A \frac{X_A - X_I}{|\mathbf{R}_A - \mathbf{R}_I|^3}$$

Hellmann-Feynman Forces in DFT

$$F_{X_I} = Z_I\left(\int d\mathbf{r} n(\mathbf{r})\frac{x - X_I}{|\mathbf{r} - \mathbf{R}_I|^3} - \sum_{A\neq I} Z_A \frac{X_A - X_I}{|\mathbf{R}_A - \mathbf{R}_I|^3}\right)$$

This allows for the calculation of equilibrium geometries – the nuclear coordinates where the forces acting upon the nuclei, due to the electrons and other nuclei, vanish.

Calculation of the Dynamical Matrix

The calculation of the force constants require the calculation of second-derivatives of $V(R)$
There are two main approaches to obtain $\Phi^{(2)}_{ab}$ from DFT

Finite displacements methods

- Atoms are displaced from the equilibrium $\mathbf{R}_0$ position and the energies and/or forces are obtained with DFT to later calculate the force-constants taking numerical derivatives.
- These methods are valid also for empirical potentials

Perturbative methods

- Quantum mechanical perturbation theory is used to the change in the electronic density and wave functions, from which the force-constants can be calculated.
- Valid only for DFT approaches, not empirical potentials

I will only present the first one.

Calculation of the Dynamical Matrix: Finite Displacements

It is possible to directly obtain the force-constants matrix by calculating with DFT atomic forces in slightly distorted supercells

Hellmann-Feynman Forces in a periodic system

In the harmonic approximation the force of an atom can be obtained from the force-constants as

$$F_a(\mathbf{L}_a) = -\sum_{\mathbf{L}_b b} \Phi^{(2)}_{ab}(\mathbf{L}_a, \mathbf{L}_b) u_b(\mathbf{L}_b)$$

Force constants

Therefore, the force-constants are

$$\Phi^{(2)}_{ab}(\mathbf{L}_a, \mathbf{L}_b) = -\frac{\partial F_a(\mathbf{L}_a)}{\partial u_b(\mathbf{L}_b)}$$

By translationnal symmetry, it is sufficient to know

$$\Phi^{(2)}_{ab}(\mathbf{L}) = -\frac{\partial F_a(\mathbf{L})}{\partial u_b(0)}$$

Calculation of the Dynamical Matrix: Finite Displacements

- The idea is to calculate these derivatives by finite differences
- Take a supercell, displace one atom that belongs to the unit cell as $\mathbf{R}_{b0}(0) + u_b(0)$, and calculate by DFT the Hellmann-Feynman forces on the atoms of the supercell. Then,

$$\Phi^{(2)}_{ab}(\mathbf{L}) = -\frac{\partial F_a(\mathbf{L})}{\partial u_b(0)} = -\frac{F_a(\mathbf{L}; \mathbf{R}_{0b}(0) + u_b(0)) - F_a(\mathbf{L}; \mathbf{R}_{0b}(0))}{u_b(0)}$$

- Repeat the procedure for all the displacements needed to generate all the force-constants for a lattice vector within the supercell

Reciprocal Dynamical matrix

Due to periodic boundary boundary conditions set by the supercell, the dynamical matrix can be calculated at any $q \in 1BZ$ by Fourier transform

$$D_{ab}(q) = \frac{1}{N_{sc}} \sum_{\mathbf{L}_{sc}} \frac{\Phi^{(2)}_{ab}(\mathbf{L}_{sc})}{\sqrt{m_a m_b}} e^{iq.\mathbf{L}_{sc}}$$

where the sum is limited to the N_{sc} $\mathbf{L}_{sc}$ vectors within the supercell

What have we learned so far?

- Single-point DFT calculation
- Approximate functionals
- Geometry optimization
- Dynamical Matrix Calculation

$\rightsquigarrow$ In principle you now have all the tools to compute a phonon spectrum from DFT