

Introduction to Computational Materials Science

for Advanced Experimental Physics

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Introduction

Objectives

- ▶ Understand the methods underlying software based on density functional theory and perturbation theory for the calculation of structural, electronic, and phononic properties of crystalline solids.
- ▶ Informed use of ABINIT, a software that you will use to compute several properties of some crystalline solids, on the basis of these theories.

References

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- ▶ Giannozzi & Baroni, "Density-Functional Perturbation Theory", Yip, *Materials Modeling Handbook*, Sec. 1.10, Springer, 2005
- ▶ Atkins & Friedman, *Molecular Quantum Mechanics*, Oxford University Press, 2011
- ▶ Martin, *Electronic Structure: Basic Theory and Practical Methods*, Cambridge University Press, 2020
- ▶ Baroni et al., "Phonons and Related Crystal Properties from Density-Functional Perturbation Theory", *Rev. Mod. Phys.* **73**(2) 515–562, 2001

Many-Electron Problem

Many-Body Hamiltonian I

We start by considering a system of electrons and nuclei described by the many-body Hamiltonian operator:

$$\hat{H}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = \hat{T}_e(\{\mathbf{r}_i\}) + \hat{T}_N(\{\mathbf{R}_I\}) + \hat{U}_{ee}(\{\mathbf{r}_i\}) + \hat{U}_{NN}(\{\mathbf{R}_I\}) + \hat{U}_{eN}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})$$

- ▶ We use SI units. However, atomic units are often used in the literature. A short summary of atomic units is in the Appendix.
- ▶ $\hat{T}_e(\{\mathbf{r}_i\})$ represents the total kinetic energy of the electrons:

$$\hat{T}_e(\{\mathbf{r}_i\}) = \sum_i \hat{T}_e(\mathbf{r}_i) = -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\mathbf{r}_i}^2}{m_e}$$

where $\hat{T}_e(\mathbf{r}_i)$ represents the kinetic energy of the i -th electron, whose position vector is \mathbf{r}_i .

Many-Body Hamiltonian II

- ▶ $\hat{T}_N(\{\mathbf{R}_I\})$ represents the total kinetic energy of the nuclei:

$$\hat{T}_N(\{\mathbf{R}_I\}) = \sum_I \hat{T}_N(\mathbf{R}_I) = -\frac{\hbar^2}{2} \sum_I \frac{\nabla_{\mathbf{R}_I}^2}{M_I}$$

where \hat{T}_I represents the kinetic energy of the I -th nucleus, whose position vector and mass are \mathbf{R}_I and M_I .

- ▶ $\hat{U}_{ee}(\{\mathbf{r}_i\})$ represents the potential energy due to the Coulomb repulsion between the electrons:

$$\hat{U}_{ee}(\{\mathbf{r}_i\}) = \frac{1}{2} \sum_{i \neq j} \hat{U}_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

where $\hat{U}_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ represents the potential energy between the i -th and j -th electrons.

Many-Body Hamiltonian III

- ▶ $\hat{U}_{\text{NN}}(\{\mathbf{R}_I\})$ represents the potential energy due to the Coulomb repulsion between the nuclei:

$$\hat{U}_{\text{NN}}(\{\mathbf{r}_i\}) = \frac{1}{2} \sum_{I \neq J} \hat{U}_{IJ}(\mathbf{R}_I, \mathbf{R}_J) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

where $\hat{U}_{IJ}(\mathbf{R}_I, \mathbf{R}_J)$ represents the potential energy between the I -th and J -th nuclei, whose atomic numbers are Z_I and Z_J .

- ▶ $\hat{U}_{\text{eN}}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})$ represents the potential energy due to the Coulomb attraction between the electrons and nuclei:

$$\hat{U}_{\text{eN}}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = \sum_{il} \hat{U}_{il}(\mathbf{r}_i, \mathbf{R}_I) = -\frac{e^2}{4\pi\epsilon_0} \sum_{il} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$

where $\hat{U}_{il}(\mathbf{r}_i, \mathbf{R}_I)$ represents the potential energy between the i -th electron and the I -th nucleus.

Born-Oppenheimer Approximation I

The Born-Oppenheimer approximation enables the separation of the system of electrons and nuclei into two sub-systems:

- ▶ The electrons interact among themselves and with the nuclei as if the latter were fixed in space at each instant.
- ▶ The nuclei interact among themselves and feel only an “average” potential energy from the electrons.

These leads to two separate equations for electrons and nuclei that, although coupled, simplify calculations.

Born-Oppenheimer Approximation II

- ▶ The properties of the system of electrons and nuclei are determined by solving the corresponding Schroedinger equation:

$$\hat{H}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = W \Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})$$

where W and $\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})$ are total energy and many-body wavefunction.

- ▶ For a given set of fixed nuclear coordinates $\{\mathbf{R}_I\}$, the many-electron Hamiltonian is:

$$\hat{H}_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = \hat{T}_e(\{\mathbf{r}_i\}) + \hat{U}_{ee}(\{\mathbf{r}_i\}) + \hat{U}_{eN}(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$$

- ▶ Solving the many-electron Schroedinger equation:

$$\hat{H}_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})\psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = E(\{\mathbf{R}_I\})\psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$$

provides many-electron states of energy $E(\{\mathbf{R}_I\})$ and wavefunction $\psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$.

Born-Oppenheimer Approximation III

- ▶ These states depend parametrically on the nuclear coordinates $\{\mathbf{R}_I\}$, but describe only the dynamics of the electrons, treating the nuclei as external classical particles fixed in space, whose sole role is to generate an “external” potential felt by the electrons.
- ▶ Parametric dependence is separated from actual independent variables by a semicolon.

Born-Oppenheimer Approximation IV

The Born-Oppenheimer approximation takes advantage of the large mass difference between electrons and nuclei, to approximate the many-body wavefunction as:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \approx X(\{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$$

where $\psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$ is an eigenfunction of the many-electron Hamiltonian $\hat{H}_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$ having eigenvalue $E(\{\mathbf{R}_I\})$, and $X(\{\mathbf{R}_I\})$ is an eigenfunction of the nuclear Hamiltonian:

$$\hat{H}_N(\{\mathbf{R}_I\}) = \hat{T}_N(\{\mathbf{R}_I\}) + \hat{U}_{NN}(\{\mathbf{R}_I\}) + E(\{\mathbf{R}_I\})$$

having eigenvalue W equal to the total energy of the many-body system.

Born-Oppenheimer Approximation V

- ▶ The original many-body Schroedinger equation is transformed into a system of two “smaller” Schroedinger equations, one for the electrons and one for the nuclei:

$$\begin{cases} \hat{H}_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = E(\{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \\ \hat{H}_N(\{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}) = W \chi(\{\mathbf{R}_I\}) \end{cases}$$

- ▶ Because of their much lighter mass, electrons are much faster than nuclei and their dynamics can be studied by fixing the nuclear coordinates at each instant.
- ▶ On the other hand, because they are much slower, nuclei cannot follow the electron dynamics instantaneously and only feel an effective potential generated by the electrons, given by $E(\{\mathbf{R}_I\})$.
- ▶ To confirm that the many-electron wavefunction depends only parametrically on the nuclear coordinates, write $\psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = \phi(\{\mathbf{r}_i\}) \chi(\{\mathbf{R}_I\})$ and plug it into the many-electron Schroedinger equation: $\chi(\{\mathbf{R}_I\})$ cancels out.

Proof of the Born-Oppenheimer Approximation I

1. We write the many-body wavefunction as:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = X(\{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$$

2. We plug it into the many-body Schroedinger equation:

$$\begin{aligned} X(\{\mathbf{R}_I\}) \hat{H}_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) + \\ \left[\hat{T}_N(\{\mathbf{R}_I\}) + U_{NN}(\{\mathbf{R}_I\}) \right] X(\{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = \\ W X(\{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \end{aligned}$$

3. We consider the following vector identity, neglecting the terms that relate the electron dynamics to the nuclear one:

$$\begin{aligned} \nabla_{\mathbf{R}_I}^2 X(\{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \approx \\ \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \nabla_{\mathbf{R}_I}^2 X(\{\mathbf{R}_I\}) + \cancel{X(\{\mathbf{R}_I\}) \nabla_{\mathbf{R}_I}^2 \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})} + \\ \cancel{2 \nabla_{\mathbf{R}_I} X(\{\mathbf{R}_I\}) \nabla_{\mathbf{R}_I} \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})} \end{aligned}$$

Proof of the Born-Oppenheimer Approximation II

4. As consequence, we can write:

$$\hat{T}_N(\{\mathbf{R}_I\}) X(\{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \approx \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \hat{T}_N(\{\mathbf{R}_I\}) X(\{\mathbf{R}_I\})$$

5. We replace this expression into the many-body problem and, by re-arranging the equation, obtain the “compatibility” equation:

$$\frac{1}{\psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})} \hat{H}_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) + \frac{1}{X(\{\mathbf{R}_I\})} \left[\hat{T}_N(\{\mathbf{R}_I\}) + U_{NN}(\{\mathbf{R}_I\}) \right] X(\{\mathbf{R}_I\}) = W$$

Proof of the Born-Oppenheimer Approximation III

6. The first LHS term describes the electron dynamics and depends on $(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})$, while the second LHS term describes the nuclear dynamics and depends on $(\{\mathbf{R}_I\})$. Their sum can be equal to the constant W only if the electron-related term is a function of the nuclear coordinates only, that is:

$$\hat{H}_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = E(\{\mathbf{R}_I\}) \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$$

This is the many-electron Schroedinger equation.

7. Substituting the many-electron Schroedinger equation into the “compatibility” equation leads to the nuclear Schroedinger equation, proving the Born-Oppenheimer approximation:

$$\underbrace{\left[\hat{T}_N(\{\mathbf{R}_I\}) + \hat{U}_{NN}(\{\mathbf{R}_I\}) + E(\{\mathbf{R}_I\}) \right]}_{\hat{H}_N(\{\mathbf{R}_I\})} X(\{\mathbf{R}_I\}) = W X(\{\mathbf{R}_I\})$$

Determining the Many-Electron Ground State I

The many-electron problem obtained can be generalized to:

$$\hat{H}_e(\{\mathbf{r}_i\}; \{\lambda\}) \psi(\{\mathbf{r}_i\}; \{\lambda\}) = E(\{\lambda\}) \psi(\{\mathbf{r}_i\}; \{\lambda\})$$

with:

$$\hat{H}_e(\{\mathbf{r}_i\}; \{\lambda\}) = \hat{T}_e(\{\mathbf{r}_i\}) + \hat{U}_{\text{int}}(\{\mathbf{r}_i\}) + \hat{U}_{\text{ext}}(\{\mathbf{r}_i\}; \{\lambda\})$$

- ▶ $\hat{U}_{\text{int}}(\{\mathbf{r}_i\}) = \hat{U}_{\text{ee}}(\{\mathbf{r}_i\})$ is “internal” potential energy of the electrons due to the Coulomb repulsion among them.
- ▶ $\hat{U}_{\text{ext}}(\{\mathbf{r}_i\}; \{\lambda\}) = \sum_i u_{\text{ext}}(\mathbf{r}_i; \{\lambda\})$ is the potential energy of the electrons due to some “external” source.
- ▶ Each electron feels the same external potential $u_{\text{ext}}(\mathbf{r}_i; \{\lambda\})$, which may depend on a set of parameters $\{\lambda\}$, such as the nuclear coordinates $\{\mathbf{R}_I\}$ in our previous case.

Determining the Many-Electron Ground State II

- ▶ For a given set of $\{\lambda\}$, the many-electron Schrodinger equation is solved by an infinite set of eigenstates.
- ▶ We are interested in the so-called ground state $\psi_0(\{\mathbf{r}_i\}; \{\lambda\})$, that is, the eigenstate with the smallest energy, denoted by $E_0(\{\lambda\})$, which we assume to be non-degenerate.
- ▶ To simplify the notation, we omit $\{\lambda\}$ when not necessary.

The ground state can be determined by applying the variational principle, stating that the expectation value of the Hamiltonian is minimal and equal to the ground-state energy when calculated w.r.t. the ground-state wavefunction.

Determining the Many-Electron Ground State III

- ▶ One can associate to each acceptable wavefunction $\psi(\{\mathbf{r}_i\})$ the corresponding Hamiltonian expectation value (energy), that is, define the functional (see Appendix):

$$E[\psi(\{\mathbf{r}_i\})] = \langle \psi(\{\mathbf{r}_i\}) | \hat{H}_e(\{\mathbf{r}_i\}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} \geq E_0$$

where $E[\psi_0(\{\mathbf{r}_i\})] = E_0$.

- ▶ The ground state can be determined by minimizing the functional w.r.t. the wavefunction:

$$\min_{\psi(\{\mathbf{r}_i\})} E[\psi(\{\mathbf{r}_i\})] = E[\psi_0(\{\mathbf{r}_i\})] = E_0$$

under the normalization constraint $\langle \psi(\{\mathbf{r}_i\}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} = 1$.

Determining the Many-Electron Ground State IV

- ▶ In practice, this is done by choosing a trial wavefunction with parametric dependence on a set of parameters $\{\nu\}$ and minimizing the energy functional w.r.t. these parameters:

$$\min_{\{\nu\}} E[\psi_{\text{trial}}(\{\mathbf{r}_i\}; \{\nu\})] = \min_{\{\nu\}} E(\{\nu\}) \geq E_0$$

- ▶ The values obtained for $\{\nu\}$ provides the trial wavefunction that is “closest” to the ground-state one.

Because the wavefunction depends on the coordinates of each electron, this approach is feasible only for a small number of electrons, and becomes quickly intractable as the number of electrons increases.

Electron Density I

- ▶ The operator representing the electron density, that is, the number of electrons per unit volume, is defined as:

$$\hat{n}(\mathbf{r}; \{\mathbf{r}_i\}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$$

- ▶ Then, the electron density of a system of N electrons is:

$$\begin{aligned} n(\mathbf{r}) &= \langle \psi(\{\mathbf{r}_i\}) | \hat{n}(\mathbf{r}; \{\mathbf{r}_i\}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} \\ &= N \int d\mathbf{r}_2 \dots d\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 \end{aligned}$$

- ▶ One can also define a joint electron density operator:

$$\hat{n}(\mathbf{r}, \mathbf{r}'; \{\mathbf{r}_i\}) = \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j)$$

Electron Density II

- ▶ Then, the joint electron density of a system of N electrons is:

$$\begin{aligned}n(\mathbf{r}, \mathbf{r}') &= \langle \psi(\{\mathbf{r}_i\}) | \hat{n}(\mathbf{r}, \mathbf{r}; \{\mathbf{r}_i\}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} \\&= N(N-1) \int d\mathbf{r}_3 \dots d\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)|^2\end{aligned}$$

- ▶ Electron density and joint electron density are related by:

$$n(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}) n(\mathbf{r}') + \Delta n(\mathbf{r}, \mathbf{r}')$$

where $\Delta n(\mathbf{r}, \mathbf{r}') = 0$ for systems of independent electrons.

Potentials as Electron Density Functionals

The expectation value of external and internal potentials can be expressed as functionals of the electron density and joint electron density.

- ▶ The expectation value of the internal potential is:

$$\langle \psi(\{\mathbf{r}_i\}) | \hat{U}_{\text{int}}(\{\mathbf{r}_i\}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = U_{\text{int}}[n(\mathbf{r}, \mathbf{r}')]$$

It can be seen as a functional of $n(\mathbf{r}, \mathbf{r}')$.

- ▶ The expectation value of the external potential is:

$$\langle \psi(\{\mathbf{r}_i\}) | \hat{U}_{\text{ext}}(\{\mathbf{r}_i\}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} = \int d\mathbf{r} n(\mathbf{r}) u_{\text{ext}}(\mathbf{r}) = U_{\text{ext}}[n(\mathbf{r}); u_{\text{ext}}(\mathbf{r})]$$

For a given $u_{\text{ext}}(\mathbf{r})$, it can be seen as a functional of $n(\mathbf{r})$.

Proof of Internal Potential Density Functional Form

$$\begin{aligned} \langle \psi(\{\mathbf{r}_i\}) | \hat{U}_{\text{int}}(\{\mathbf{r}_i\}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} &= \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \langle \psi(\{\mathbf{r}_i\}) | \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \langle \psi(\{\mathbf{r}_i\}) | \sum_{i \neq j} \int d\mathbf{r} d\mathbf{r}' \frac{\delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}'|} | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \langle \psi(\{\mathbf{r}_i\}) | \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \langle \psi(\{\mathbf{r}_i\}) | \hat{n}(\mathbf{r}, \mathbf{r}; \{\mathbf{r}_i\}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \end{aligned}$$

Proof of External Potential Density Functional Form

$$\begin{aligned} \langle \psi(\{\mathbf{r}_i\}) | \hat{U}_{\text{ext}}(\{\mathbf{r}_i\}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} &= \\ &= \langle \psi(\{\mathbf{r}_i\}) | \sum_i u_{\text{ext}}(\mathbf{r}_i) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} \\ &= \langle \psi(\{\mathbf{r}_i\}) | \sum_i \int d\mathbf{r} \delta(\mathbf{r} - \mathbf{r}_i) u_{\text{ext}}(\mathbf{r}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} \\ &= \int d\mathbf{r} \langle \psi(\{\mathbf{r}_i\}) | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} u_{\text{ext}}(\mathbf{r}) \\ &= \int d\mathbf{r} \langle \psi(\{\mathbf{r}_i\}) | \hat{n}(\mathbf{r}; \{\mathbf{r}_i\}) | \psi(\{\mathbf{r}_i\}) \rangle_{\{\mathbf{r}_i\}} u_{\text{ext}}(\mathbf{r}) \\ &= \int d\mathbf{r} n(\mathbf{r}) u_{\text{ext}}(\mathbf{r}) \end{aligned}$$

The Role of Density in Density Functional Theory

Density functional theory (DFT) shows that all the properties of a system of interacting electrons subject to an external potential are in principle fully determined by the ground-state density alone, and provides recipes for its calculation.

- ▶ There is a one-to-one correspondence between the ground-state electron density $n_0(\mathbf{r})$ and the external potential $u_{\text{ext}}(\mathbf{r})$.
- ▶ The total energy of a system of interacting electrons is a functional of the physically acceptable electron densities that is minimal at the ground-state electron density (variational theorem).
- ▶ Starting from these facts, the many-electron problem can be transformed into an equivalent single-electron problem.
- ▶ The degrees of freedom are significantly reduced, making the problem of determining the ground-state properties of interacting electrons tractable also for a large number of electrons.

Density Functional Theory (DFT)

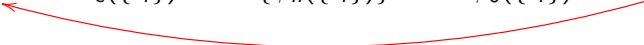
The First Hohenberg-Kohn Theorem

For a system of interacting electrons subject to an external potential, $u_{\text{ext}}(\mathbf{r})$, there is a one-to-one correspondence between the ground-state electron density $n_0(\mathbf{r})$ and $u_{\text{ext}}(\mathbf{r})$:

$$n_0(\mathbf{r}) \longleftrightarrow \{u_{\text{ext}}(\mathbf{r}) + c \mid c \in \mathbb{R}\}$$

- ▶ It is trivial that $u_{\text{ext}}(\mathbf{r})$ uniquely determines $n_0(\mathbf{r})$.
- ▶ At the same time, $n_0(\mathbf{r})$ uniquely defines $u_{\text{ext}}(\mathbf{r})$.

Corollary. The properties of a system of interacting electrons are fully determined by $n_0(\mathbf{r})$ alone.

$$u_{\text{ext}}(\mathbf{r}) \longrightarrow \hat{H}_e(\{\mathbf{r}_i\}) \longrightarrow \{\psi_n(\{\mathbf{r}_i\})\} \longrightarrow \psi_0(\{\mathbf{r}_i\}) \longrightarrow n_0(\mathbf{r})$$


Proof of the First Hohenberg-Kohn Theorem I

1. It is trivial that for a given $u_{\text{ext}}(\mathbf{r})$, there is a unique $n_0(\mathbf{r})$.
2. We need to prove that, for a given $n_0(\mathbf{r})$, there is a unique $u_{\text{ext}}(\mathbf{r})$ s.t. $n_0(\mathbf{r})$ is the ground-state electron density.
3. This is done by showing that $u_{\text{ext}}^{(1)}(\mathbf{r}) \neq u_{\text{ext}}^{(2)}(\mathbf{r})$ implies $n_0^{(1)}(\mathbf{r}) \neq n_0^{(2)}(\mathbf{r})$ through proof by contradiction.

Proof of the First Hohenberg-Kohn Theorem II

4. If $\hat{H}_e^{(i)}(\{\mathbf{r}_i\})$ is the many-electron Hamiltonian corresponding to $u_{\text{ext}}^{(i)}(\mathbf{r})$, with ground-state eigenvalue, eigenfunction, and electron density $E_0^{(i)}$, $\psi_0^{(i)}(\{\mathbf{r}_i\})$, and $n_0^{(i)}(\mathbf{r})$, respectively, then:

$$\begin{aligned} & \langle \psi_0^{(2)}(\{\mathbf{r}_i\}) | \hat{H}_e^{(1)}(\{\mathbf{r}_i\}) | \psi_0^{(2)}(\{\mathbf{r}_i\}) \rangle \\ &= \langle \psi_0^{(2)}(\{\mathbf{r}_i\}) | \hat{H}_e^{(2)}(\{\mathbf{r}_i\}) + \hat{U}_{\text{ext}}^{(1)}(\{\mathbf{r}_i\}) - \hat{U}_{\text{ext}}^{(2)}(\{\mathbf{r}_i\}) | \psi_0^{(2)}(\{\mathbf{r}_i\}) \rangle \\ &= E_0^{(2)} + \int d\mathbf{r} n_0^{(2)}(\mathbf{r}) [u_{\text{ext}}^{(1)}(\mathbf{r}) - u_{\text{ext}}^{(2)}(\mathbf{r})] > E_0^{(1)} \end{aligned}$$

5. Similarly, one can obtain:

$$E_0^{(1)} + \int d\mathbf{r} n_0^{(1)}(\mathbf{r}) [u_{\text{ext}}^{(2)}(\mathbf{r}) - u_{\text{ext}}^{(1)}(\mathbf{r})] > E_0^{(2)}$$

6. These inequalities are incompatible if $n_0^{(1)}(\mathbf{r}) = n_0^{(2)}(\mathbf{r})$, proving the theorem.

The Hohenberg-Kohn Functional I

- ▶ Because $n_0(\mathbf{r})$ uniquely determines $u_{\text{ext}}(\mathbf{r})$, the latter can be seen as having a universal parametric dependence on the former:

$$u_{\text{ext}}(\mathbf{r}) \mapsto u_{\text{ext}}(\mathbf{r}; n_0(\mathbf{r}))$$

- ▶ As consequence, the ground-state electron density uniquely identifies the many-electron system at hand, which can be expressed as a universal parametric dependence of the Hamiltonian:

$$\hat{H}_e(\{\mathbf{r}_i\}) \mapsto \hat{H}_e(\{\mathbf{r}_i\}; n_0(\mathbf{r}))$$

- ▶ Similarly, the correspondence between the system of interacting electrons considered and its ground-state wavefunction can be expressed through a parametric dependence of the latter on the ground-state electron density:

$$\psi_0(\{\mathbf{r}_i\}) \mapsto \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r}))$$

The Hohenberg-Kohn Functional II

It follows that the ground-state energy of a system of interacting electrons, and its components, are functionals of the ground-state electron density:

$$E_0[n_0(\mathbf{r})] = \langle \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \hat{H}_{\text{ext}}(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r})) \rangle_{\{\mathbf{r}_i\}}$$

$$T_e[n_0(\mathbf{r})] = \langle \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \hat{T}_e(\{\mathbf{r}_i\}) | \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r})) \rangle_{\{\mathbf{r}_i\}}$$

$$U_{\text{int}}[n_0(\mathbf{r})] = \langle \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \hat{U}_{\text{int}}(\{\mathbf{r}_i\}) | \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r})) \rangle_{\{\mathbf{r}_i\}}$$

$$U_{\text{ext}}[n_0(\mathbf{r})] = \langle \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \hat{U}_{\text{ext}}(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r})) \rangle_{\{\mathbf{r}_i\}}$$

- ▶ For the many-electron system identified by $n_0(\mathbf{r})$, one can consider the expectation value of the energy w.r.t. to the ground-state wavefunction of another many-electron system, having ground-state electron density $n(\mathbf{r}) \neq n_0(\mathbf{r})$.
- ▶ This leads to the definition of the Hohenberg-Kohn functional.

The Hohenberg-Kohn Functional III

For the many-electron system identified by $n_0(\mathbf{r})$, the Hohenberg-Kohn functional is defined as:

$$E^{\text{HK}}[n(\mathbf{r}); n_0(\mathbf{r})] = T_e[n(\mathbf{r})] + U_{\text{int}}[n(\mathbf{r})] + U_{\text{ext}}[n(\mathbf{r}); n_0(\mathbf{r})]$$

with:

$$E^{\text{HK}}[n(\mathbf{r}); n_0(\mathbf{r})] = \langle \psi_0(\{\mathbf{r}_i\}; n(\mathbf{r})) | \hat{H}_e(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \psi_0(\{\mathbf{r}_i\}; n(\mathbf{r})) \rangle_{\{\mathbf{r}_i\}}$$

$$T_e[n(\mathbf{r})] = \langle \psi_0(\{\mathbf{r}_i\}; n(\mathbf{r})) | \hat{T}_e(\{\mathbf{r}_i\}) | \psi_0(\{\mathbf{r}_i\}; n(\mathbf{r})) \rangle_{\{\mathbf{r}_i\}}$$

$$U_{\text{int}}[n(\mathbf{r})] = \langle \psi_0(\{\mathbf{r}_i\}; n(\mathbf{r})) | \hat{U}_{\text{int}}(\{\mathbf{r}_i\}) | \psi_0(\{\mathbf{r}_i\}; n(\mathbf{r})) \rangle_{\{\mathbf{r}_i\}}$$

$$U_{\text{ext}}[n(\mathbf{r}); n_0(\mathbf{r})] = \langle \psi_0(\{\mathbf{r}_i\}; n(\mathbf{r})) | \hat{U}_{\text{ext}}(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \psi_0(\{\mathbf{r}_i\}; n(\mathbf{r})) \rangle_{\{\mathbf{r}_i\}}$$

where $n(\mathbf{r})$ can be the ground-state electron density of any many-electron system.

The Hohenberg-Kohn Functional IV

- $T_e[n(\mathbf{r})]$ and $U_{\text{int}}[n(\mathbf{r})]$ are unchanged because the corresponding operators do not depend on $u_{\text{ext}}(\mathbf{r}; n_0(\mathbf{r}))$; they are universal, but their form is unknown.
 1. For example, we have shown that the internal potential energy functional can be written in terms of the joint electron density:

$$U_{\text{int}}[n(\mathbf{r}, \mathbf{r}')] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

2. By recalling that $n(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}) n(\mathbf{r}') + \Delta n(\mathbf{r}, \mathbf{r}')$, one can write:

$$U_{\text{int}}[n(\mathbf{r}), \Delta n(\mathbf{r}, \mathbf{r}')] = \underbrace{\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{U_{\text{H}}[n(\mathbf{r})]} + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r} d\mathbf{r}' \frac{\Delta n(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

The Hohenberg-Kohn Functional V

- ▶ $U_H[n(\mathbf{r})]$ is called the Hartree functional, its explicit form is known, and corresponds to the classical potential energy of the electron density.
- ▶ On the other hand, the second RHS term describes non-classical interactions among the electrons, its explicit dependence on the electron density is unknown, and hinders the determination of an explicit form for $U_{\text{int}}[n(\mathbf{r})]$.
- ▶ Finally, we have already determined the explicit form of the external potential energy functional:

$$U_{\text{ext}}[n(\mathbf{r}); n_0(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) u_{\text{ext}}(\mathbf{r}; n_0(\mathbf{r}))$$

The Second Hohenberg-Kohn Theorem

For the many-electron system with ground-state electron density $n_0(\mathbf{r})$, the Hohenberg-Kohn functional is minimal at $n_0(\mathbf{r})$, and its minimum gives the ground-state energy E_0 :

$$\min_{n(\mathbf{r})} E^{\text{HK}}[n(\mathbf{r}); n_0(\mathbf{r})] = E^{\text{HK}}[n_0(\mathbf{r}); n_0(\mathbf{r})] = E_0$$

- ▶ This is the electron density analogous of the variational principle for wavefunctions, with the advantage that n depends only on \mathbf{r} , while ψ depends on $\{\mathbf{r}_i\}$.
- ▶ Unfortunately, the explicit form of the Hohenberg-Kohn functional is unknown and approximations must be introduced.

Corollary. $E^{\text{HK}}[n(\mathbf{r}); n_0(\mathbf{r})]$ alone is enough to determine the exact ground-state energy and electron density.

Proof of the Second Hohenberg-Kohn Theorem I

1. Let $n(\mathbf{r})$ be a trial electron density and $\psi_0(\mathbf{r}; n(\mathbf{r}))$ the ground-state wavefunction of the corresponding many-electron system.
2. For this density, the Hohenberg-Kohn functional associated to the many-electron system having ground-state electron density $n_0(\mathbf{r})$ takes the value:

$$E^{\text{HK}}[n(\mathbf{r}); n_0(\mathbf{r})] = \langle \psi_0(\{\mathbf{r}_i\}; n(\mathbf{r})) | \hat{H}_e(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \psi_0(\{\mathbf{r}_i\}; n(\mathbf{r})) \rangle_{\{\mathbf{r}_i\}}$$

3. On the other hand, it takes the following value at the ground-state electron density:

$$E^{\text{HK}}[n_0(\mathbf{r}); n_0(\mathbf{r})] = \langle \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \hat{H}_e(\{\mathbf{r}_i\}; n_0(\mathbf{r})) | \psi_0(\{\mathbf{r}_i\}; n_0(\mathbf{r})) \rangle_{\{\mathbf{r}_i\}}$$

Proof of the Second Hohenberg-Kohn Theorem II

4. Therefore, $E^{\text{HK}}[n(\mathbf{r}); n_0(\mathbf{r})]$ is the expectation value of the Hamiltonian operator w.r.t. a wavefunction different from its ground-state eigenfunction, while $E^{\text{HK}}[n_0(\mathbf{r}); n_0(\mathbf{r})]$ is exactly the expectation value of the Hamiltonian operator w.r.t. to its ground-state eigenfunction, that is, E_0 .
5. Because of the variational principle for wavefunctions, it readily follows that:

$$E^{\text{HK}}[n(\mathbf{r}); n_0(\mathbf{r})] \geq E^{\text{HK}}[n_0(\mathbf{r}); n_0(\mathbf{r})] = E_0$$

hence the theorem is proven.

Determining the Ground-State Electron Density

- ▶ In analogy to the variational method for determining the ground-state wavefunction, one can determine the ground-state electron density by minimizing the Hohenberg-Kohn functional w.r.t. the electron density:

$$\min_{\{\nu\}} E^{\text{HK}}[n(\mathbf{r}; \{\nu\}); n_0(\mathbf{r})] = \min_{\{\nu\}} E(\{\nu\}; n_0(\mathbf{r})) \geq E_0$$

under the normalization constraint:

$$\int d\mathbf{r} n(\mathbf{r}; \{\nu\}) = N$$

where N is the number of electrons.

- ▶ Notice that, although $n_0(\mathbf{r})$ is not known a priori, it enters the Hohenberg-Kohn functional only through $u_{\text{ext}}(\mathbf{r}; n_0(\mathbf{r}))$, which is usually known.
- ▶ The true difficulty is due to the kinetic and internal potential energy terms, for which explicit expressions are unknown, leading to the introduction of approximations.

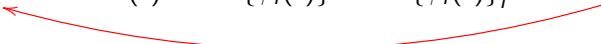
Kohn-Sham Ansatz

For each system of interacting electrons, there exists a system of non-interacting electrons with the same ground-state density $n_0(\mathbf{r})$, called the auxiliary Kohn-Sham system.

- ▶ If $\hat{H}_e^{\text{KS}}(\mathbf{r}) = \hat{T}_e(\mathbf{r}) + \hat{U}^{\text{KS}}(\mathbf{r})$ is the single-electron Hamiltonian of the auxiliary Kohn-Sham system, and $\hat{H}_e^{\text{KS}}(\mathbf{r}) \phi_i^{\text{KS}}(\mathbf{r}) = \epsilon_i^{\text{KS}} \phi_i^{\text{KS}}(\mathbf{r})$ with $\langle \phi_i^{\text{KS}}(\mathbf{r}) | \phi_j^{\text{KS}}(\mathbf{r}) \rangle = \delta_{ij}$, then:

$$n_0(\mathbf{r}) = \sum_i^{\text{occ}} \phi_i^{\text{KS}*}(\mathbf{r}) \phi_i^{\text{KS}}(\mathbf{r})$$

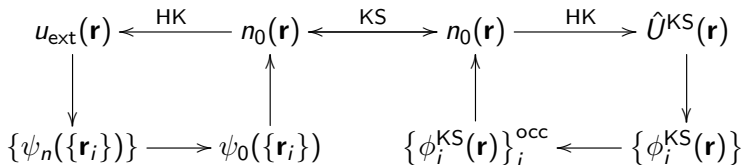
- ▶ The first Hohenberg-Kohn theorem exists also for non-interacting electrons:

$$\hat{U}^{\text{KS}}(\mathbf{r}) \longrightarrow \hat{H}^{\text{KS}}(\mathbf{r}) \longrightarrow \{\phi_i(\mathbf{r})\} \longrightarrow \{\phi_i(\mathbf{r})\}_i^{\text{occ}} \longrightarrow n_0(\mathbf{r})$$


Kohn-Sham Approach

In the Kohn-Sham approach, one obtains the ground-state electron density of a many-electron system by determining the single-electron eigenstates of the auxiliary Kohn-Sham system of non-interacting electrons.

- ▶ The Kohn-Sham approach can be summarized as follows:



- ▶ It is principle exact, but approximate in practice because the explicit form of $T[n(\mathbf{r})]$ and $U_{\text{int}}[n(\mathbf{r})]$ is unknown.
- ▶ We now discuss how to obtain $\hat{U}^{\text{KS}}(\mathbf{r})$ for a given $u_{\text{ext}}(\mathbf{r})$.

Exchange-Correlation Functional I

- ▶ Because of the first Hohenberg-Kohn theorem for non-interacting electrons, the set of occupied single-electron eigenfunctions of the auxiliary Kohn-Sham system can be seen as having a universal parametric dependence on the ground-state electron density:

$$\{\phi_i(\mathbf{r})\}_i^{\text{occ}} \mapsto \{\phi_i(\mathbf{r}; n_0(\mathbf{r}))\}_i^{\text{occ}}$$

- ▶ As consequence, the expectation value of the kinetic energy of the auxiliary Kohn-Sham system is a functional of $n_0(\mathbf{r})$:

$$T_e^{\text{KS}}[n_0(\mathbf{r})] = \sum_i^{\text{occ}} \langle \phi_i^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r})) | \hat{T}_e(\mathbf{r}) | \phi_i^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r})) \rangle_{\mathbf{r}_i}$$

The exchange-correlation functional is defined as:

$$U_{\text{xc}}[n_0(\mathbf{r})] = T_e[n_0(\mathbf{r})] - T_e^{\text{KS}}[n_0(\mathbf{r})] + U_{\text{int}}[n_0(\mathbf{r})] - U_{\text{H}}[n_0(\mathbf{r})]$$

Exchange-Correlation Functional II

- ▶ $U_{xc}[n_0(\mathbf{r})]$ is universal by construction, since it consists of the combination of functionals that do not depend on $u_{\text{ext}}(\mathbf{r}; n_0(\mathbf{r}))$, that is, universal themselves, which are $T_e[n_0(\mathbf{r})]$, $T_e^{\text{KS}}[n_0(\mathbf{r})]$, $U_{\text{int}}[n_0(\mathbf{r})]$, and $U_H[n_0(\mathbf{r})]$.
- ▶ The Hohenberg-Kohn functional associated to the system having ground-state electron density $n_0(\mathbf{r})$ can be rewritten as:

$$E^{\text{HK}}[n(\mathbf{r}); n_0(\mathbf{r})] = T_e^{\text{KS}}[n(\mathbf{r})] + U_H[n(\mathbf{r})] + U_{xc}[n(\mathbf{r})] + U_{\text{ext}}[n(\mathbf{r}); n_0(\mathbf{r})]$$

- ▶ Basically, the exchange-correlation functional describes many-body effects that have no classical counterpart.
- ▶ The exchange-correlation functional is the only term of the Hohenberg-Kohn functional whose explicit dependence on the electron density is unknown and it is hence approximated; the theory would be exact otherwise.

Kohn-Sham Equations I

The potential energy of the auxiliary Kohn-Sham system is:

$$U^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r})) = u_{\text{ext}}(\mathbf{r}) + U_{\text{H}}(\mathbf{r}; n_0(\mathbf{r})) + U_{\text{xc}}(\mathbf{r}; n_0(\mathbf{r}))$$

- ▶ $U_{\text{H}}(\mathbf{r}; n(\mathbf{r}))$ is the Hartree potential, equal to the functional derivative (see Appendix) of the Hartree functional:

$$U_{\text{H}}(\mathbf{r}; n(\mathbf{r})) = \frac{\delta U_{\text{H}}}{\delta n}(\mathbf{r}) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- ▶ $U_{\text{xc}}(\mathbf{r}; n(\mathbf{r}))$ is the exchange-correlation potential, equal to the functional derivative of the exchange-correlation functional:

$$U_{\text{xc}}(\mathbf{r}; n(\mathbf{r})) = \frac{\delta U_{\text{xc}}}{\delta n}(\mathbf{r})$$

Kohn-Sham Equations II

The ground-state electron density of the many-electron system is obtained by solving the following system of equations, called Kohn-Sham equations:

$$\begin{cases} \hat{H}^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r})) \phi_i^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r})) = \varepsilon_i^{\text{KS}}(n_0(\mathbf{r})) \phi_i^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r})) \\ n_0(\mathbf{r}) = \sum_i^{\text{occ}} \phi_i^{\text{KS}*}(\mathbf{r}; n_0(\mathbf{r})) \phi_i^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r})) \end{cases}$$

- ▶ The ground-state electron density is given by the occupied eigenfunctions of the Kohn-Sham Hamiltonian.
- ▶ At the same time, the Kohn-Sham Hamiltonian is defined by the ground-state electron density.
- ▶ Since the solution to the problem defines the problem itself, the Kohn-Sham equations must be solved self-consistently.

Kohn-Sham Equations III

- ▶ The ground-state energy of the many-electron system is:

$$E_0 = E_0[n_0(\mathbf{r})] = \sum_i^{\text{occ}} \varepsilon_i^{\text{KS}}(n_0(\mathbf{r})) - U_{\text{H}}[n_0(\mathbf{r})] + U_{\text{xc}}[n_0(\mathbf{r})] - \int d\mathbf{r} \frac{\delta U_{\text{xc}}}{\delta n}(\mathbf{r}) n(\mathbf{r})$$

Proof of the Kohn-Sham Equations I

1. The Kohn-Sham equations are obtained by minimizing the functional $E^{\text{HK}}[n(\mathbf{r}); n_0(\mathbf{r})]$ with respect to electron density $n(\mathbf{r})$, according to the second Hohenberg-Kohn theorem.
2. Since, according to the Kohn-Sham ansatz, the electron density $n(\mathbf{r})$ can be expressed in terms of the single-electron eigenfunctions of a system non-interacting electrons as:

$$n(\mathbf{r}) = \sum_i^{\text{occ}} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r})$$

the minimization can be performed w.r.t. $\{\phi_i(\mathbf{r})\}_i^{\text{occ}}$ under the orthonormalization constraints $\langle \phi_i(\mathbf{r}) | \phi_j(\mathbf{r}) \rangle = \delta_{ij}$, which also ensure $\int d\mathbf{r} n(\mathbf{r}) = N$, with N equal to the number of electrons.

Proof of the Kohn-Sham Equations II

3. The derivative of the Hohenberg-Kohn functional w.r.t. $\phi_i^*(\mathbf{r})$ is directly related to the Kohn-Sham Hamiltonian:

$$\begin{aligned}\frac{\delta E^{\text{HK}}}{\delta \phi_i^*}(\mathbf{r}) &= \frac{\delta T_e^{\text{KS}}}{\delta \phi_i^*}(\mathbf{r}) + \left[\frac{\delta U_{\text{ext}}}{\delta n}(\mathbf{r}) + \frac{\delta U_{\text{H}}}{\delta n}(\mathbf{r}) + \frac{\delta U_{\text{xc}}}{\delta n}(\mathbf{r}) \right] \frac{\delta n}{\delta \phi_i^*}(\mathbf{r}) \\ &= \hat{H}^{\text{KS}}(\mathbf{r}; n(\mathbf{r})) \phi_i(\mathbf{r})\end{aligned}$$

as can be shown by computing the functional derivatives:

$$\begin{aligned}\frac{\delta T_e^{\text{KS}}}{\delta \phi_i^*}(\mathbf{r}) &= \hat{T}_e(\mathbf{r}) \phi_i(\mathbf{r}) & \frac{\delta U_{\text{ext}}}{\delta n}(\mathbf{r}) &= u_{\text{ext}}(\mathbf{r}) & \frac{\delta U_{\text{H}}}{\delta n}(\mathbf{r}) &= U_{\text{H}}(\mathbf{r}; n(\mathbf{r})) \\ \frac{\delta U_{\text{xc}}}{\delta n}(\mathbf{r}) &= U_{\text{xc}}(\mathbf{r}; n(\mathbf{r})) & \frac{\delta n}{\delta \phi_i^*}(\mathbf{r}) &= \phi_i(\mathbf{r}) & \frac{\delta \langle \phi_i | \phi_i \rangle}{\delta \phi_i^*}(\mathbf{r}) &= \phi_i(\mathbf{r})\end{aligned}$$

The functional derivatives are functions of \mathbf{r} that may depend parametrically on the function at which they are calculated, that is, $n(\mathbf{r})$.

Proof of the Kohn-Sham Equations III

4. According to the Lagrange multipliers method, the Hohenberg-Kohn functional is minimized w.r.t. $\phi_i^*(\mathbf{r})$ under the constraints $\langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle = 1$ when:

$$\frac{\delta E^{\text{HK}}}{\delta \phi_i^*}(\mathbf{r}) - \varepsilon_i \frac{\delta \langle \phi_i | \phi_i \rangle}{\delta \phi_i^*}(\mathbf{r}) = 0$$

where ε_i are the Lagrange multipliers.

5. Substituting the expressions obtained before, one obtains:

$$\hat{H}^{\text{KS}}(\mathbf{r}; n(\mathbf{r})) \phi_i(\mathbf{r}) - \varepsilon_i \phi_i(\mathbf{r}) = 0$$

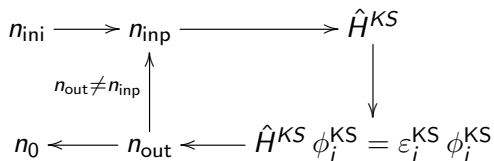
hence proving the Kohn-Sham equations.

Comments on the Kohn-Sham Equations

- ▶ The Kohn-Sham equations are single-electron equations with many-body effects incorporated in a mean way into $U^{\text{KS}}(\mathbf{r})$.
- ▶ Conceptually, their solution provides the exact ground-state of the corresponding system of interacting electrons.
- ▶ In practice, approximate expressions for $U_{\text{xc}}(\mathbf{r}; n(\mathbf{r}))$ are used because its explicit form is unknown, whose quality influences the accuracy of the results.
- ▶ The energies $\varepsilon_i^{\text{KS}}$ are formally Lagrange multipliers and do not correspond to the true single-electron energies.
- ▶ Identification of $\varepsilon_i^{\text{KS}}$ with single-electron energies must be justified and often heuristically corrected case-by-case.
- ▶ Experience shows that, despite an underestimation of the band-gap in semiconductors/insulators, the general trend of the dispersion curves $\varepsilon_i(\mathbf{k})$ resembles the true single-electron band structure; we will adopt this approximation.

Solving the Kohn-Sham Equations

- ▶ Because \hat{U}^{KS} depends parametrically on $n(\mathbf{r})$, \hat{H}^{KS} cannot be defined without already knowing its eigenfunctions.
- ▶ Since the solution to the problem defines the problem itself, the Kohn-Sham equations must be solved self-consistently:



In practice, at least three more ingredients are needed:

- ▶ Approximate expressions for $U_{\text{xc}}[n(\mathbf{r})]$ and $U_{\text{xc}}(\mathbf{r})$.
- ▶ A basis to expand $\phi_i^{\text{KS}}(\mathbf{r})$, so that the problem can be represented in matrix form and solved numerically.
- ▶ A convenient way to treat the external potential $u_{\text{ext}}(\mathbf{r})$.

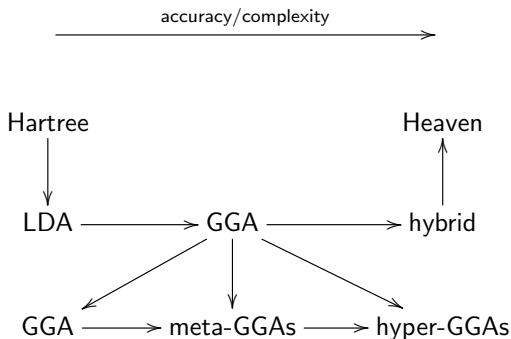
DFT Practical Implementation

Exchange-Correlation Functional Approximations

- ▶ In general, the exchange-correlation functional is expressed as the sum of an exchange and a correlation term:

$$U_{xc}[n(\mathbf{r})] = U_x[n(\mathbf{r})] + U_c[n(\mathbf{r})]$$

- ▶ There are several models to approximate the exchange-correlation functional, whose accuracy increase with complexity:



Local Density Approximation (LDA) I

- ▶ The exchange-correlation functional is local and expressed in terms of the exchange-correlation energy density $\epsilon_{xc}^{LDA}(n(\mathbf{r}))$:

$$U_{xc}^{LDA}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}^{LDA}(n(\mathbf{r}))$$

- ▶ $\epsilon_{xc}^{LDA}(n(\mathbf{r}))$ point-wise equals the exchange-correlation energy per electron of a homogeneous electron gas of same density.
- ▶ One possible form has been derived by parametrizing numerical results obtained with Monte Carlo calculations:

$$\epsilon_{xc}^{LDA}(r_s(\mathbf{r})) = \epsilon_x^{LDA}(r_s(\mathbf{r})) + \epsilon_c^{LDA}(r_s(\mathbf{r}))$$

with:

$$\epsilon_x^{LDA}(r_s(\mathbf{r})) = \frac{0.4582}{r_s(\mathbf{r})}$$

and:

$$\epsilon_c^{LDA}(r_s(\mathbf{r})) = \begin{cases} -0.1423/(1 + 1.0529 \sqrt{r_s(\mathbf{r})} + 0.3334 r_s(\mathbf{r})) & \text{for } r_s(\mathbf{r}) \geq 1 \\ -0.0480 + 0.0311 \ln r_s(\mathbf{r}) - 0.0116 r_s(\mathbf{r}) + 0.0020 r_s(\mathbf{r}) \ln r_s(\mathbf{r}) & \text{for } r_s(\mathbf{r}) \leq 1 \end{cases}$$

Local Density Approximation (LDA) II

- ▶ Above, the energy is expressed in Hartree, while r_s is a dimensionless parameter given by $(4\pi/3)(r_s(\mathbf{r}) a_B)^3 = 1/n(\mathbf{r})$.
- ▶ The corresponding exchange-correlation potential is:

$$U_{xc}^{\text{LDA}}(\mathbf{r}; n(\mathbf{r})) = \frac{\delta U_{xc}^{\text{LDA}}}{\delta n}(\mathbf{r}; n(\mathbf{r})) = \epsilon_{xc}^{\text{LDA}}(n(\mathbf{r})) + \frac{d\epsilon_{xc}^{\text{LDA}}(n(\mathbf{r}))}{dn(\mathbf{r})}$$

- ▶ LDA is exact for an homogeneous gas of interacting electrons, hence is suited for systems with slowly varying electron density.

Generalized Gradient Approximation (GGA)

- ▶ The exchange-correlation energy density can be expanded in terms of the gradient of the electron density and higher-order differentiation terms:

$$\epsilon_{xc}(n(\mathbf{r}), \nabla_{\mathbf{r}}n(\mathbf{r}), \dots)$$

- ▶ In the GGA, differentiation terms above 1st order are dropped:

$$U_{xc}^{GGA}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}^{GGA}(n(\mathbf{r}), \nabla_{\mathbf{r}}n(\mathbf{r}))$$

- ▶ Many forms exist for $\epsilon_{xc}^{GGA}(n(\mathbf{r}), \nabla_{\mathbf{r}}n(\mathbf{r}))$, depending on the properties of interest.
- ▶ The Perdew-Burke-Ernzerhof (PBE) model is the most used.

Meta-Generalized Gradient Approximation (MGGA)

- ▶ In MGGA functionals, also the Laplacian of the density is retained to improve accuracy:

$$U_{xc}^{\text{MGGA}}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}^{\text{MGGA}}(n(\mathbf{r}), \nabla_{\mathbf{r}} n(\mathbf{r}), \nabla_{\mathbf{r}}^2 n(\mathbf{r}))$$

- ▶ To improve numerical stability, the kinetic energy density is used instead of the Laplacian of the electron density:

$$\tau(\mathbf{r}) = \frac{\hbar}{2m_e} \sum_i^{\text{occ}} |\nabla_{\mathbf{r}} \phi_i^{\text{KS}}(\mathbf{r})|^2$$

- ▶ Therefore, MGGA functionals take the form:

$$U_{xc}^{\text{MGGA}}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}^{\text{MGGA}}(n(\mathbf{r}), \nabla_{\mathbf{r}} n(\mathbf{r}), \tau(\mathbf{r}))$$

Hybrid Functionals

- ▶ Hybrid functionals include fractions of the exact Hartree-Fock exchange energy, calculated as:

$$U_x^{\text{HF}}[\{\phi_i^{\text{KS}}(\mathbf{r})\}_i^{\text{occ}}] = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j}^{\text{occ}} \int d\mathbf{r} d\mathbf{r}' \frac{\phi_i^{\text{KS}*}(\mathbf{r}) \phi_j^{\text{KS}*}(\mathbf{r}') \phi_j^{\text{KS}}(\mathbf{r}) \phi_i^{\text{KS}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- ▶ For example, the PBE0 hybrid functional has the form:

$$U_{\text{xc}}^{\text{PBE0}} = U_{\text{xc}}^{\text{PBE}} + \frac{1}{4} (U_x^{\text{HF}} - U_x^{\text{PBE}})$$

- ▶ Becke's B3LYP is the most famous hybrid functional, obtained by including many exchange-correlation terms and fitting adjustable parameters to atomic and molecular data.
- ▶ Hybrid functionals correct most LDA/GGA errors, but require much more computational power and/or time.

Matrix Form of the Kohn-Sham Equations I

- ▶ To solve the Kohn-Sham equations numerically, we need to express them in matrix form.
- ▶ This is done by expanding the Kohn-Sham orbitals as a linear combination of a suitable complete orthonormal set of functions $\{\phi_j(\mathbf{r})\}_j$, called a basis set:

$$\phi_i^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r})) = \sum_j c_{ij}(n_0(\mathbf{r})) \phi_j(\mathbf{r})$$

- ▶ Then, the Kohn-Sham Hamiltonian $\hat{H}^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r}))$ can be represented in matrix form:

$$\mathbf{H}^{\text{KS}}(n_0(\mathbf{r})) = \left[\langle \phi_j(\mathbf{r}) | \hat{H}^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r})) | \phi_k(\mathbf{r}) \rangle_{\mathbf{r}} \right]_{jk}$$

Matrix Form of the Kohn-Sham Equations II

- ▶ The Kohn-Sham single-electron energies $\varepsilon_i^{\text{KS}}(n_0(\mathbf{r}))$ and orbitals $\phi_i^{\text{KS}}(\mathbf{r}; n_0(\mathbf{r}))$ can be determined by solving the eigenvalue equation in matrix form (secular equation):

$$\mathbf{H}^{\text{KS}}(n_0(\mathbf{r})) \mathbf{c}_i(n_0(\mathbf{r})) = \varepsilon_i^{\text{KS}}(n_0(\mathbf{r})) \mathbf{c}_i(n_0(\mathbf{r}))$$

where $\mathbf{c}_i(n_0(\mathbf{r})) = [c_{ij}(n_0(\mathbf{r}))]_j^T$.

- ▶ The parametric dependence on the electron density is shown to remind that the problem must be solved self-consistently.
- ▶ Expansion of KS orbitals would require an infinite basis set to be exact. In practice, the basis set must be finite. The number of eigenvalues that are obtained by solving the secular equation equals the basis set size.

Plane-Wave Representation in Crystalline Solids I

- ▶ In a crystalline solids, the periodicity of the nuclear arrangement renders the Kohn-Sham potential periodic:

$$\hat{U}_{\text{KS}}(\mathbf{r}) = \hat{U}_{\text{KS}}(\mathbf{r} + \mathbf{t}) \quad \forall \mathbf{t} = \sum_{i=1}^3 n_i \mathbf{t}_i$$

where $\{\mathbf{t}_i\}_{i=1}^3$ are the primitive translation vectors of the underlying Bravais lattice, and $n_i = 0, 1, \dots, N_i - 1$, with N_i equal to the number of unit cells in the direction of \mathbf{t}_i .

- ▶ On the other hand, $\left\{ \mathbf{g} = \sum_{i=1}^3 m_i \mathbf{g}_i : m_i \in \mathbb{Z} \right\}$ forms the so-called reciprocal lattice, whose primitive translation vectors are $\{\mathbf{g}_i : \mathbf{g}_i \cdot \mathbf{t}_j = 2\pi \delta_{ij} \text{ for } j = 1, 2, 3\}_{i=1}^3$

Plane-Wave Representation in Crystalline Solids II

- ▶ The Bloch theorem can be applied to Kohn-Sham orbitals, that is, $\varepsilon_i^{\text{KS}} \mapsto \varepsilon_{n\mathbf{k}}^{\text{KS}}$ and $\phi_i^{\text{KS}}(\mathbf{r}) \mapsto \phi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r})$, where:

$$\begin{aligned}\phi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r}) &= \exp(i\mathbf{k} \cdot \mathbf{r}) u_{n\mathbf{k}}^{\text{KS}}(\mathbf{r}) \quad u_{n\mathbf{k}}^{\text{KS}}(\mathbf{r}) = u_{n\mathbf{k}}^{\text{KS}}(\mathbf{r} + \mathbf{t}) \quad \forall \mathbf{t} \\ &= \exp(-i\mathbf{k} \cdot \mathbf{r}) \phi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r} + \mathbf{t}) \quad \forall \mathbf{t} \\ &= \sum_{\mathbf{g}} c_{n\mathbf{k}}(\mathbf{g}) W_{\mathbf{k}+\mathbf{g}}(\mathbf{r})\end{aligned}$$

- ▶ The last expression shows that plane waves of wave vector different from \mathbf{k} by a reciprocal lattice vector:

$$W_{\mathbf{k}+\mathbf{g}}(\mathbf{r}) = \frac{1}{\sqrt{N\Omega}} \exp[i(\mathbf{k} + \mathbf{g}) \cdot \mathbf{r}]$$

where $\Omega = \mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3$ is the unit cell volume, form a complete orthonormal set for the expansion of $\phi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r})$.

Plane-Wave Representation in Crystalline Solids III

- ▶ If $N_i \rightarrow \infty$, periodic boundary conditions can be imposed, and the electron wavevector \mathbf{k} equals:

$$\mathbf{k} = \sum_{i=1}^3 \frac{n_i}{N_i} \mathbf{g}_i \quad \forall n_i \in \mathbb{Z}$$

- ▶ Distinct solutions are found only within the first Brillouin zone:

$$\text{BZ} = \{\mathbf{k} : k < |\mathbf{k} - \mathbf{g}| \quad \forall \mathbf{g}\}$$

- ▶ Therefore, for each band index n , we have a number of wavefunctions equal to the number of unit cells $N = N_1 N_2 N_3$; the curves $\varepsilon_n^{\text{KS}}(\mathbf{q})$ define the Kohn-Sham electronic band structure.
- ▶ At the same time, for each \mathbf{k} , a different Kohn-Sham equation in matrix form is obtained, whose solutions are indexed by n and equal the number of plane waves used for the expansion.
- ▶ One has to make the problem finite, by limiting the number of plane waves and by choosing a suitable grid of \mathbf{k} points.

Plane-Wave Cut-Off

- ▶ In codes implementing density-functional theory on a plane wave basis set, the basis set is made finite by defining an energy cut-off E_{cut} .
- ▶ For each \mathbf{k} , the only plane waves used are the ones having wave vector $\mathbf{k} + \mathbf{g}$ such that the corresponding free-electron kinetic energy is less than the cut-off energy:

$$\left\{ W_{\mathbf{k}+\mathbf{g}}(\mathbf{r}) : \langle W_{\mathbf{k}+\mathbf{g}}(\mathbf{r}) | \hat{T}_e(\mathbf{r}) | W_{\mathbf{k}+\mathbf{g}}(\mathbf{r}) \rangle = \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{g}|^2 < E_{\text{cut}} \right\}_{\mathbf{g}}$$

- ▶ For each \mathbf{k} , a number of Kohn-Sham orbitals equal to the size of the plane-wave basis set can be obtained.
- ▶ The cut-off needed to obtain accurate results depends on the system. It should be chosen with a convergence study, that is, by changing its values until the corresponding variation of the results is less than a desired tolerance.

k Points Grid I

- ▶ For many quantities, it is necessary to perform integrals in \mathbf{k} across the set of inequivalent solutions, that is, the BZ.
- ▶ For example, the average value of a function $f(\mathbf{k})$ is:

$$\bar{f} = \frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} d\mathbf{k} f(\mathbf{k})$$

- ▶ Numerically, one uses a discrete number $N_{\mathbf{k}}$ of \mathbf{k} points (grid), and the integral is approximated as:

$$\bar{f} = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} f(\mathbf{k})$$

- ▶ It is crucial to define the grid of \mathbf{k} points in an optimal way to obtain accurate results.

k Points Grid II

- ▶ Monkhorst and Pack have proposed a simple formula, valid for any crystal, that provides a uniform grid of **k** points:

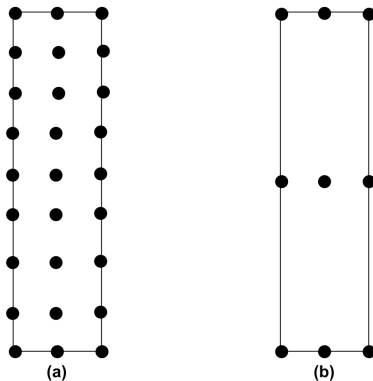
$$\left\{ \mathbf{k} = \sum_{i=1}^3 \frac{2 n_i - N_i - 1}{2 N_i} \mathbf{g}_i \quad \text{for } n_i = 1, 2, \dots, N_i \right\}$$

where N_i is the number of **k** points desired along \mathbf{g}_i .

- ▶ Since one has to solve a Kohn-Sham system for each **k** point, it is important to limit the size of the grid to the minimum that enables one to obtain the results with the desired accuracy.
- ▶ As for the plane-wave cut-off energy, a convergence study should be performed also w.r.t. the size of the **k** points grid.

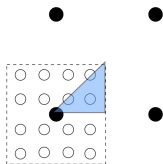
k Points Grid III

- ▶ Grids whose points are uniformly distributed are preferred over those that have different point densities in different directions.
- ▶ For example, grid (a) is better than grid (b) in the figure.



k Points Grid IV

- ▶ Crystals may be invariant w.r.t. other symmetry operations in addition to translations, such as rotations.
- ▶ These operations may connect BZ \mathbf{k} points: $f(\mathbf{k}_1) \leftrightarrow f(\mathbf{k}_2)$.
- ▶ Properties across the full BZ can be obtained from the subset of \mathbf{k} points unrelated to others, called Irreducible Brillouin Zone (IBZ).
- ▶ A weight $w_{\mathbf{k}}$ can be assigned to each IBZ \mathbf{k} point depending on the number of related BZ \mathbf{k} points, so that:



$$\bar{f} = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}}^{\text{IBZ}} w_{\mathbf{k}} f(\mathbf{k})$$

- ▶ This saves a significant amount of computational time.

Smearing I

- ▶ In the Kohn-Sham approach, the ground-state electron density of a crystal at 0 K is:

$$n_0(\mathbf{r}) \propto \sum_n \sum_{\mathbf{k}}^{\text{BZ}} f_{n\mathbf{k}} \phi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r})$$

where $f_{n\mathbf{k}} \in \{0, 1\}$ is the occupation of the $n\mathbf{k}$ -th orbital.

- ▶ In insulators at 0 K, for a given n , $f_{n\mathbf{k}}$ has the same value for all \mathbf{k} vectors, and hardly changes from one step to the next of the self-consistent cycle.
- ▶ In metals at 0 K, for a given n , $f_{n\mathbf{k}}$ changes value between different \mathbf{k} vectors, and most likely changes from one step to the next of the self-consistent cycle.
- ▶ This causes serious convergence issues w.r.t. the number of \mathbf{k} points in metals, where very fine grids would be needed.

Smearing II

- ▶ To overcome this numerical issue, the occupation number can be replaced by a function that varies smoothly between 0 and 1, called smearing function:

$$f(\varepsilon) = \frac{1}{\sigma} \tilde{\delta}\left(\frac{\varepsilon}{\sigma}\right)$$

that becomes the step function as $\sigma \rightarrow 0$, where σ is the smearing parameter.

- ▶ The smeared ground-state electron density is:

$$n_0(\mathbf{r}; \sigma) \propto \sum_n \sum_{\mathbf{k}}^{\text{BZ}} \frac{1}{\sigma} \tilde{\delta}\left(\frac{\varepsilon_F - \varepsilon_{n\mathbf{k}}^{\text{KS}}}{\sigma}\right) \phi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r})$$

where ε_F is the Fermi level.

Smearing III

- ▶ Typical smearing functions are:

- ▶ Fermi-Dirac:

$$\tilde{\delta}(x) = \frac{1}{1 + \exp(x)}$$

- ▶ Marzari-Vandebilt:

$$\tilde{\delta}(x) = \frac{2 (2 - x \sqrt{2})}{\sqrt{\pi}} \exp \left(\frac{1}{\sqrt{2}} - x \right)^2$$

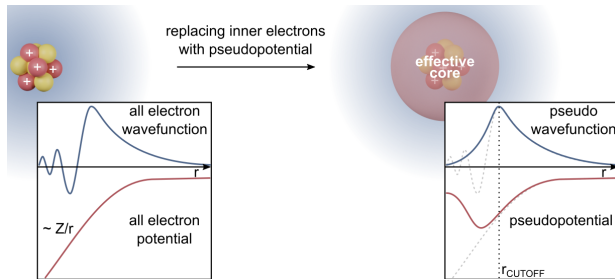
- ▶ σ is a convergence parameter and it should be chosen as small as possible while ensuring convergence.

Pseudo-Potential Approximation I

- ▶ Plane-wave basis sets have some weaknesses if one wants to consider all the electrons of the crystal in the calculations:
 - ▶ Low-energy occupied orbitals (core/inner electrons) are tightly bound to the nuclei, where they are sharply peaked.
 - ▶ High-energy occupied orbitals (valence/outer electrons) rapidly oscillates around the nuclei, where the potential is very strong.
- ▶ A very large number of plane waves is required to accurately describe the sharp wavefunction features, increasing computational demands.
- ▶ Fortunately, most physical properties of solids are determined by the valence electrons.
- ▶ Then, one can replace the strong potential acting on the valence electrons because of the nuclei and the tightly bound core electrons with an effective potential acting only on the valence electrons, called pseudo-potential (PP).

Pseudo-Potential Approximation II

- ▶ The pseudo-potential can be interpreted as the potential acting on the valence electrons that generated by the nuclei screened by the core electrons.
- ▶ The pseudo-potential is much smoother than the original. As consequence, the new valence electron wavefunction, called pseudo-wavefunction, is smoother too. This significantly reduces the number of plane waves needed.



Pseudo-Potential Approximation III

- So, the full Hamiltonian is replaced by a pseudo-Hamiltonian:

$$\begin{aligned}\hat{H}_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) &= \hat{T}_e(\{\mathbf{r}_i\}) + \hat{U}_{ee}(\{\mathbf{r}_i\}) + \hat{U}_{eN}(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \\ &\quad \downarrow \\ \hat{H}_e^{\text{PP}}(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) &= \hat{T}_e(\{\mathbf{r}_i\}_i^{\text{out}}) + \hat{U}_{ee}(\{\mathbf{r}_i\}_i^{\text{out}}) + \hat{U}_{eN}^{\text{PP}}(\{\mathbf{r}_i\}_i^{\text{out}}; \{\mathbf{R}_I\})\end{aligned}$$

- The pseudo-potential is given by:

$$\hat{U}_{eN}^{\text{PP}}(\{\mathbf{r}_i\}_i^{\text{out}}; \{\mathbf{R}_I\}) = \sum_i^{\text{out}} u_{eN}^{\text{PP}}(\mathbf{r}_i; \{\mathbf{R}_I\})$$

with:

$$u_{eN}^{\text{PP}}(\mathbf{r}; \{\mathbf{R}_I\}) = \sum_{\mathbf{R}_I} u_{\mathbf{R}_I}^{\text{PP}}(\mathbf{r} - \mathbf{R}_I)$$

where $u_{\mathbf{R}_I}^{\text{PP}}(\mathbf{r})$ is the atomic pseudo-potential generated by the I -th nucleus together with its core electrons.

Atomic Pseudo-Potentials I

- ▶ In general, the pseudo-potential $u_{\mathbf{R}_I}^{\text{PP}}(\mathbf{r})$ is assumed to depend only on the atomic species α and be independent on its environment (transferability):

$$u_{\mathbf{R}_I}^{\text{PP}}(\mathbf{r} - \mathbf{R}_I) \mapsto u_{\alpha}^{\text{PP}}(\mathbf{r} - \mathbf{R}_I)$$

- ▶ There is no unique recipe to determine $u_{\alpha}^{\text{PP}}(\mathbf{r})$, but the approach is similar for any pseudo-potential model and assure a reasonable quality:
 1. An all-electron (AE) self-consistent atomic calculation is performed with $u_{\text{ext}}(\mathbf{r})$ equal to the atomic potential $u_{\alpha}(\mathbf{r})$:

$$\hat{H}_{\alpha}^{\text{AE}}(\mathbf{r}) \phi_{\alpha i}^{\text{AE}}(\mathbf{r}) = \varepsilon_{\alpha i}^{\text{AE}} \phi_{\alpha i}^{\text{AE}}(\mathbf{r})$$

to determine the all-electron Kohn-Sham eigenvalues and eigenfunctions.

Atomic Pseudo-Potentials II

2. A pseudo-potential model is chosen to describe nucleus and core electrons, usually having the form:

$$u_{\alpha}^{\text{PP}}(\mathbf{r}; \{\lambda\}) = \begin{cases} u(\mathbf{r}; \{\lambda\}) & \text{for } r < r_{\text{cut}} \\ u_{\alpha}(\mathbf{r}) & \text{for } r > r_{\text{cut}} \end{cases}$$

where $\{\lambda\}$ is a set of adjustable parameters.

3. Self-consistent calculations are performed to determine eigenvalues and eigenfunctions of the Kohn-Sham Hamiltonian describing the valence electrons subject to the atomic pseudo-potential $u_{\alpha}^{\text{PP}}(\mathbf{r}; \{\lambda\})$ as a function of $\{\lambda\}$:

$$\hat{H}_{\alpha}^{\text{PP}}(\mathbf{r}; \{\lambda\}) \phi_{\alpha i}^{\text{PP}}(\mathbf{r}; \{\lambda\}) = \varepsilon_{\alpha i}^{\text{PP}}(\{\lambda\}) \phi_{\alpha i}^{\text{PP}}(\mathbf{r}; \{\lambda\})$$

4. These calculations are repeated until a set $\{\lambda\}$ satisfying certain conditions is found.

Norm-Conserving Pseudo-Potentials

Norm-conserving pseudo-potentials have the following conditions for all valence electrons:

- ▶ Equal AE and PP eigenvalues:

$$\varepsilon_{\alpha i}^{\text{AE}} = \varepsilon_{\alpha i}^{\text{PP}}(\{\lambda\}) \quad \forall i \in \text{valence}$$

- ▶ Equal AE and PP eigenfunctions beyond the core radius:

$$\phi_{\alpha i}^{\text{AE}}(\mathbf{r}) = \phi_{\alpha i}^{\text{PP}}(\mathbf{r}; \{\lambda\}) \text{ for } r > r_c \quad \forall i \in \text{valence}$$

- ▶ Equal AE and PP charge in the core region:

$$\int_0^{r_c} dr r^2 |\phi_{\alpha i}^{\text{AE}}(r)|^2 = \int_0^{r_c} dr r^2 |\phi_{\alpha i}^{\text{PP}}(r; \{\lambda\})|^2 \quad \forall i \in \text{valence}$$

where only the radial part of the wave-function is integrated.

- ▶ Reproduced scattering properties.

Comments on Pseudo-Potentials

- ▶ PP models can be rather complex, and one usually arrives to a pseudo-potential different for each angular momentum.
- ▶ Norm-conserving pseudo-potentials are termed “ab initio”, in the sense that they are obtained from calculations.
- ▶ On the other hand, empirical pseudo-potentials are obtained by fitting the chosen model to experimental data.
- ▶ A smaller r_c generally leads to better accuracy and transferability, but requires more plane waves, leading to the naming hard potentials.
- ▶ A larger r_c generally leads to reduced accuracy and transferability, but requires less plane waves, leading the naming soft potentials.
- ▶ Ultra-soft pseudo-potentials have been introduced by Vanderbilt, which require less plane waves for the same accuracy, but need more operation per computational cycle, for large systems, this leads to improved performance.

Density Functional Perturbation Theory (DFPT)

Equilibrium Nuclear Coordinates I

- ▶ In the Born-Oppenheimer approximation, if the nuclei have position vectors $\{\mathbf{R}_I\}$, their potential energy is:

$$E_{\text{tot}}(\{\mathbf{R}_I\}) = E_0(\{\mathbf{R}_I\}) + U_{\text{NN}}(\{\mathbf{R}_I\})$$

This is called adiabatic surface.

- ▶ The classical force acting on the I -th nucleus is:

$$\mathbf{F}_I(\{\mathbf{R}_I\}) = -\nabla_{\mathbf{R}_I} E_{\text{tot}}(\{\mathbf{R}_I\}) = -\nabla_{\mathbf{R}_I} E_0(\{\mathbf{R}_I\}) - \nabla_{\mathbf{R}_I} U_{\text{NN}}(\{\mathbf{R}_I\})$$

- ▶ A given atomic configuration is an equilibrium configuration if:

$$\{\mathbf{R}_{I0}\} = \{\mathbf{R}_I : \mathbf{F}_J(\{\mathbf{R}_I\}) = 0 \ \forall J\}$$

that is, if it is a minimum of the adiabatic surface, which could be local.

Equilibrium Nuclear Coordinates II

- ▶ The gradient of the electronic ground-state energy can be expressed in terms of the ground-state electron density and the gradient of the external potential, which is usually known:

$$\nabla_{\mathbf{R}_I} E_0(\{\mathbf{R}_I\}) = \int d\mathbf{r} n_0(\mathbf{r}; \{\mathbf{R}_I\}) \nabla_{\mathbf{R}_I} u_{\text{ext}}(\mathbf{r}; \{\mathbf{R}_I\})$$

- ▶ Therefore, once the ground-state for a given atomic configuration has been obtained, the nuclear forces are readily available.
- ▶ One can modify the given nuclear configuration depending on the direction of the nuclear forces to find one at which all these forces vanish, that is, an equilibrium configuration; this is called structural relaxation.
- ▶ Clearly, there is not way to be certain that the relaxed structure is the global minimum of the adiabatic surface, and the equilibrium configuration found depends on the starting point of the search.

Proof of the Ground-State Energy Gradient Expression

Starting from the Hellmann-Feynman theorem (see Appendix):

$$\begin{aligned}\nabla_{\mathbf{R}_I} E_0(\{\mathbf{R}_I\}) &= \langle \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) | \nabla_{\mathbf{R}_I} \hat{H}_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) | \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \rangle_{\{\mathbf{r}_i\}} \\&= \langle \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) | \nabla_{\mathbf{R}_I} \hat{U}_{\text{ext}}(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) | \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \rangle_{\{\mathbf{r}_i\}} \\&= \langle \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) | \nabla_{\mathbf{R}_I} \sum_i u_{\text{ext}}(\mathbf{r}_i; \{\mathbf{R}_I\}) | \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \rangle_{\{\mathbf{r}_i\}} \\&= \langle \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) | \nabla_{\mathbf{R}_I} \sum_i \int d\mathbf{r} \delta(\mathbf{r} - \mathbf{r}_i) u_{\text{ext}}(\mathbf{r}; \{\mathbf{R}_I\}) | \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \rangle_{\{\mathbf{r}_i\}} \\&= \int d\mathbf{r} \langle \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \rangle_{\{\mathbf{r}_i\}} \nabla_{\mathbf{R}_I} u_{\text{ext}}(\mathbf{r}; \{\mathbf{R}_I\}) \\&= \int d\mathbf{r} n_0(\mathbf{r}; \{\mathbf{R}_I\}) \nabla_{\mathbf{R}_I} u_{\text{ext}}(\mathbf{r}; \{\mathbf{R}_I\})\end{aligned}$$

Harmonic Approximation I

- ▶ We consider the equilibrium atomic configuration $\{\mathbf{R}_{I0}\}$.
- ▶ Then, we express the position vector of the I -th nucleus as $\mathbf{R}_I = \mathbf{R}_{I0} + \mathbf{u}_I$, where \mathbf{u}_I is its displacement from its equilibrium position.
- ▶ As consequence, the adiabatic surface can be expressed in terms of the nuclear displacements:

$$E_{\text{tot}}(\{\mathbf{R}_I\}) \mapsto E_{\text{tot}}(\{\mathbf{u}_I\})$$

- ▶ For small displacements, one can expand the adiabatic surface in Taylor series around the equilibrium configuration considered:

$$E_{\text{tot}}(\{\mathbf{u}_I\}) = E_{\text{tot}}(\{0\}) + \frac{1}{2} \sum_{I\alpha, J\beta} \underbrace{\frac{\partial^2 E_{\text{tot}}}{\partial u_{I\alpha} \partial u_{J\beta}} \Big|_{\{0\}}}_{D_{I\alpha, J\beta}} u_{I\alpha} u_{J\beta} + \dots$$

where α and β denote the Cartesian directions.

Harmonic Approximation II

- ▶ First-order terms are missing because the equilibrium configuration is a critical point of the adiabatic surface.
- ▶ In the harmonic approximation, only the terms up to second order are retained.
- ▶ The $D_{I\alpha,J\beta}$ values are called interatomic force constants and $\mathbf{D} = [D_{I\alpha,J\beta}]_{I\alpha,J\beta}$ is called dynamical matrix.
- ▶ Then, the force acting on the I -th nucleus along α is:

$$F_{I\alpha} = -\frac{\partial E_{\text{tot}}(\{\mathbf{u}_J\})}{\partial u_{I\alpha}} = -\sum_{J\beta} D_{I\alpha,J\beta} u_{J\beta}$$

- ▶ The classical nuclear dynamics follows the coupled equations:

$$M_I \ddot{u}_{I\alpha} = -\sum_{J\beta} D_{I\alpha,J\beta} u_{J\beta} \quad \forall I\alpha$$

Phonons I

- ▶ In a crystal, the position vector of each nucleus can be written as the sum of the translation vector associated to its unit cell and its position relative to the unit cell origin. If \mathbf{t}_n is the former and \mathbf{d}_ν the latter at the equilibrium configuration considered:

$$\mathbf{R}_I = \underbrace{\mathbf{t}_n + \mathbf{d}_\nu}_{\mathbf{R}_{I0}} + \underbrace{\mathbf{u}_{n\nu}}_{\mathbf{u}_I}$$

- ▶ With the re-indexing $I \mapsto n\nu$, the equations of motions become:

$$M_\nu \ddot{u}_{n\nu\alpha} = - \sum_{n'\nu'\alpha'} D_{n\nu\alpha, n'\nu'\alpha'} u_{n'\nu'\alpha'} \quad \forall n\nu\alpha$$

- ▶ They can be solved by assuming:

$$u_{n\nu\alpha}(t) = u_{\nu\alpha}(\mathbf{q}, \omega) \exp[i(\mathbf{q} \cdot \mathbf{t}_n - \omega t)]$$

which is a phonon of wave vector \mathbf{q} and frequency ω .

Phonons II

- ▶ Plugging the phonon form into the equations of motion leads to the following system of equations:

$$M_\nu \omega^2 u_{\nu,\alpha}(\mathbf{q}, \omega) = \underbrace{\sum_{\nu'\alpha'} \sum_{n'} D_{n\nu\alpha, n'\nu'\alpha'} \exp[-i\mathbf{q} \cdot (\mathbf{t}_n - \mathbf{t}_{n'})]}_{D_{\nu\alpha, \nu'\alpha'}(\mathbf{q})} u_{\nu'\alpha'}(\mathbf{q}, \omega) \quad \forall \nu\alpha$$

- ▶ $D_{\nu\alpha, \nu'\alpha'}(\mathbf{q})$ is the element of the dynamical matrix in reciprocal space. It does not depend on n because:

$$D_{n\nu\alpha, n'\nu'\alpha'} = D_{m\nu\alpha, m'\nu'\alpha'} \quad \text{if} \quad \mathbf{t}_n - \mathbf{t}_{n'} = \mathbf{t}_m - \mathbf{t}_{m'}$$

- ▶ The equations of motion have non-trivial solution if:

$$\det([D_{\nu\alpha, \nu'\alpha'}(\mathbf{q}) - M_\mu \omega^2(\mathbf{q}) \delta_{\alpha\alpha'} \delta_{\nu\nu'}]_{\nu\alpha, \nu'\alpha'}) = 0$$

- ▶ The number of solutions per \mathbf{q} vector $\{\omega_i(\mathbf{q})\}$ equals the number of atoms per unit cell times the three space coordinates.

Phonons III

- ▶ As for electrons, periodic boundary conditions give:

$$\mathbf{q} = \sum_{i=1}^3 \frac{n_i}{N_i} \mathbf{g}_i \quad \forall n_i \in \mathbb{Z}$$

- ▶ Again, inequivalent solutions are found only for $\mathbf{q} \in \text{BZ}$.
- ▶ Therefore, for each band index i , there is a number of solutions equal to the number of unit cells; the curves $\omega_i(\mathbf{q})$ form the phonon band structure, and are three times the number of atoms per unit cell.
- ▶ For any crystal, $\omega_i(\mathbf{q} \rightarrow 0) \rightarrow 0$ for three bands; this can be used to cross-check calculations.

Linear Response I

- ▶ Nuclear dynamics around an equilibrium configuration is governed by the interatomic force constants, that is, the second derivatives of the adiabatic surface w.r.t. nuclear displacements at the equilibrium configuration.
- ▶ The first derivatives vanish at the equilibrium configuration:

$$\frac{\partial E_{\text{tot}}}{\partial u_{n\nu\alpha}}(\{0\}) = \frac{\partial U_{\text{NN}}}{\partial u_{n\nu\alpha}}(\{0\}) + \int d\mathbf{r} n_0(\mathbf{r}; \{0\}) \frac{\partial u_{\text{ext}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; \{0\}) = 0$$

Linear Response II

- ▶ On the other hand, the second derivatives can be expressed in terms of the linear responses of the ground-state electron density w.r.t. to a nuclear displacement:

$$\begin{aligned} \frac{\partial^2 E_{\text{tot}}}{\partial u_{n\nu\alpha} \partial u_{n'\nu'\alpha'}}(\{0\}) &= \frac{\partial^2 U_{\text{NN}}}{\partial u_{n\nu\alpha} \partial u_{n'\nu'\alpha'}}(\{0\}) + \\ &\quad \int d\mathbf{r} n_0(\mathbf{r}; \{0\}) \frac{\partial^2 u_{\text{ext}}}{\partial u_{n\nu\alpha} \partial u_{n'\nu'\alpha'}}(\mathbf{r}, \{0\}) + \\ &\quad \int d\mathbf{r} \underbrace{\frac{\partial n_0}{\partial u_{n'\nu'\alpha'}}(\mathbf{r}; \{0\})}_{\text{linear response}} \frac{\partial u_{\text{ext}}}{\partial u_{n\nu\alpha}}(\mathbf{r}, \{0\}) \end{aligned}$$

- ▶ As the other terms are known once the calculation of the electronic ground-state at the equilibrium configuration is done, the linear responses are the only missing ingredients to fully describe phonons.

Density Functional Perturbation Theory (DFPT) I

- ▶ DFPT enables the calculation of the linear response of the ground-state electron density w.r.t. a small displacement of the nuclei from their equilibrium configuration, needing as input only ground-state properties at the equilibrium configuration.
- ▶ For a small displacement $u_{n\nu\alpha} \neq 0$ around equilibrium, the linear response of the ground-state electron density is related to the linear response of the occupied Kohn-Sham orbitals:

$$\frac{\partial n_0}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0) = 2 \Re \left[\sum_i^{\text{occ}} \phi_i^{\text{KS}*}(\mathbf{r}; 0) \frac{\partial \phi_i^{\text{KS}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0) \right] \quad (1)$$

Density Functional Perturbation Theory (DFPT) II

- At the same time, the linear response of each Kohn-Sham orbital can be calculated separately by solving:

$$\left[\hat{H}^{\text{KS}}(\mathbf{r}; 0) - \varepsilon_i^{\text{KS}}(0) \right] \frac{\partial \phi_i^{\text{KS}}}{\partial u_{n\nu\alpha}}(\mathbf{r}, 0) = \left[\langle \phi_i(\mathbf{r}; 0)^{\text{KS}} | \frac{\partial U^{\text{KS}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0) | \phi_i^{\text{KS}}(\mathbf{r}; 0) \rangle - \frac{\partial U^{\text{KS}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0) \right] \phi_i^{\text{KS}}(\mathbf{r}; 0) \quad (2)$$


Density Functional Perturbation Theory (DFPT) III

- Finally, from the definition of the Kohn-Sham potential:

$$\begin{aligned} \frac{\partial U^{\text{KS}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0) = & \frac{\partial u_{\text{ext}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0) + \\ & \underbrace{\frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial n}{\partial u_{n\nu\alpha}}(\mathbf{r}'; 0)}_{\frac{\partial U_{\text{H}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0)} + \\ & \underbrace{\int d\mathbf{r}' \frac{\delta U_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r}')} \frac{\partial n}{\partial u_{n\nu\alpha}}(\mathbf{r}'; 0)}_{\frac{\partial U_{\text{xc}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0)} \quad (3) \end{aligned}$$

Density Functional Perturbation Theory (DFPT) IV

- ▶ Equations 1, 2 and 3 form a system that must be solved self-consistently, because of the following connection between the unknown terms:

$$\frac{\partial U^{\text{KS}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0) \longrightarrow \left\{ \frac{\partial \phi_i^{\text{KS}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0) \right\}_i^{\text{occ}} \longrightarrow \frac{\partial n_0}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0)$$


All other terms are known from the equilibrium ground-state.

- ▶ It is important to notice that empty Kohn-Sham orbitals (conduction states) are in principle not required.

Proof of Density Functional Perturbation Theory I

1. Equations 1 and 3 are readily derived by simply applying definitions.
2. To obtain Equation 2, the first step is to linearize the following terms w.r.t. a small displacement $u_{n\nu\alpha}$ around equilibrium:

$$U^{KS}(\mathbf{r}, u_{n\nu\alpha}) \approx U^{KS}(\mathbf{r}, 0) + \frac{\partial U^{KS}}{\partial u_{n\nu\alpha}}(\mathbf{r}, 0) u_{n\nu\alpha}$$

$$\phi_i^{KS}(\mathbf{r}, u_{n\nu\alpha}) \approx \phi_i^{KS}(\mathbf{r}, 0) + \frac{\partial \phi_i^{KS}}{\partial u_{n\nu\alpha}}(\mathbf{r}, 0) u_{n\nu\alpha}$$

$$\varepsilon_i^{KS}(u_{n\nu\alpha}) \approx \varepsilon_i^{KS}(0) + \frac{\partial \varepsilon_i^{KS}}{\partial u_{n\nu\alpha}}(0) u_{n\nu\alpha}$$

Proof of Density Functional Perturbation Theory II

3. Then, one applies first-order perturbation theory (see Appendix) to the Kohn-Sham Hamiltonian:

$$\hat{H}^{\text{KS}}(\mathbf{r}; u_{n\nu\alpha}) = \underbrace{\hat{T}_{\mathbf{r}} + U^{\text{KS}}(\mathbf{r}; 0)}_{\hat{H}^{\text{KS}}(\mathbf{r}; 0) : \text{unperturbed Hamiltonian with known eigenstates}} + \overbrace{\frac{\partial U^{\text{KS}}}{\partial u_{n\nu\alpha}}(\mathbf{r}, 0) u_{n\nu\alpha}}^{\text{perturbation}}$$

while recalling that:

$$\frac{\partial \varepsilon_i^{\text{KS}}}{\partial u_{n\nu\alpha}}(0) = \langle \phi_i^{\text{KS}}(\mathbf{r}; 0) | \frac{\partial U^{\text{KS}}}{\partial u_{n\nu\alpha}}(\mathbf{r}; 0) | \phi_i^{\text{KS}}(\mathbf{r}; 0) \rangle$$

Monochromatic Perturbation I

- ▶ So far, we have developed DFPT by considering perturbations due to a single atomic displacement instead of a phonon of given wave vector \mathbf{q} (monochromatic perturbation).
- ▶ If one considers phonons, it can be proven that the elements of the dynamical matrix in reciprocal space can be written as:

$$\begin{aligned} D_{\nu\alpha,\nu'\alpha'}(\mathbf{q}) &= \sum_{n'} D_{0\nu\alpha,n'\nu'\alpha'} \exp(i\mathbf{q} \cdot \mathbf{t}'_n) \\ &= \frac{1}{N} \frac{\partial^2 E_{\text{tot}}}{\partial u_{\nu\alpha}^*(\mathbf{q}) \partial u_{\nu'\alpha'}(\mathbf{q})}(\{0\}) \end{aligned}$$

where N is the number of unit cells of the crystal.

Monochromatic Perturbation II

- ▶ Then, one can apply the linear response equation:

$$\begin{aligned} \frac{1}{N} \frac{\partial^2 E_{\text{tot}}}{\partial u_{\nu\alpha}^*(\mathbf{q}) \partial u_{\nu'\alpha'}(\mathbf{q})}(\{0\}) &= \frac{1}{N} \frac{\partial^2 U_{\text{NN}}}{\partial u_{\nu\alpha}^*(\mathbf{q}) \partial u_{\nu'\alpha'}(\mathbf{q})}(\{0\}) + \\ &\int_{\Omega} d\mathbf{r} n_0(\mathbf{r}; \{0\}) \frac{\partial u_{\text{ext}}^2}{\partial u_{\nu\alpha}^*(\mathbf{q}) \partial u_{\nu'\alpha'}(\mathbf{q})}(\mathbf{r}, \{0\}) + \\ &\int_{\Omega} d\mathbf{r} \frac{\partial n_0}{\partial u_{\nu'\alpha'}(\mathbf{q})}(\mathbf{r}; \{0\}) \left(\frac{\partial u_{\text{ext}}}{\partial u_{\nu\alpha}(\mathbf{q})}(\mathbf{r}, \{0\}) \right)^* \end{aligned}$$

and extend the DFPT equations to the case of monochromatic perturbations; Ω is the unit cell.

- ▶ The equations are basically the same as before, except that the integrals must be calculated only on the unit cell.

Fourier Interpolation I

- ▶ We have defined the dynamical matrix in reciprocal space as the matrix whose elements are the Fourier components of the interatomic force constants:

$$D_{\nu\alpha,\nu'\alpha'}(\mathbf{q}) = \sum_{n'} D_{0\nu\alpha,n'\nu'\alpha'} \exp(i\mathbf{q} \cdot \mathbf{t}_{n'})$$

- ▶ As DFPT calculations are relatively expensive, this can be used to speed up calculations:
 1. One starts by calculating the dynamical matrix on a uniform grid $\{\mathbf{q}_i \text{ for } i = 1, \dots, N_q\}$
 2. Then, one determines the interatomic force constants on the basis of the properties of the discrete Fourier transform:

$$\bar{D}_{0\nu\alpha,n'\nu'\alpha'} = \frac{1}{N_q} \sum_{i=1}^{N_q} D_{\nu\alpha,\nu'\alpha'}(\mathbf{q}_i) \exp(i\mathbf{q}_i \cdot \mathbf{t}_{n'})$$

Fourier Interpolation II

3. Finally, one interpolates the dynamical matrix elements at other wave vectors $\mathbf{q} \notin \{\mathbf{q}_i \text{ for } i = 1, \dots, N_q\}$ by:

$$\overline{D}_{\nu\alpha,\nu'\alpha'}(\mathbf{q}) = \sum_{n'} \overline{D}_{0\nu\alpha,n'\nu'\alpha'} \exp(i\mathbf{q} \cdot \mathbf{t}_{n'})$$

4. The overbar indicates that this is an approximation whose accuracy depends on the quality of the grid of \mathbf{q} points used to obtain the interatomic force constants.
5. Clearly, the grid should be chosen small enough to make the calculations feasible, but large enough to reach the required accuracy. In principle, also this grid is a converge parameter.

DFPT vs Frozen Phonons Technique

- ▶ The frozen phonon technique keeps all atoms locked at their equilibrium position and compute phonons by local perturbations, that is, by slightly moving atom by atom from their starting position.
- ▶ The calculation of the dynamical matrix at a generic point of the BZ has the problem that a crystal with a small distortion (that is, froze-in) loses the original periodicity unless $\mathbf{q} = 0$.
- ▶ Computation of the dynamical matrix at any $\mathbf{q} \neq 0$ requires a super-cell big enough to recover periodicity.
- ▶ The computational effort needed to determine the forces grows as the cube of the supercell size, making the frozen phonon technique quite slow from the computational point of view.
- ▶ DFPT on the other hand, maps perturbations (phonons) incommensurate with the unperturbed system periodicity onto the original periodic system, removing the need to work with super-cells.

Appendix

Atomic Units

Fundamental constants:

- ▶ $a_B = \frac{\hbar^2}{m_e e^2} = 0.529 \text{ \AA} \text{ (Bohr)}$
- ▶ $Ry = \frac{\hbar^2}{2 m_e a_B^2} = \frac{e^2}{2 a_B} = 13.606 \text{ eV (Rydberg)}$
- ▶ $Ha = \frac{e^2}{a_B} = 27.21 \text{ eV (Hartree)}$
- ▶ $\alpha^{-1} = \frac{c \hbar}{e^2} = 137.036$

Hartree atomic units:

- ▶ $e = 1$
- ▶ $\hbar = 1$
- ▶ $m_e = 1$
- ▶ $4 \pi \epsilon_0 = 1$
- ▶ Unit of energy: Ha
- ▶ Unit of length: a_B
- ▶ Velocity of light: α^{-1}

Rydberg atomic units:

- ▶ $e^2 = 2$,
- ▶ $\hbar = 1$,
- ▶ $m_e = 1/2$
- ▶ $4 \pi \epsilon_0 = 1$
- ▶ Unit of energy: Ry
- ▶ Unit of length: a_B
- ▶ Velocity of light: $2 \alpha^{-1}$

Functionals

- ▶ A functional F is a mapping that associates to each function $f(x)$ of a given set of functions \mathcal{F} a number $F[f(x)]$:

$$F : f(x) \in \mathcal{F} \mapsto F[f(x)] \in \mathbb{C}$$

- ▶ The functional differential is defined as the derivative:

$$\delta F[f(x); g(x)] = \lim_{\epsilon \rightarrow 0} \frac{F[f(x) + \epsilon g(x)] - F[f(x)]}{\epsilon}$$

The derivative is “directional” because dependent on $g(x)$.

- ▶ The functional differential can be expressed as:

$$\delta F[f(x); g(x)] = \int_x dx \frac{\delta F}{\delta f}(x) g(x)$$

where $\frac{\delta F}{\delta f}(x)$ is a function of x called functional derivative of F at f .

Hellmann-Feynman's Theorem I

Given an Hermitian operator $\hat{H}(\mathbf{r}, \lambda)$ dependent on a continuous parameter λ , if $\psi(\mathbf{r}; \lambda)$ is an eigenfunction having eigenvalue $E(\lambda)$, then:

$$\frac{dE}{d\lambda}(\lambda) = \langle \psi(\mathbf{r}; \lambda) | \frac{d\hat{H}(\mathbf{r}; \lambda)}{d\lambda}(\lambda) | \psi(\mathbf{r}; \lambda) \rangle_{\mathbf{r}}$$

Hellmann-Feynman's Theorem II

- The theorem can be readily proven:

$$\begin{aligned}\frac{dE}{d\lambda}(\lambda) &= \frac{d}{d\lambda} \langle \psi(\mathbf{r}; \lambda) | \hat{H}(\mathbf{r}; \lambda) | \psi(\mathbf{r}; \lambda) \rangle_{\mathbf{r}}(\lambda) \\ &= \left\langle \frac{d\psi}{d\lambda}(\mathbf{r}; \lambda) | \hat{H}(\mathbf{r}; \lambda) | \psi(\mathbf{r}; \lambda) \right\rangle_{\mathbf{r}} + \langle \psi(\mathbf{r}; \lambda) | \hat{H}(\mathbf{r}; \lambda) | \frac{d\psi}{d\lambda}(\mathbf{r}; \lambda) \rangle_{\mathbf{r}} \\ &\quad + \langle \psi(\mathbf{r}; \lambda) | \frac{d\hat{H}}{d\lambda}(\mathbf{r}; \lambda) | \psi(\mathbf{r}; \lambda) \rangle_{\mathbf{r}} \\ &= E(\lambda) \left\langle \frac{d\psi}{d\lambda}(\mathbf{r}; \lambda) | \psi(\mathbf{r}; \lambda) \right\rangle_{\mathbf{r}} + E(\lambda) \left\langle \psi(\mathbf{r}; \lambda) | \frac{d\psi}{d\lambda}(\mathbf{r}; \lambda) \right\rangle_{\mathbf{r}} \\ &\quad + \langle \psi(\mathbf{r}; \lambda) | \frac{d\hat{H}}{d\lambda}(\mathbf{r}; \lambda) | \psi(\mathbf{r}; \lambda) \rangle_{\mathbf{r}} \\ &= E(\lambda) \frac{d}{d\lambda} \langle \psi(\mathbf{r}; \lambda) | \psi(\mathbf{r}; \lambda) \rangle_{\mathbf{r}}(\lambda) + \langle \psi(\mathbf{r}; \lambda) | \frac{d\hat{H}}{d\lambda}(\mathbf{r}; \lambda) | \psi(\mathbf{r}; \lambda) \rangle_{\mathbf{r}} \\ &= \langle \psi(\mathbf{r}; \lambda) | \frac{d\hat{H}}{d\lambda}(\mathbf{r}; \lambda) | \psi(\mathbf{r}; \lambda) \rangle_{\mathbf{r}}\end{aligned}$$

First-Order Perturbation Theory

Given an Hamiltonian operator $\hat{H}^{(0)}$ with known eigenvalues and eigenfunctions $E_n^{(0)}$ and $\psi_n^{(0)}$, eigenvalues and eigenfunctions of the Hamiltonian operator $\hat{H}^{(0)} + \hat{H}^{(1)}$, where $\hat{H}^{(1)}$ is a “small” perturbation, can be approximated as $E_n^{(0)} + E_n^{(1)}$ and $\psi_n^{(0)} + \psi_n^{(1)}$, where:

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle$$

and:

$$\left(\hat{H}^{(0)} - E_n^{(0)} \right) \psi_n^{(1)} = \left(E_n^{(1)} - \hat{H}^{(1)} \right) \psi_n^{(0)}$$