Periodic HF/DFT

Marek Krośnicki, Valera Veryazov

March 2025



- $\hat{H}\Psi(r) = E\Psi(r)$
- introducing basis: H_{ab}
- what is the range of indexes a,b?
- Point group symmetry and labels: they help us reduce the size and classify solutions: $F^{\alpha}C^{\alpha} = \epsilon S^{\alpha}C^{\alpha}$
- in infinite crystal $\Phi(x + R_n) = \Phi(x)$, but we don't want a and b to run infinite.

Symmetry - Space groups



Figure: NiO. Space group No. 225 Fm-3m

An infinite three-dimensional lattice may be defined in therms of linear independent real basic lattice vectors \boldsymbol{a} , \boldsymbol{b} , \boldsymbol{c}

 $\boldsymbol{t_n} = n_1 \boldsymbol{a}_1 + n_2 \boldsymbol{a}_2 + n_3 \boldsymbol{a}_3$

where $\mathbf{n} = (n_1, n_2, n_3)$ "Lattice points" – points in \mathbb{R}^3 having lattice vectors as their position vectors Every symmetry operation is pair of R(T)-rotation and t_n -pure translation

$$\boldsymbol{R}(T) \cdot \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} t_x \\ t_y \\ t_z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$$

shorter

$$R(T) \cdot \mathbf{x} + \mathbf{t}(T) = \mathbf{x}'$$
$$\{R(T)|\mathbf{t}(T)\}\mathbf{x} = \mathbf{x}'$$

Born and von Karman cyclic boundary conditions



Small parallelepiped (4x4x4 conventional unit cell).

For every eigenfunction of electronic Hamiltonian \hat{H}_e

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + N_1 \mathbf{a}_1) = \psi(\mathbf{r} + N_2 \mathbf{a}_2) = \psi(\mathbf{r} + N_3 \mathbf{a}_3)$$

Were N_1 , N_2 , N_3 are very large integers. This means that symmetry operator

$$P(T)\psi(\mathbf{r}) = \psi(\{\mathbf{R}(T)|\mathbf{t}(T)\}^{-1}\mathbf{r})$$

 $P(\{\mathbf{1}|N_j a_j\}) = P(\{\mathbf{1}|\mathbf{0}\})$

$P(\{\mathbf{1}|N_{j}a_{j}\}) = P(\{\mathbf{1}|\mathbf{0}\})$

$$P(\{\mathbf{1}|\mathbf{t}_{n}\}) = P(\{\mathbf{1}|\mathbf{0}\})P(\{\mathbf{1}|\mathbf{t}_{n}\}) = P(\{\mathbf{1}|\mathbf{t}_{n} + m_{1}N_{1}\mathbf{a}_{1} + m_{2}N_{2}\mathbf{a}_{2} + m_{3}N_{3}\mathbf{a}_{3}\})$$

it holds for any t_n and any set of integers m_1, m_2, m_3 therefore we have finite number $N = N_1 N_2 N_3$ of different $P(\{1|t_n\})$ operators

$$P(\{\mathbf{1}|n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3\}) \quad 0 \le n_j < N_j, \quad j = 1, 2, 3.$$

$$P(\{\mathbf{1}|N_j \mathbf{a}_j\}) = P(\{\mathbf{1}|\mathbf{a}_j\})^{N_j} = P(\{\mathbf{1}|\mathbf{0}\})$$
 for $j = 1, 2, 3$

Considering that T group is finite and Abelian it follows that we have one-dimensional representation

$$\Gamma(\{\mathbf{1}|\boldsymbol{a}_j\}) = [c_j]$$
 and $c_j^{N_j} = 1$

so that

$$c_j = \exp(-2\pi i p_j/N_j), \quad j=1,2,3$$

where $p_j \in \{0, 1, \dots, N_j - 1\}$ is an integer . Finally

 $\Gamma(\{\mathbf{1}|n_j \mathbf{a}_j\}) = [\exp(-2\pi i p_j n_j / N_j)]$

Introducing translational symmetry

$$\Gamma(\{\mathbf{1}|n_{j}\boldsymbol{a}_{j}\}) = [\exp(-2\pi i p_{j} n_{j} / N_{j})]$$
$$\Gamma(\{\mathbf{1}|\boldsymbol{t}_{n}\}) = \left[e^{-2\pi i [(p_{1}n_{1}/N_{1}) + (p_{2}n_{2}/N_{2}) + (p_{3}n_{3}/N_{3})]}\right]$$
$$\boldsymbol{t}_{n} = n_{1}\boldsymbol{a}_{1} + n_{2}\boldsymbol{a}_{2} + n_{3}\boldsymbol{a}_{3}$$

There are $N = N_1 N_2 N_3$ different sets of integers (p_1, p_2, p_3) which label N irreps of group T.

We define allowed **K** vectors (CAPITAL **K**)

$$\mathbf{K} \cdot \mathbf{t_n} = 2\pi [(p_1 n_1/N_1) + (p_2 n_2/N_2) + (p_3 n_3/N_3)]$$
 where $K_j = 2\pi p_j/N_j$
 $\Gamma^{\mathbf{K}}(\{\mathbf{1}|\mathbf{t_n}\}) = \left[e^{-i\mathbf{K}\cdot\mathbf{t_n}}\right]$

$$\Gamma^{\boldsymbol{K}}(\{\boldsymbol{1}|\boldsymbol{t_n}\}) = \begin{bmatrix} e^{-i\boldsymbol{K}\cdot\boldsymbol{t_n}} \end{bmatrix}$$
$$\boldsymbol{K} = K_1\boldsymbol{b}_1 + K_2\boldsymbol{b}_2 + K_3\boldsymbol{b}_3 \quad \text{and} \quad \boldsymbol{a_m}\boldsymbol{b}_j = 2\pi\delta_{mj}$$

Basic lattice vectors of the reciprocal lattice

$$oldsymbol{b}_1 = rac{2\pioldsymbol{a}_2 imes oldsymbol{a}_3}{oldsymbol{a}_1 \cdot (oldsymbol{a}_2 imes oldsymbol{a}_3)} \quad oldsymbol{b}_2 = rac{2\pioldsymbol{a}_3 imes oldsymbol{a}_1}{oldsymbol{a}_1 \cdot (oldsymbol{a}_2 imes oldsymbol{a}_3)} \quad oldsymbol{b}_3 = rac{2\pioldsymbol{a}_1 imes oldsymbol{a}_2}{oldsymbol{a}_1 \cdot (oldsymbol{a}_2 imes oldsymbol{a}_3)}$$

 $\mathbf{K} \cdot \mathbf{t_n} = 2\pi [(p_1 n_1 / N_1) + (p_2 n_2 / N_2) + (p_3 n_3 / N_3)]$ where $K_i = 2\pi p_i / N_i$



Figure: Brillouin zone for hexagonal lattice (source wiki) Periodic HF/DFT

Marek Krośnicki, Valera Veryazov

$$\Gamma^{\kappa}(\{\mathbf{1}|\boldsymbol{t}_{n}\}) = \left[e^{-i\boldsymbol{K}\cdot\boldsymbol{t}_{n}}\right]$$

$$P(\{\mathbf{1}|\boldsymbol{t}_{n}\})\psi_{1}^{k}(\boldsymbol{r}) = \Gamma^{k}(\{\mathbf{1}|\boldsymbol{t}_{n}\})\psi_{1}^{k}(\boldsymbol{r}) = e^{-i\boldsymbol{k}\cdot\boldsymbol{t}_{n}}\psi_{1}^{k}(\boldsymbol{r})$$

$$P(\{\mathbf{1}|\boldsymbol{t}_{n}\})\psi_{1}^{k}(\boldsymbol{r}) = \psi_{1}^{k}(\{\mathbf{1}|\boldsymbol{t}_{n}\}^{-1}\boldsymbol{r}) = \psi_{1}^{k}(\boldsymbol{r}-\boldsymbol{t}_{n})$$

$$\psi_{1}^{k}(\boldsymbol{r}-\boldsymbol{t}_{n}) = e^{-i\boldsymbol{k}\cdot\boldsymbol{t}_{n}}\psi_{1}^{k}(\boldsymbol{r})$$

Bloch functions

This is true for Bloch wave: $\psi_{1k}(\mathbf{r}) = e^{\mathbf{k}\cdot\mathbf{r}}u_{1k}(\mathbf{r})$ where $u_k(\mathbf{r}) = u_k(\mathbf{r} - \mathbf{t}_n)$ for any \mathbf{t}_n . The electronic energy eigenfunctions must be a basis functions of the irreducible representations Γ^{κ} of group T

- $\hat{H}(\mathbf{r})\psi_{l\mathbf{k}}(\mathbf{r}) = E_l(\mathbf{k})\psi_{l\mathbf{k}}(\mathbf{r})$
- $\psi_{lk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{lk}(\mathbf{r})$ where $u_{lk}(\mathbf{r}) = u_{lk}(\mathbf{r} \mathbf{t}_n)$
- $\psi_{I,(k+\kappa_i)}(\mathbf{r}) = \psi_{Ik}(\mathbf{r})$ K_i reciprocal lattice, \mathbf{k} reciprocal space

Example of Brillouin zones in 3D: FCC,



HF-Roothaan

How HF-Roothaan equations will look like $FC = \epsilon SC$? For HFR we need a basis set

Localized basis set
 We can define set {φ₁^k(r),...,φ_m^k(r)} of localized functions in the unit reference cell:

$$\psi_{\mu \mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{t}_{n} \in N} \exp(i\mathbf{k} \cdot \mathbf{t}_{n}) \varphi_{\mu}^{\mathbf{k}}(\mathbf{r} - \mathbf{t}_{n})$$

The sum goes over all t_n vectors of the direct lattice in the unit reference cell • $F(\mathbf{k})C(\mathbf{k}) = \epsilon(\mathbf{k})S(\mathbf{k})C(\mathbf{k})$

Fourier Transform of a function in BvK "Box"

Lets take a periodic function $f(\mathbf{r})$ and make a FT and FT⁻¹

$$ilde{f}(oldsymbol{G}) = rac{1}{\Omega} \int f(oldsymbol{r}) e^{-ioldsymbol{G}oldsymbol{r}} doldsymbol{r}$$
 $f(oldsymbol{r}) = \int ilde{f}(oldsymbol{G}) e^{ioldsymbol{G}oldsymbol{r}} doldsymbol{G}$

We can select a discrete G grid centred around origin of coordinate system in reciprocal lattice.

$$G_m = m_1 b_1 + m_2 b_2 + m_3 b_3$$
 $m_j = 0, 1, \dots, M_j - 1$

FT along one direction



$$f(x) \rightarrow f_m = f(x_m)$$

$$ilde{f}(q)
ightarrow ilde{f}_n = ilde{f}(q_n)$$

$$f(x_m)$$
 is sampled on $x_m = m \frac{L_1}{M_1}$ where $m = 0, \ldots, M_1 - 1$
 $\tilde{f}(q_n)$ is sampled on $q_n = n \frac{2\pi}{L_1}$ where $n = 0, \ldots, M_1 - 1$

Parallelepiped (4x4x4 conventional unit cell). Length of x edge is $L_1 = N_1 |\mathbf{a}_1|$

$$f(x_m)$$
 is sampled on $x_m = m \frac{L_1}{M_1}$ where $m = 0, ..., M_1 - 1$
 $\tilde{f}(q_n)$ is sampled on $q_n = n \frac{2\pi}{L_1}$ where $n = 0, ..., M_1 - 1$
 $\tilde{f}(q_n) = \frac{1}{M_1} \sum_{m=0}^{M_1 - 1} f_m e^{-i(2\pi n)m/M_1}$ (k-space)
 $f(x_m) = \sum_{n=0}^{M_1 - 1} \tilde{f}_n e^{i(2\pi n)m/M_1}$ (x-space)

$$\tilde{f}(n_1, n_2, n_3) = \frac{1}{M} \sum_{m_1, m_2, m_3=0}^{M_j - 1} f_{m_1, m_2, m_3} e^{-i(2\pi n_1)m_1/M_1} e^{-i(2\pi n_2)m_2/M_2} e^{-i(2\pi n_3)m_3/M_3}$$

(k-space)

$$f(x_{m_1}, x_{m_2}, x_{m_3}) = \sum_{n_1, n_2, n_3=0}^{M_j-1} \tilde{f}_{n_1, n_2, n_3} e^{i(2\pi n_1)m_1/M_1} e^{i(2\pi n_2)m_2/M_2} e^{i(2\pi n_3)m_3/M_3}$$

(x-space) where $M = M_1 M_2 M_3$, j = 1, 2, 3.

Nyquist-Shannon-Kotelnikov Sampling Theorem

A continuous signal that has been band-limited (i.e.), it contains no frequencies higher than a certain f_{max} can be perfectly reconstructed from its discrete samples if the sampling rate f_s is at least twice the highest frequency component of the signal $f_s \ge 2f_{max}$. If the signal is sampled below this rate, aliasing occurs, meaning different frequency components overlap and distort the original signal.



$$\psi_{lk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{lk}(\mathbf{r})$$
 where $u_{lk}(\mathbf{r}) = u_{lk}(\mathbf{r}-\mathbf{t_n})$
 $u_{lk}(\mathbf{r}) = \sum_{|\mathbf{G}| \le G_{max}} c_{lk}(\mathbf{G}) \exp\{i\mathbf{G}\cdot\mathbf{r}\}$

G is a grid of **G** vectors.

$$\psi_{l\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{l\boldsymbol{k}}(\boldsymbol{r}) = \sum_{|\boldsymbol{G}| \leq G_{max}} c_{l\boldsymbol{k}}(\boldsymbol{G})e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}}$$





E_{cut} =const, variation of lattice constant



E_{cut} =const, variation of lattice constant

Increase of cell size:

- finer (denser) k-points grid
- A larger basis set can cause the energy vs. lattice constant function to exhibit artificial behaviour.



Charge density

Let us set $G_{max} = 2mE_{cut}/\hbar^2$. In case of single determinant KS-DFT with orbitals

$$\psi_{l\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{l\boldsymbol{k}}(\boldsymbol{r}) = \sum_{|\boldsymbol{G}| \leq G_{max}} c_{l\boldsymbol{k}}(\boldsymbol{G}) e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}}$$

we can calculate charge density

$$n(\mathbf{r}) = \sum_{l,\mathbf{k}} f_{l\mathbf{k}} \psi_{l\mathbf{k}}^*(\mathbf{r}) \psi_{l\mathbf{k}}(\mathbf{r})$$

We will apply convolution theorem of Fourier transform

$$ilde{n}(\boldsymbol{G}) = \sum_{l, \boldsymbol{k}} \sum_{|\boldsymbol{G}'| \leq G_{max}} f_l \tilde{\psi}_{l \boldsymbol{k}}(\boldsymbol{G}') \tilde{\psi}_{l \boldsymbol{k}}(\boldsymbol{G} - \boldsymbol{G}')$$

Maximal value $|\boldsymbol{G} - \boldsymbol{G}'| = 2 \max |\boldsymbol{G}|$. Therefore for charge density we need denser grid

$$\frac{\hbar^2}{2m}|\boldsymbol{G}|^2 \le 4E_{cut}$$

How to select k grid, 4x4x1



 $\Psi_{AB} = \Psi_{ab,n} = \Psi_{ab,k}$, where A,B - belongs to a large unit cell, a,b - belongs to primitive unite cell, n - number of unit cell, k - k-point corresponding to this unit cell

- k-point sampling must be fine enough to accurately reconstruct the energy bands and density of states.
- If the k-point grid is too coarse (below the "Nyquist rate"), important details of the band structure can be missed or misrepresented (aliasing effects), leading to errors in total energy etc.
- Metallic systems require denser k-point grids because
- Insulators and semiconductors can tolerate coarser grids, but too few k-points may still lead to incorrect band gap estimations.

Example of Brillouin zones in 3D: FCC



• numerical integration of Brillouin zone (BZ) over a discrete grid of k-points

$$rac{1}{\Omega_k}\int_{BZ}dkpproxrac{1}{N_k}\sum_k\cdots$$

A calculation with 8 k-points is very similar to large unit cell calculation, containing 8 primitive unit cells. If k-points are generated as a result of expanding the primitive unit cell $2\times2\times2$, it is identical to calculation with a largre unit cell of the same size.

- Can one make calculation of NaCl with primitive unit cell and one k-point? The result will be very strange, since for example, there is no interaction between Na and Na.
- If one uses not a primitive unit cell of NaCl, but say, expanded by 8x8x8, it is enough to use only one Gamma point
- Can one make calculation of a huge unit cell with and one k-point?
- if the function is fluctuating a lot, one needs more points for integration.

- Cyclic model: the topology of space makes a loop, so one has a circle of atoms instead of a linear chain. Distance larger than a translation vector (size of the cycle) does not exit.
- Periodic model: a unit cell is periodically repeated.
- Does cyclic model identical to periodic model? No!
- Think about interactions! What is the 'radius' of Coulomb? Overlap ? Density?
- Not all interactions/terms are cell-periodic

- TB tight binding
- Semi-empirical
- HF
- DFT
- local MP2, CC, with excitations only in some area.

 $\hat{F} = \hat{T} + \hat{V} + \hat{J} - \hat{K},$

kinetic, one-electron interaction with nuclei, Coulomb and Exchange.

if μ is an index for an atomic orbital in *zero* cell, ν is an index for an atomic orbital located in cell **T**:

$$F_{\mu
u}(\mathbf{k}) = \sum_{\mathbf{T}} e^{i\mathbf{kT}} F_{\mu
u}(\mathbf{T})^{\dagger}$$

Coulomb is local operator, but exchange requires integration over whole space. So, what is 'whole space' in periodic model? If integration of exchange is not limited, it diverges..

- Insulators
- Metals
- Mott insulators
- 'failure' of band theory: NiO
- band theory and symmetry of the crystal

The language of one-electron energies (HOMO-LUMO, band structure, DOS) is simple, intuitive, but not accurate. The total energy is not the sum of one-electron terms. So, for accurate description of

electron excitations one needs not only the ground state, but also excited states.

- CASTEP
- CRYSTAL
- CP2K
- Gaussian
- pySCF
- Quantum ESPRESSO
- Turbomole
- VASP
- WIEN2k