

Plane Wave Density Functional Theory from Scratch

Course Philosophy	3
Recap	5
Plane waves	26
Potentials	46
Ewald summation	57
Self-consistent field procedure	69



Section

Course Philosophy

- ▶ Building a PW-DFT code *from scratch* is an ambitious though feasible goal.
- ▶ Limitations to ensure feasibility
 - ▶ Only Γ -point
 - ▶ Cubic unit cell
 - ▶ No pseudopotentials
 - ▶ Restricted (no spin-polarization)
- ▶ Focusing on the ingredients (so that you can cook at home)
- ▶ Learning by doing (exercises + workouts)
- ▶ Fully working educational code (PyPWFDT) to dissect



Section

Recap

We start with the (in)famous time-independent non-relativistic Schrödinger equation

$$\hat{\mathcal{H}}\psi = E\psi$$

where the Hamiltonian operator $\hat{\mathcal{H}}$ is given (in atomic units) by

$$\hat{\mathcal{H}} = \underbrace{-\sum_{i=1}^N \frac{1}{2} \nabla_i^2}_{E_{\text{kin}} \text{ electrons}} - \underbrace{\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2}_{E_{\text{kin}} \text{ nuclei}} - \underbrace{\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}}_{\text{nuc-el attraction}} + \underbrace{\sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}}_{\text{el-el repulsion}} + \underbrace{\sum_{A=1}^M \sum_{A>B}^M \frac{Z_A Z_B}{R_{AB}}}_{\text{nuc-nuc repulsion}}$$

Nuclei are much heavier than electrons, hence we consider the motion of the electrons to occur under the static presence of the nuclei.

$$\hat{\mathcal{H}} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{A>B}^M \frac{Z_A Z_B}{R_{AB}}$$

by which the result is termed the **electronic** Hamiltonian

$$\hat{\mathcal{H}}_{\text{elec}} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

Note that the nucleus-nucleus repulsion is still used, but only as a static term to the total electronic energy.

We have a system of multiple electrons, so we need a wave function that can handle that. A naive implementation is to simply consider a product of one-electron wave functions

$$\Psi_{\text{Hartree}} = \chi_i(\vec{\mathbf{x}}_1) \chi_j(\vec{\mathbf{x}}_2) \cdots \chi_N(\vec{\mathbf{x}}_N)$$

which is called a Hartree product. Assuming that the spinorbitals form an orthonormal set

$$\langle \chi_i(\vec{\mathbf{x}}_1) | \chi_j(\vec{\mathbf{x}}_1) \rangle = \delta_{ij}$$

then

$$\hat{\mathcal{H}}_{\text{elec}} \Psi_{\text{Hartree}} = (\epsilon_1 + \epsilon_2 + \cdots + \epsilon_N) \Psi_{\text{Hartree}}$$

The chance to find any of the electrons is given by

$$|\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\vec{x}_1 d\vec{x}_2 \dots d\vec{x}_N = |\chi_i(\vec{x}_1)|^2 d\vec{x}_1 |\chi_j(\vec{x}_2)|^2 d\vec{x}_2 \dots |\chi_N(\vec{x}_N)|^2 d\vec{x}_N$$

For each of the electrons, that chance does not depend on the position of the other electrons. In other words, electron motion is fundamentally uncorrelated in this wave function. That cannot be right!

In reality, electrons will repel each other and thus the chance to find electron 1 at position \vec{x}_1 depends on the position of, e.g., electron 2 at position \vec{x}_2 .

But there is an even more fundamental problem. The Hartree product allows us to distinguish between individual electrons. Electrons are fundamentally **indistinguishable** particles and hence the many-electron wave function should have this property embedded.

Remember, the $\vec{\mathbf{x}}$ are the electrons and the χ_i are the spin-orbitals.

$$|\Psi(\vec{\mathbf{x}}_1, \vec{\mathbf{x}}_2, \dots, \vec{\mathbf{x}}_N)\rangle = (N!)^{-1/2} \begin{vmatrix} \chi_i(\vec{\mathbf{x}}_1) & \chi_j(\vec{\mathbf{x}}_1) & \cdots & \chi_k(\vec{\mathbf{x}}_1) \\ \chi_i(\vec{\mathbf{x}}_2) & \chi_j(\vec{\mathbf{x}}_2) & \cdots & \chi_k(\vec{\mathbf{x}}_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(\vec{\mathbf{x}}_N) & \chi_j(\vec{\mathbf{x}}_N) & \cdots & \chi_k(\vec{\mathbf{x}}_N) \end{vmatrix}$$

$$|\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)\rangle = (N!)^{-1/2} \begin{vmatrix} \chi_i(\vec{x}_1) & \chi_j(\vec{x}_1) & \cdots & \chi_k(\vec{x}_1) \\ \chi_i(\vec{x}_2) & \chi_j(\vec{x}_2) & \cdots & \chi_k(\vec{x}_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(\vec{x}_N) & \chi_j(\vec{x}_N) & \cdots & \chi_k(\vec{x}_N) \end{vmatrix}$$

- ▶ Satisfies anti-symmetry principle
- ▶ Electrons become (exchange-)correlated

$$|\Psi(\vec{\mathbf{x}}_1, \vec{\mathbf{x}}_2, \dots, \vec{\mathbf{x}}_N)\rangle = (N!)^{-1/2} \begin{vmatrix} \chi_i(\vec{\mathbf{x}}_1) & \chi_j(\vec{\mathbf{x}}_1) & \cdots & \chi_k(\vec{\mathbf{x}}_1) \\ \chi_i(\vec{\mathbf{x}}_2) & \chi_j(\vec{\mathbf{x}}_2) & \cdots & \chi_k(\vec{\mathbf{x}}_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(\vec{\mathbf{x}}_N) & \chi_j(\vec{\mathbf{x}}_N) & \cdots & \chi_k(\vec{\mathbf{x}}_N) \end{vmatrix}$$

Important

This is still an **uncorrelated** wave function because electrons with opposite spin remain uncorrelated.

Inserting a Slater determinant

$$|\Psi(\vec{\mathbf{x}}_1, \vec{\mathbf{x}}_2, \dots, \vec{\mathbf{x}}_N)\rangle = (N!)^{-1/2} \begin{vmatrix} \chi_i(\vec{\mathbf{x}}_1) & \chi_j(\vec{\mathbf{x}}_1) & \cdots & \chi_k(\vec{\mathbf{x}}_1) \\ \chi_i(\vec{\mathbf{x}}_2) & \chi_j(\vec{\mathbf{x}}_2) & \cdots & \chi_k(\vec{\mathbf{x}}_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(\vec{\mathbf{x}}_N) & \chi_j(\vec{\mathbf{x}}_N) & \cdots & \chi_k(\vec{\mathbf{x}}_N) \end{vmatrix}$$

into

$$\hat{\mathcal{H}}_{\text{elec}} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

$$\begin{aligned}
 E = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle &= \underbrace{\sum_i^N \langle \chi_i | -\frac{1}{2} \nabla^2 | \chi_i \rangle}_{\text{kinetic energy}} + \underbrace{\sum_i^N \langle \chi_i | \sum_{A=1}^M \frac{Z_A}{r_{i,a}} | \chi_i \rangle}_{\text{nuclear attraction}} \cdots \\
 &\cdots + \frac{1}{2} \sum_i^N \sum_j^N \left[\underbrace{\langle \chi_i \chi_j | \frac{1}{r_{ij}} | \chi_i \chi_j \rangle}_{\text{coulomb repulsion}} - \underbrace{\langle \chi_i \chi_j | \frac{1}{r_{ij}} | \chi_j \chi_i \rangle}_{\text{exchange}} \right]
 \end{aligned}$$

Hartree-Fock is a **wave function** based method, can we switch to only using the **electron density** and are there advantages to that?

The electrons are under the influence of an **external potential** due to the nuclei

$$\nu_{\text{ext}}(\vec{r}) \equiv \sum_i -\frac{Z_i}{|\vec{r} - \vec{R}_i|}.$$

In combination with the **number of electrons**, this determines all the ground state properties (up to an arbitrary constant) of the system.

Suppose there are two different external potentials that yield the same electron density. These would have different Hamiltonians and thus a different ground state wave function. From the variational principle we can then state

$$\begin{aligned} E_1 &< \langle \Psi_2 | \hat{\mathcal{H}}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{\mathcal{H}}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{\mathcal{H}}_1 - \hat{\mathcal{H}}_2 | \Psi_2 \rangle \\ &= E_2 + \int \rho(\vec{r}) [\nu_{\text{ext},1}(\vec{r}) - \nu_{\text{ext},2}(\vec{r})] d\vec{r}. \end{aligned}$$

And by swapping E_1 and E_2 we would then find the contradiction

$$E_1 + E_2 < E_2 + E_1.$$

Suppose we have a system of M nuclei and N electrons, then its energy as function of the electron density ρ is given by

$$\begin{aligned}
 E_\nu[\rho] &= \underbrace{T[\rho(\vec{r})]}_{\text{kinetic}} + \underbrace{V[\rho(\vec{r})]}_{\text{nuclear attraction}} + \underbrace{U[\rho(\vec{r})]}_{\text{electron-electron}} \\
 &= \int \rho(\vec{r}) \nu_{\text{ext}}(\vec{r}) d\vec{r} + F_{\text{HK}}[\rho]
 \end{aligned}$$

where $F_{\text{HK}}[\rho]$ is a so-called **universal** functional

$$F_{\text{HK}}[\rho] = T[\rho] + U[\rho],$$

To find the ground state electron density $\rho_0(\vec{r})$, we are tasked by looking for that $\rho_0(\vec{r})$ that minimizes $E_\nu[\rho]$.

$$E_\nu[\rho] = T[\rho(\vec{r})] + V[\rho(\vec{r})] + U[\rho(\vec{r})]$$

This procedure is however hindered by having no explicit expressions for $T[\rho(\vec{r})]$ and the non-classical part of $U[\rho(\vec{r})]$.

Instead of solving for a system of **interacting** electrons, we use a fictitious proxy system of **non-interacting** electrons with the **same density** as the interacting system. For that system, the Hamiltonian is very simple

$$\hat{\mathcal{H}}_s = \sum_i^N \frac{1}{2} \nabla_i^2 + \sum_i^N \nu_s(\vec{r}_i)$$

Application of a Slater determinant on this Hamiltonian would yield

$$\hat{h}_s \chi_i = \left(-\frac{1}{2} \nabla^2 + \nu_s(\vec{r}) \right) \chi_i = \epsilon_i \chi_i$$

Because the electrons are (assumed) to be **non-interacting**, the expressions for the kinetic energy and the total electron density become very simple

$$T_s[\rho] = \sum_i^N \langle \chi_i | -\frac{1}{2} \nabla^2 | \chi_i \rangle$$

$$\rho(\vec{r}) = |\chi_i(\vec{r})|^2.$$

A non-interacting system is of course not equal to an interacting system, and this discrepancy has to be fixed. The trick to solve this is to **transfer** the interacting part of $T[\rho]$ to a so-called exchange-correlation functional as defined by

$$E_{xc}[\rho] \equiv (T[\rho] - T_s[\rho]) + \left(V_{ee}[\rho] - \underbrace{J[\rho]}_{\text{classical e-e}} \right)$$

by which the universal function $F[\rho]$ becomes

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho].$$

DFT:

$$\begin{aligned}
 E[\rho] &= T_s[\rho] + \int v(\vec{r})\rho(\vec{r}) d\vec{r} + J[\rho] + E_{xc}[\rho] \\
 &= \left[\sum_i \int \chi_i^* \left(-\frac{1}{2} \nabla_i^2 \right) \chi_i d\vec{r} \right] + \int v(\vec{r})\rho(\vec{r}) d\vec{r} + J[\rho] + E_{xc}[\rho].
 \end{aligned}$$

HF:

$$\begin{aligned}
 E = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle &= \sum_i^N \langle \chi_i | -\frac{1}{2} \nabla^2 | \chi_i \rangle + \sum_i^N \langle \chi_i | \sum_{A=1}^M \frac{Z_A}{r_{i,A}} | \chi_i \rangle \cdots \\
 &\cdots + \frac{1}{2} \sum_i^N \sum_j^N \left[\langle \chi_i \chi_j | \frac{1}{r_{ij}} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \frac{1}{r_{ij}} | \chi_j \chi_i \rangle \right]
 \end{aligned}$$

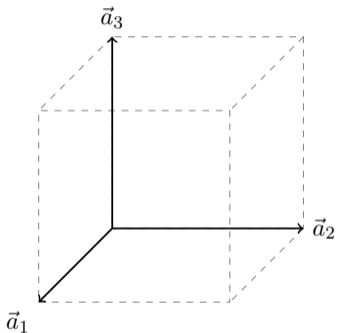
Kohn-Sham method: one-electron orbitals

$$\hat{h}_s \chi_i = \left(-\frac{1}{2} \nabla^2 + \nu_s(\vec{r}) \right) \chi_i = \epsilon_i \chi_i$$



Section

Plane waves



Unitcell matrix:

$$\mathbf{M} = \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix}.$$

Volume:

$$\Omega = \det |\mathbf{M}| = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

Plane wave:

$$\phi(\vec{G}, \vec{r}) = \frac{1}{\sqrt{\Omega}} \exp(i\vec{G} \cdot \vec{r})$$

Plane wave vectors:

$$\vec{G}_{i_1, i_2, i_3} = \left(i_1 - \frac{N_1}{2}\right) \vec{b}_1 + \left(i_2 - \frac{N_2}{2}\right) \vec{b}_2 + \left(i_3 - \frac{N_3}{2}\right) \vec{b}_3$$

Reciprocal matrix vectors:

$$\begin{aligned} \vec{b}_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\Omega} \\ \vec{b}_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\Omega} \\ \vec{b}_3 &= 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\Omega} \end{aligned}$$

Reciprocal matrix:

$$\mathbf{B} = \begin{pmatrix} \vec{b}_1 \\ \vec{b}_2 \\ \vec{b}_3 \end{pmatrix} = 2\pi (\mathbf{M}^T)^{-1}$$

$$\begin{aligned}\langle \phi(\vec{G}, \vec{r}) | \phi(\vec{G}, \vec{r}) \rangle &= \frac{1}{\Omega} \int_{\Omega} d\vec{r} \exp(-i\vec{G} \cdot \vec{r}) \exp(+i\vec{G} \cdot \vec{r}) \\ &= \frac{1}{\Omega} \int_{\Omega} d\vec{r} 1 = \frac{\Omega}{\Omega} = 1.\end{aligned}$$

👁 Observe

- ▶ Complex-conjugate is taken for the *ket*
- ▶ Results in “cancellation” of exponential term
- ▶ Effectively integration over unit cell volume

$$\begin{aligned}\langle \phi(\vec{G}', \vec{r}) | \phi(\vec{G}, \vec{r}) \rangle &= \frac{1}{\Omega} \int_{\Omega} d\vec{r} \exp(-i\vec{G}' \cdot \vec{r}) \exp(+i\vec{G} \cdot \vec{r}) \\ &= \frac{1}{\Omega} \int_{\Omega} d\vec{r} \exp(i(\vec{G} - \vec{G}') \cdot \vec{r}) \\ &= \delta_{\vec{G}, \vec{G}'}\end{aligned}$$

 Observe

- ▶ $(\vec{G} - \vec{G}') \cdot \vec{r}$ always corresponds to a multiple of 2π
- ▶ $\exp(i \cdot 2\pi \cdot n) = 1$ for $n \in \mathbb{Z}$ (recall the unit circle)

Any function inside the unitcell \mathbf{M} that admits to

$$u(\vec{r}) = u(\vec{r} + \vec{R})$$

can be represented by a linear combination of plane waves

$$u(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{u}(\vec{G}) \exp(i\vec{G} \cdot \vec{r})$$

Given

$$u(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{u}(\vec{G}) \exp(i\vec{G} \cdot \vec{r})$$

we can find $\tilde{u}(\vec{G})$ via

$$\begin{aligned} \langle \phi(\vec{G}', \vec{r}) | u(\vec{r}) \rangle &= \int_{\Omega} d\vec{r} \frac{1}{\Omega} \sum_{\vec{G}} \tilde{u}(\vec{G}) \exp(i(\vec{G} - \vec{G}') \cdot \vec{r}) \\ &= \sum_{\vec{G}} \tilde{u}(\vec{G}) \delta_{\vec{G}, \vec{G}'} \\ &= \tilde{u}(\vec{G}'). \end{aligned}$$

The equality

$$u(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{u}(\vec{G}) \exp(i\vec{G} \cdot \vec{r})$$

is only true for an infinitely large set of plane waves. Typically we use a number of plane waves smaller than ∞ by defining a cut-off energy such that

$$\frac{1}{2} |\vec{G}|^2 < E_{\text{cut}}.$$

For sufficiently large sets, the top equation remains approximately true (tunable to within proper numerical approximation).

- ▶ Finding the plane wave expansion coefficients $\{\tilde{u}(\vec{G})\}$ can be done via numerical integration on a per-plane wave basis. This is however very inefficient.
- ▶ Finding **all** plane wave expansion coefficients $\{\tilde{u}(\vec{G})\}$ **simultaneously** exploits certain overlap in operations.

Method: Fast Fourier Transforms

Superfast and trivially parallelizable algorithm for obtaining plane waves

Implementation of Fast Fourier Transform (FFT) differs between software packages.

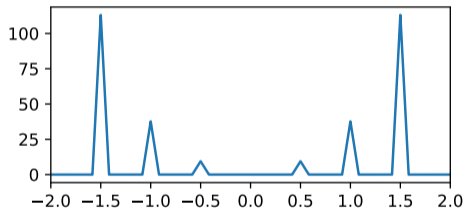
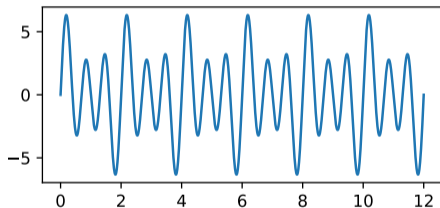
Always read the documentation! Most packages define the **inverse** DFT, in one dimension, via

$$a_m = \frac{1}{n} \sum_{k=0}^{n-1} A_k \exp\left(2\pi i \frac{mk}{n}\right)$$

Or in three dimensions, using our notation, as

$$a_{xyz} = \frac{1}{N_x N_y N_z} \sum_{\vec{G}} \tilde{a}(\vec{G}) \exp\left(i\vec{G} \cdot (x, y, z)^T\right)$$

$$y = \sin\left(2\pi \cdot \frac{1}{2}x\right) + 2 \sin(2\pi \cdot x) + 4 \sin\left(2\pi \cdot \frac{3}{2}x\right)$$



(left) Original signal; (right) FFT

The typical implementation

$$a_{xyz} = \frac{1}{N_x N_y N_z} \sum_{\vec{G}} \tilde{a}(\vec{G}) \exp \left(i\vec{G} \cdot (x, y, z)^T \right)$$

differs from our definition

$$u(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{u}(\vec{G}) \exp \left(i\vec{G} \cdot \vec{r} \right)$$

- ▶ The FFT algorithm is **agnostic** about our unit cell. It simply takes a bunch of numbers (3D-array) and spits out the corresponding expansion coefficients.
- ▶ Resulting coefficients need to be **corrected** to comply with our definition
- ▶ **Reciprocal space vectors \vec{G}** need to be established to use the plane-wave basis in further calculations.

Points

1. Sample unit cell using equidistant sampling points
2. Reformat as ordered 3D array
($z > y > x$)
3. Insert into FFT algorithm
4. Correct coefficients by factor $\frac{N_x N_y N_z}{\sqrt{\Omega}}$

\vec{G} -vectors

1. Calculate G-vectors per dimension
2. Consolidate into 3D vector field

```

1 import numpy as np
2
3 npts = 64 # number of data points per cartesian direction
4 sz = 10 # size of the cubic unit cell
5
6 c = np.linspace(0, sz, npts, endpoint=False)
7 z, y, x = np.meshgrid(c, c, c, indexing='ij')
8
9 r = np.zeros((npts,npts,npts,3))
10 r[:, :, :, 0] = x
11 r[:, :, :, 1] = y
12 r[:, :, :, 2] = z
13
14 # build Gaussian
15 r -= (5,5,5) # put Gaussian at the center
16 r2 = np.einsum('ijkl,ijkl->ijk', r, r)
17 psi = (2.0 / np.pi)**(3/4) * np.exp(-r2)
18
19 ct = np.sqrt(sz**3) / npts**3
20 psi_fft = np.fft.fftn(psi) * ct

```




```

1 def build_fft_vectors(sz, npts):
2     # calculate plane wave vector coefficients in one dimension
3     k = np.fft.fftfreq(npts) * 2.0 * np.pi * (npts / sz)
4
5     # construct plane wave vectors
6     k3, k2, k1 = np.meshgrid(k, k, k, indexing='ij')
7
8     kvec = np.zeros((npts,npts,npts,3))
9     kvec[:, :, :, 0] = k1
10    kvec[:, :, :, 1] = k2
11    kvec[:, :, :, 2] = k3
12
13    k2 = np.einsum('ijkl,ijkl->ijk', kvec, kvec)
14
15    return kvec, k2

```

⚠ Important

- ▶ From the perspective of your computer, the arrays are just chunks of number. They carry no metadata; only you can interpret them.
- ▶ The scalar fields and vectors fields are **"aligned"**. Do not change their order nor their shape.
- ▶ Stick to the "protocol" when building and working with these numerical objects.

Given a wave function ψ as expanded using the plane-wave basis set (PWBS):

$$\psi(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{\psi}(\vec{G}) \exp(i\vec{G} \cdot \vec{r})$$

We can easily evaluate the kinetic energy via

$$E_{\text{kin}} = \frac{1}{2} \sum_{\vec{G}} |\tilde{\psi}(\vec{G})|^2 \cdot |\vec{G}|^2$$

Provided

$$\psi(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{\psi}(\vec{G}) \exp(i\vec{G} \cdot \vec{r})$$

the kinetic energy can be easily derived to correspond to

$$\begin{aligned} E_{\text{kin}} &= \left\langle \psi(\vec{r}) \left| -\frac{1}{2} \nabla^2 \right| \psi(\vec{r}) \right\rangle \\ &= \frac{1}{2} \sum_{\vec{G}'} \sum_{\vec{G}} \tilde{\psi}(\vec{G}') \tilde{\psi}(\vec{G}) |\vec{G}'|^2 \langle \phi(\vec{G}') | \phi(\vec{G}) \rangle \\ &= \frac{1}{2} \sum_{\vec{G}'} \sum_{\vec{G}} \tilde{\psi}(\vec{G}') \tilde{\psi}(\vec{G}) |\vec{G}'|^2 \delta_{\vec{G}, \vec{G}'} \\ &= \frac{1}{2} \sum_{\vec{G}} |\tilde{\psi}(\vec{G})|^2 \cdot |\vec{G}|^2 \end{aligned}$$

From here on, we introduce the following notation for the FFT according to prevalent in numerical implementations

$$\tilde{\psi}(\vec{G}) = \mathcal{F} [\psi(\vec{r})]$$

and according to a conventional plane-wave basis set via

$$\tilde{\psi}\vec{G} = \mathcal{F}_{\text{pw}} [\psi(\vec{r})]$$

There also exist the inverse transforms, indicated by " $^{-1}$ ", e.g.

$$\psi(\vec{r}) = \mathcal{F}^{-1} [\tilde{\psi}(\vec{G})]$$





סניטעה ווערס

Section

Potentials

- ▶ Nucleus-electron (external potential)
- ▶ Electron-electron (Hartree potential; Classical electron-electron interactions)
- ▶ Exchange-correlation (Non-classical electron-electron interactions)

There are also nuclear-nuclear interactions, which we will treat in the next section.

An easy way to solve for a classical electrostatic potential, either electron-electron or nucleus-electron is via solving **Poisson's equation** .

$$\nabla^2 \varphi(\vec{r}) = -4\pi \rho(\vec{r})$$

ρ acts as the **charge density** , either electron density of nuclear point charges.

Suppose that

$$\rho(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{\rho}(\vec{G}) \exp(i\vec{G} \cdot \vec{r}).$$

the Poisson equation can be easily solved, yielding

$$\varphi(\vec{r}) = -\frac{4\pi}{\sqrt{\Omega}} \sum_{\vec{G}} \frac{\tilde{\rho}(\vec{G})}{|\vec{G}|^2} \exp(i\vec{G} \cdot \vec{r}).$$

The term corresponding to $\vec{G} = \vec{0}$ diverges, so we remove this term.

$$\varphi(\vec{r}) = -\frac{4\pi}{\sqrt{\Omega}} \sum_{\vec{G} \neq \vec{0}} \frac{\tilde{\rho}(\vec{G})}{|\vec{G}|^2} \exp(i\vec{G} \cdot \vec{r}).$$

This term correspond to the average charge in the unit cell. For a neutral system, this term *should* be zero. More specifically, all the divergent terms for electrostatic interactions (e-e, e-n and n-n) should cancel out.

Given an electron density, $\rho(\vec{r})$ we can thus easily construct the Hartree potential via consecutive forward and backward FFTs

$$\varphi(\vec{r}) = \mathcal{F}_{\text{pw}}^{-1} \left[+ \frac{4\pi}{|\vec{G}|^2} \mathcal{F}_{\text{pw}} [\rho(\vec{r})] \right]_{\vec{G} \neq \vec{0}} .$$

⚠ Note

Observe the “+” sign in the above equation because ρ corresponding to the electron density is negative charge.

```
1 # construct charge density
2 rho = np.power(psi,2)
3 fft_rho = np.fft.fftn(rho)
4
5 # build fft vectors
6 kvec, k2 = build_fft_vectors(sz, npts)
7
8 # build the Hartree potential in reciprocal space
9 with np.errstate(divide='ignore', invalid='ignore'):
10     fft_hartree = 4.0 * np.pi * fft_rho / k2
11     fft_hartree[~np.isfinite(fft_hartree)] = 0.0
12
13 # perform inverse FFT
14 hartree = np.fft.ifftn(fft_hartree)
```

For the nuclear attraction, the charge field are simply point charges

$$\rho_{\text{nuc}}(\vec{r}) = \sum_j q_j \delta(\vec{r} - \vec{R}_j).$$

and thus the Fourier transform has a nice analytical solution

$$\begin{aligned} \langle \phi(\vec{G}, \vec{r}) | u(\vec{r}) \rangle &= \frac{1}{\sqrt{\Omega}} \int_{\Omega} d\vec{r} \sum_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}) \cdot \delta(\vec{r} - \vec{R}_j) \\ &= \frac{1}{\sqrt{\Omega}} \exp(i\vec{G} \cdot \vec{R}_j) \end{aligned}$$

And we only need a backward transform for the nuclear potential

$$v_{\text{ext}} = -\frac{4\pi}{\sqrt{\Omega}} \mathcal{F}_{\text{pw}}^{-1} \left[\sum_{\vec{G} \neq \vec{0}} |\vec{G}|^{-2} \sum_j \exp(i\vec{G} \cdot \vec{R}_j) \right].$$

Mind the exclusion of the divergent term!

```

1 def build_external_potential(npts, sz):
2     """
3     Calculate the external potential by single nucleus with charge Z=1
4     """
5     # build fft vectors
6     kvec, k2 = build_fft_vectors(sz, npts)
7     R = (sz/2, sz/2, sz/2)
8
9     # generate structure factor and nuclear attraction field
10    sf = np.exp(-1j * kvec @ R) / np.sqrt(sz**3)
11    ct = np.sqrt(sz**3) / npts**3
12    with np.errstate(divide='ignore', invalid='ignore'):
13        nupotg = -4.0 * np.pi / k2
14        nupotg[0,0,0] = 0
15
16    vnuc = np.fft.ifftn(sf * nupotg) / ct
17
18    return vnuc

```

- ▶ Treats non-classical electron-electron interaction
- ▶ Best evaluated in real-space
- ▶ Fixed recipes available; outside the scope of this lecture
- ▶ Most simple type is **SVWN5** (LDA)
 - ▶ Slater exchange (**S**)
 - ▶ Correlation by Padé-approximant of Vosko, Wilk and Nusair, equation 5 of their paper (**VWN5**)
- ▶ Great numerical libraries readily available (**libXC**)

3,4



Section

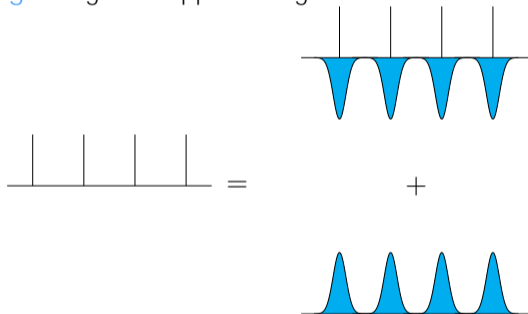
Ewald summation

In a periodic unit cell, the atoms within the cell interact with all the atoms both inside the unit cell, as well as those in neighboring super cells.

$$E_{\text{nuc-nuc}} = \frac{1}{2} \sum_i q_i \sum_{j \neq i, \vec{n}} \frac{q_j}{r_{ij} + \vec{n}},$$

This is a slowly (conditionally converging) series! The **Ewald method** tackles this.

A set of point charges (left) is the sum of a set of **screened** charges (right-top) plus a correction of **screening** charges of opposite sign.



At large distance, the contribution of **screened** charges rapidly decays.

1. A long-range contribution due to the *compensating* charge cloud: ν_{lr}
2. A short-range contribution due to the *screened* charges: ν_{sr}
3. A correction term for the on-site spurious self-interaction: ν_s
4. An electroneutrality term ν_{en}

Apologies!

In the following slides, I am going to show the derivation of these terms. You might experience “math-overload”. Just try to hang on.

The compensating charge cloud corresponds to Gaussians, thus their charge density corresponds to

$$\rho_c(\vec{r}) = \sum_j q_j \left(\frac{\alpha}{\pi}\right)^{3/2} \exp\left(-\alpha |\vec{r} - \vec{R}_j|^2\right).$$

Applying an analytical Fourier transform yields

$$\begin{aligned} \rho_c(\vec{G}) &= \frac{1}{\sqrt{\Omega}} \int_{\Omega} d\vec{r} \exp\left(-i\vec{G} \cdot \vec{r}\right) \sum_j q_j \left(\frac{\alpha}{\pi}\right)^{3/2} \exp\left(-\alpha |\vec{r} - \vec{R}_j|^2\right) \\ &= \frac{1}{\sqrt{\Omega}} \sum_j q_j \exp\left(-i\vec{G} \cdot \vec{R}_j\right) \exp\left(-\frac{|\vec{G}|^2}{4\alpha}\right) \end{aligned}$$

Solving the Poisson equation for

$$\rho_c(\vec{G}) = \frac{1}{\sqrt{\Omega}} \sum_j q_j \exp(-i\vec{G} \cdot \vec{R}_j) \exp\left(-\frac{|\vec{G}|^2}{4\alpha}\right)$$

gives

$$\nu_{\text{lr}}(\vec{G}) = \frac{4\pi}{|\vec{G}|^2 \sqrt{\Omega}} \sum_j q_j \exp(-i\vec{G} \cdot \vec{R}_j) \exp\left(-\frac{|\vec{G}|^2}{4\alpha}\right)$$

yielding the following energy contribution

$$E_{\text{lr}} = \frac{2\pi}{\Omega} \sum_{\vec{G} \neq 0} \sum_{i,j} \frac{q_i q_j}{|\vec{G}|^2} \exp\left(i\vec{G} \cdot (\vec{R}_i - \vec{R}_j)\right) \exp\left(-\frac{|\vec{G}|^2}{4\alpha}\right)$$

Ignoring any imaginary components, we can simplify the following

$$E_{\text{lr}} = \frac{2\pi}{\Omega} \sum_{\vec{G} \neq 0} \sum_{i,j} \frac{q_i q_j}{|\vec{G}|^2} \exp\left(i\vec{G} \cdot (\vec{R}_i - \vec{R}_j)\right) \exp\left(-\frac{|\vec{G}|^2}{4\alpha}\right)$$

to

$$E_{\text{lr}} = \frac{2\pi}{\Omega} \sum_{\vec{G} \neq 0} \sum_{i,j} \frac{q_i q_j}{|\vec{G}|^2} \cos\left(\vec{G} \cdot (\vec{R}_i - \vec{R}_j)\right) \exp\left(-\frac{|\vec{G}|^2}{4\alpha}\right)$$

Solving the Poisson equation for a centered Gaussian charge

$$\nabla^2 \nu_s(r) = -4\pi q_j \left(\frac{\alpha}{\pi}\right)^{3/2} \exp(-\alpha r^2)$$

yields

$$\nu_s(r) = \frac{q_i}{r} \operatorname{erf}(\sqrt{\alpha}r),$$

which evaluated at $r = 0$ gives

$$\nu_s(0) = 2q_i \sqrt{\frac{\alpha}{\pi}},$$

Interaction of

$$\nu_s(0) = 2q_i \sqrt{\frac{\alpha}{\pi}},$$

with a point charge yields the following energy term

$$\begin{aligned} E_s &= \frac{1}{2} \sum_i q_i \cdot \nu_s(0) \\ &= \sqrt{\frac{\alpha}{\pi}} \sum_i q_i^2. \end{aligned}$$

For the interaction between a point charge with the field of **screening** charges, we find - from the previous results - the following potential

$$\begin{aligned} \nu_{\text{sr}} &= \sum_j \frac{q_j}{r} - \frac{q_j}{r} \operatorname{erf}(\sqrt{\alpha}r) \\ &= \sum_j \frac{q_j}{r} \operatorname{erfc}(\sqrt{\alpha}r) \end{aligned}$$

which gives the following energy term

$$E_{\text{sr}} = \frac{1}{2} \sum_{\vec{n} \neq \vec{0}} \sum_{i \neq j} \frac{q_i q_j}{|\vec{r}_{ij} + \vec{n}|} \operatorname{erfc}(\sqrt{\alpha}|\vec{r}_{ij} + \vec{n}|)$$

Because the Ewald sum is executed for a non-neutral system, we have to reintroduce the $\tilde{\rho}(\vec{G} = \vec{0})$ term. Since

$$\rho_{\text{bg}} = \frac{\sum_i q_i}{\Omega}$$

we find that

$$\begin{aligned} E_{\text{en}} &= \frac{1}{2} \int_{\Omega} d\vec{r} \rho_{\text{bg}} \nu_{\text{sr}} \\ &= \frac{\sum_{i,j} q_i q_j}{\Omega} \int_{\Omega} d\vec{r} \frac{1}{r} \text{erfc}(\sqrt{\alpha}r) \\ &= \frac{\pi}{2\alpha\Omega} \left(\sum_i q_i \right)^2 \end{aligned}$$

In the procedure, there are two guiding parameters

- ▶ α : Width of the Gaussian, chosen such that long-range contributions by the screened charges rapidly vanish.
- ▶ E_{cut} : The number of plane waves, effectively partitions the calculation between the long- and short-range parts. A balance is sought that minimizes $\{\vec{G}\}$ and $\{\vec{n}\}$ in the equations below.

$$E_{\text{lr}} = \frac{2\pi}{\Omega} \sum_{\vec{G} \neq 0} \sum_{i,j} \frac{q_i q_j}{|\vec{G}|^2} \cos(\vec{G} \cdot (\vec{R}_i - \vec{R}_j)) \exp\left(-\frac{|\vec{G}|^2}{4\alpha}\right)$$

$$E_{\text{sr}} = \frac{1}{2} \sum_{\vec{n} \neq \vec{0}} \sum_{i \neq j} \frac{q_i q_j}{|\vec{r}_{ij} + \vec{n}|} \operatorname{erfc}(\sqrt{\alpha} |\vec{r}_{ij} + \vec{n}|)$$



Section

Self-consistent field procedure

Solving the electronic structure problem using a basis set is solving the Roothaan equations.

$$\mathbf{HC} = \mathbf{ESC}.$$

For an orthonormal basis set, this equation simplifies to

$$\mathbf{HC} = \mathbf{EC}.$$

- ▶ In localized-orbital codes, it is common practice to perform a **full diagonalization** of \mathbf{H} , yet this is infeasible in PW-codes due to the **size** of the basis set.
- ▶ Rather than full diagonalization, we seek only to find the N lowest eigenvalue-eigenvector pair for the Aufbau principle.
- ▶ As \mathbf{H} is typically a **sparse** and **diagonally dominant** matrix, very efficient routines exist.

- ▶ Very efficient method than can focus on finding lowest eigenvalue/-vector pairs.
- ▶ Does not even require full matrix \mathbf{H} , only the **result** of the operation $\vec{c}' = \mathbf{H}\vec{c}$ should be known.

$$\hat{\mathcal{H}}\tilde{\psi}(\vec{G}) = \frac{1}{2}|\vec{G}|^2 \circ \tilde{\psi}(\vec{G}) + \hat{\mathcal{F}}_{\text{pw}} \left[\hat{\mathcal{F}}_{\text{pw}}^{-1} \left[\tilde{\psi}(\vec{G}) \right] \circ \nu_{\text{eff}}(\vec{r}) \right]$$

where the effective potential is given by

$$\nu_{\text{eff}}(\vec{r}) = \nu_{\text{ext}}(\vec{r}) + \nu_U(\vec{r}) + \nu_{\text{xc}}(\vec{r}).$$

$$\hat{\mathcal{H}}\tilde{\psi}(\vec{G}) = \frac{1}{2}|\vec{G}|^2 \circ \tilde{\psi}(\vec{G}) + \hat{\mathcal{F}}_{\text{pw}} \left[\hat{\mathcal{F}}_{\text{pw}}^{-1} \left[\tilde{\psi}(\vec{G}) \right] \circ \nu_{\text{eff}}(\vec{r}) \right]$$

```
1 def matvec(psi, nu, k2):
2     return 0.5 * k2 * psi + np.fft.fftn(np.fft.ifftn(psi) * nu)
```

- ▶ Kinetic energy is evaluated in reciprocal space
- ▶ Potential is evaluated in real-space and then cast back to reciprocal space
- ▶ Answer is a vector in reciprocal space: energy contribution **per plane wave**

Suppose the lowest Kohn-Sham orbitals in the plane-wave basis set are known, we can easily form the electron density

$$\rho(\vec{r}) = 2 \sum_j^{N_{\text{elec}}/2} \left| \hat{\mathcal{F}}_{\text{pw}}^{-1} \left[\tilde{\psi}_j(\vec{G}) \right] \right|^2$$

The total electronic energy is then given by

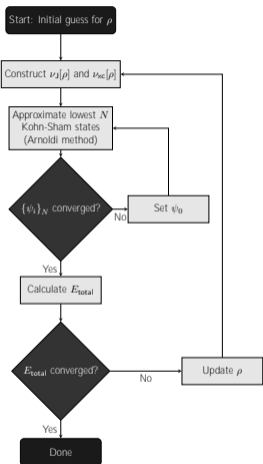
$$E_{\text{elec}} = \underbrace{\frac{1}{2} \sum_j^{N_{\text{elec}}/2} \left[\sum_{\vec{G}} |\tilde{\psi}_j(\vec{G})|^2 |\vec{G}|^2 \right]}_{\text{kinetic (reciprocal-space)}} + \underbrace{\frac{\Omega}{N} \sum_i^N \rho(\vec{r}_i) \nu_{\text{eff}}(\vec{r}_i)}_{\text{potential (real-space)}} + E_{\text{ewald}}$$

Where $\nu(\vec{r}) = \nu_{\text{ext}}(\vec{r}) + \nu_U(\vec{r}) + \nu_{xc}(\vec{r})$

$$\nu_{\text{ext}}(\vec{r}) = -\frac{4\pi}{\sqrt{\Omega}} \mathcal{F}_{\text{pw}}^{-1} \left[\sum_{\vec{G} \neq \vec{0}} |\vec{G}|^{-2} \sum_j \exp(i\vec{G} \cdot \vec{R}_j) \right]$$

$$\nu_U(\vec{r}) = \mathcal{F}_{\text{pw}}^{-1} \left[-\frac{4\pi}{|\vec{G}|^2} \mathcal{F}_{\text{pw}}[\rho(\vec{r})] \right]_{\vec{G} \neq \vec{0}} .$$

$$\nu_{xc}(\vec{r}) = -\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta \rho(\vec{r})}$$



- ▶ Because ν depends on ρ but ρ is found via ν , there is a “chicken-egg” problem which we can solve in an iterative procedure.
- ▶ Every step, ρ is refined by slowly mixing in the new solution to the old.

$$\rho \leftarrow \alpha \rho_{\text{new}} + (1 - \alpha) \rho_{\text{old}}$$

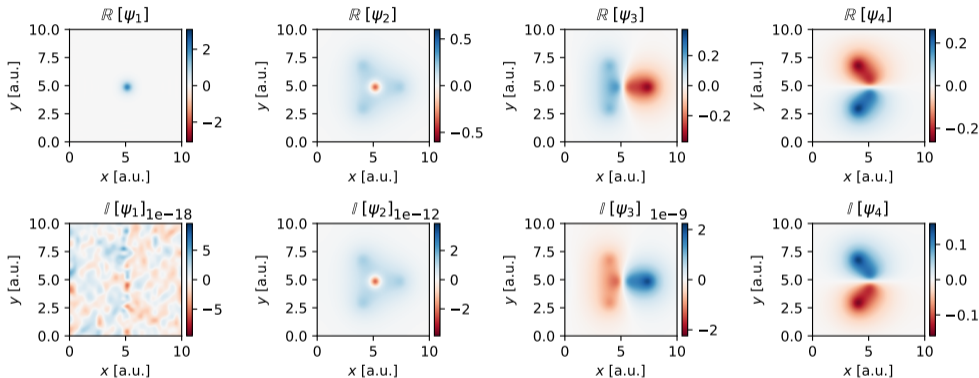
- ▶ When the calculation generates a density compliant with the field, calculation is considered converged.

- ▶ Because plane waves $\phi(\vec{r}) \in \mathbb{C}$, Kohn-Sham states are complex-valued. Orbital visualization would thus require plotting both real and imaginary parts (cumbersome).
- ▶ Solutions are unique up to a phase factor, such that

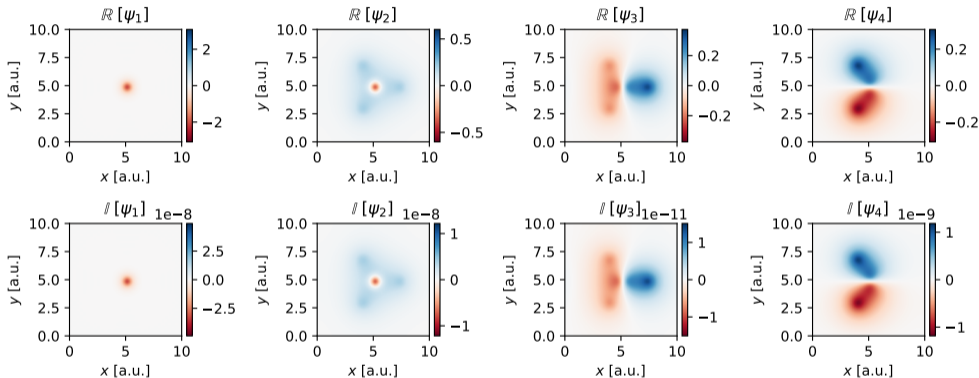
$$\psi(\vec{r})' \leftarrow \psi(\vec{r}) \cdot \exp(i\varphi)$$

- ▶ Purely for visualization purposes, we can (at least partially) cast imaginary components back to real space optimizing the following metric

$$\max_{\varphi} \left(\sum_i \mathbb{R} [\psi(\vec{r}_i) \cdot \exp(i\varphi)]^2 \right).$$



⚠ Note that ψ_4 has real and imaginary part of roughly equal size.



⚠ Note the scales for the imaginary part.

Orbital	φ (deg)	$\int_{\Omega} \mathbb{R}[\psi ^2] d\vec{r}$	$\int_{\Omega} \mathbb{R}[\psi \cdot \exp(i\varphi) ^2] d\vec{r}$
ψ_3	0.0000	1.0000	1.0000
ψ_4	31.1685	0.7321	1.0000

A rotation by a phase angle of 31 degrees ensures the ψ_4 becomes fully real-valued. Prior to the rotation, only 73% of ψ_4 resided in the real domain.

⚙️ 6,7,8