Plane Wave Density Functional Theory from Scratch

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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)

▶ Leaning by doing (exercises + workouts)

▶ Fully working educational code (PyPWDFT) to dissect

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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

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

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

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

then

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

The chance to find any of the electrons is given by

$$|\Psi\left(\vec{\mathbf{x}}_1, \vec{\mathbf{x}}_2, \cdots, \vec{\mathbf{x}}_N\right)|^2 \, \mathrm{d}\vec{\mathbf{x}}_1 \mathrm{d}\vec{\mathbf{x}}_2 \cdots \mathrm{d}\vec{\mathbf{x}}_N = |\chi_i\left(\vec{\mathbf{x}}_1\right)|^2 \, \mathrm{d}\vec{\mathbf{x}}_1 \, |\chi_j\left(\vec{\mathbf{x}}_2\right)|^2 \, \mathrm{d}\vec{\mathbf{x}}_2 \cdots |\chi_N\left(\vec{\mathbf{x}}_N\right)|^2 \, \mathrm{d}\vec{\mathbf{x}}_N$$

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!

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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.

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

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

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

▶ Satisfies anti-symmetry principle

▶ Electrons become (exchange-)correlated

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

Important

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

Inserting a Slater determinant

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

into

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

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$$E = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle = \underbrace{\sum_i^N \langle \chi_i | -\frac{1}{2}\nabla^2 | \chi_i \rangle}_{\text{kinetic energy}} + \underbrace{\sum_i^N \langle \chi_i | \sum_{A=1}^M \frac{Z_A}{r_{i,a}} | \chi_i \rangle}_{\text{nuclear attraction}} \cdots$$

$$\cdots + \frac{1}{2}\sum_i^N \sum_j^N \left[\underbrace{\langle \chi_i \chi_j | \frac{1}{r_{ij}} | \chi_i \chi_j \rangle}_{\text{coulomb repulsion}} - \underbrace{\langle \chi_i \chi_j | \frac{1}{r_{ij}} | \chi_j \chi_i \rangle}_{\text{exchange}} \right]$$

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

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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.

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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

$$E_1 < \langle \Psi_2 | \hat{\mathcal{H}}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{\mathcal{H}}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{\mathcal{H}}_1 - \hat{\mathcal{H}}_2 | \Psi_2 \rangle$$

$$= E_2 + \int \rho(\vec{r}) \left[\nu_{\text{ext},1}(\vec{r}) - \nu_{\text{ext},2}(\vec{r}) \right] \, d\vec{r}.$$

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

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

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

$$E_\nu[\rho] = \underbrace{T[\rho(\vec{r})]}_{\text{kinetic}} + \underbrace{V[\rho(\vec{r})]}_{\text{nuclear attraction}} + \underbrace{U[\rho(\vec{r})]}_{\text{electron-electron}}$$

$$= \int \rho(\vec{r})\nu_{\text{ext}}(\vec{r})d\vec{r} + F_{\text{HK}}[\rho]$$

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

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

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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 $U[\rho(\vec{r})]$.

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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

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

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

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

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

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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

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

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DFT:

$$E[\rho] = T_s[\rho] + \int v(\vec{r})\rho(\vec{r})\ d\vec{r} + J[\rho] + E_{xc}[\rho]$$

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

HF:

$$E = \langle\Psi|\hat{\mathcal{H}}|\Psi\rangle = \sum_i^N \langle\chi_i| - \frac{1}{2}\nabla^2|\chi_i\rangle + \sum_i^N \langle\chi_i|\sum_{A=1}^M \frac{Z_A}{r_{i,a}}|\chi_i\rangle \cdots$$

$$\cdots + \frac{1}{2}\sum_i^N \sum_j^N \left[\langle\chi_i\chi_j|\frac{1}{r_{ij}}|\chi_i\chi_j\rangle - \langle\chi_i\chi_j|\frac{1}{r_{ij}}|\chi_j\chi_i\rangle\right]$$

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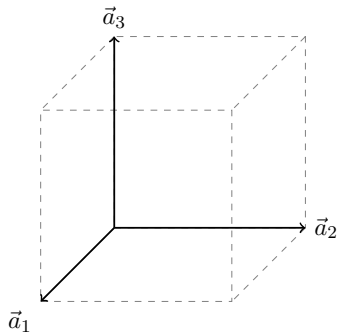Theoretical Chemistry and Spectroscopy

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Kohn-Sham method: one-electron orbitals

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

Plane waves

Unitcell matrix:

$$\mathbf{M} = \begin{pmatrix} \vec{a_1} \\ \vec{a_2} \\ \vec{a_3} \end{pmatrix}.$$

Volume:

$$\Omega = \det |\mathbf{M}| = \vec{a_1} \cdot (\vec{a_2} \times \vec{a_3})$$

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Plane wave:

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

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:

$$\vec{b_1} = 2\pi\frac{\vec{a_2} \times \vec{a_3}}{\Omega}$$

$$\vec{b_2} = 2\pi\frac{\vec{a_3} \times \vec{a_1}}{\Omega}$$

$$\vec{b_3} = 2\pi\frac{\vec{a_1} \times \vec{a_2}}{\Omega}$$

Reciprocal matrix:

$$\mathbf{B} = \begin{pmatrix} \vec{b_1} \\ \vec{b_2} \\ \vec{b_3} \end{pmatrix} = 2\pi\left(\mathbf{M}^{\mathsf{T}}\right)^{-1}$$

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$$\langle \phi(\vec{G}, \vec{r})|\phi(\vec{G}, \vec{r})\rangle = \frac{1}{\Omega} \int_{\Omega} d\vec{r} \, \exp\left(-i\vec{G}\cdot\vec{r}\right) \exp\left(+i\vec{G}\cdot\vec{r}\right)$$

$$= \frac{1}{\Omega} \int_{\Omega} d\vec{r} \, 1 = \frac{\Omega}{\Omega} = 1.$$

Observe

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

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$$\langle \phi(\vec{G}\prime, \vec{r}) | \phi(\vec{G}, \vec{r}) \rangle = \frac{1}{\Omega} \int_{\Omega} d\vec{r} \, \exp\left(-i\vec{G}\prime \cdot \vec{r}\right) \exp\left(+i\vec{G} \cdot \vec{r}\right)$$

$$= \frac{1}{\Omega} \int_{\Omega} d\vec{r} \, \exp\left(i \left(\vec{G} - \vec{G}\prime\right) \cdot \vec{r}\right)$$

$$= \delta_{\vec{G}, \vec{G}\prime}$$

👁 **Observe**

▶ $(\vec{G} - \vec{G}\prime) \cdot \vec{r}$ always corresponds to a multiple of 2π

▶ $\exp(i \cdot 2\pi \cdot n) = 0$ for $n \in \mathbb{Z}_{\neq 0}$ (recall the unit circle)

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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

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

Given

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

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

$$\langle \phi(\vec{G}\prime, \vec{r})|u(\vec{r})\rangle = \int_{\Omega} d\vec{r} \frac{1}{\Omega} \sum_{\vec{G}} \tilde{u}(\vec{G}) \exp\left(i\left(\vec{G} - \vec{G}\prime\right) \cdot \vec{r}\right)$$

$$= \sum_{\vec{G}} \tilde{u}(\vec{G}) \delta_{\vec{G},\vec{G}\prime}$$

$$= \tilde{u}(\vec{G}\prime).$$

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The equality

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

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

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

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 parallellizable algorithm for obtaining plane waves

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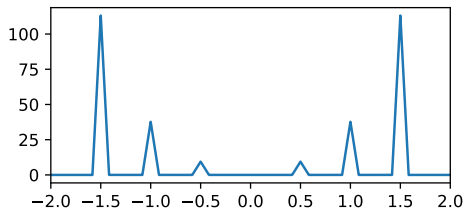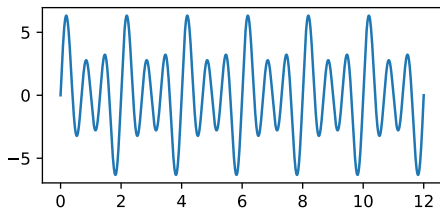Implementation of Fast Fourier Transform (FFT) differs between software packages. Always read the documentation! Most packages define the **inverse** DFT, in one dimension, via

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

Or in three dimensions, using our notation, as

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

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

(left) Original signal; (right) FFT

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The typical implementation

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

differs from our definition

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

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▶ The FFT algorithm is agnostic about our unit cell. It simply takes a a bunch of numbers (3D-array) and spits out the corresponding expansion coefficients.

▶ Resulting coefficients need to be corrected to comply with out definition

▶ Reciprocal space vectors $\vec{G}$ need to be established to use the plane-wave basis in further calculations.

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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

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```python
import numpy as np

npts = 64 # number of data points per cartesian direction
sz = 10   # size of the cubic unit cell

c = np.linspace(0, sz, npts, endpoint=False)
z, y, x = np.meshgrid(c, c, c, indexing='ij')

r = np.zeros((npts,npts,npts,3))
r[:,:,:,0] = x
r[:,:,:,1] = y
r[:,:,:,2] = z

# build Gaussian
r -= (5,5,5) # put Gaussian at the center
r2 = np.einsum('ijkl,ijkl->ijk', r, r)
psi = (2.0 / np.pi)**(3/4) * np.exp(-r2)

ct = np.sqrt(sz**3) / npts**3
psi_fft = np.fft.fftn(psi) * ct
```

```python
def build_fft_vectors(sz, npts):
    # calculate plane wave vector coefficients in one dimension
    k = np.fft.fftfreq(npts) * 2.0 * np.pi * (npts / sz)

    # construct plane wave vectors
    k3, k2, k1 = np.meshgrid(k, k, k, indexing='ij')

    kvec = np.zeros((npts,npts,npts,3))
    kvec[:,:,:,0] = k1
    kvec[:,:,:,1] = k2
    kvec[:,:,:,2] = k3

    k2 = np.einsum('ijkl,ijkl->ijk', kvec, kvec)

    return kvec, k2
```

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⚠ **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.

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

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

We can easily evaluate the kinetic energy via

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

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Provided

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

the kinetic energy can be easily derived to correspond to

$$E_{\mathsf{kin}} = \left\langle \psi(\vec{r}) \left| -\frac{1}{2}\nabla^2 \right| \psi(\vec{r}) \right\rangle$$

$$= \frac{1}{2} \sum_{\vec{G}\prime} \sum_{\vec{G}} \tilde{\psi}(\vec{G}) \tilde{\psi}(\vec{G}\prime) |\vec{G}|^2 \langle \phi(\vec{G}\prime) | \phi(\vec{G}) \rangle$$

$$= \frac{1}{2} \sum_{\vec{G}\prime} \sum_{\vec{G}} \tilde{\psi}(\vec{G}) \tilde{\psi}(\vec{G}\prime) |\vec{G}|^2 \delta_{G,G\prime}$$

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

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

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

and according to a conventional plane-wave basis set via

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

There also exist the inverse transforms, indicated by "-1", e.g.

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

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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.

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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.

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Suppose that

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

the Poisson equation can be easily solved, yielding

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

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

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

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.

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

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

⚠ Note

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

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```python
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)
```

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

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

and thus the Fourier transform has a nice analytical solution

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

$$= \frac{1}{\sqrt{\Omega}} \exp\left(i\vec{G} \cdot \vec{R}_j\right)$$

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And we only need a backward transform for the nuclear potential

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

Mind the exclusion of the divergent term!

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```python
def build_external_potential(npts, sz):
    """
    Calculate the external potential by single nucleus with charge Z=1
    """
    # build fft vectors
    kvec, k2 = build_fft_vectors(sz, npts)
    R = (sz/2, sz/2, sz/2)

    # generate structure factor and nuclear attraction field
    sf = np.exp(-1j * kvec @ R) / np.sqrt(sz**3)
    ct = np.sqrt(sz**3) / npts**3
    with np.errstate(divide='ignore', invalid='ignore'):
        nupotg = -4.0 * np.pi / k2
        nupotg[0,0,0] = 0

    vnuc = np.fft.ifftn(sf * nupotg) / ct

    return vnuc
```

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- ▶ 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`)
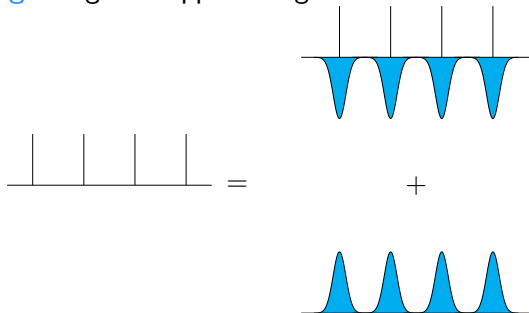- ▶ Great numerical libraries readily available (`libXC`)

⚙ 3,4

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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.

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A set of points 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.

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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.

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

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

Applying an analytical Fourier transform yields

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

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

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Solving the Poisson equation for

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

gives

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

yielding the following energy contribution

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

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Ignoring any imaginary components, we can simplify the following

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

to

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

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Solving the Poisson equation for a centered Gaussian charge

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

yields

$$\nu_{\mathsf{s}}(r) = \frac{q_i}{r} \operatorname{erf}\left(\sqrt{\alpha}\, r\right),$$

which evaluated at $r = 0$ gives

$$\nu_{\mathsf{s}}(0) = 2q_i \sqrt{\frac{\alpha}{\pi}},$$

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Interaction of

$$\nu_{\mathsf{s}}(0) = 2q_i \sqrt{\frac{\alpha}{\pi}},$$

with a point charge yields the following energy term

$$E_{\mathsf{s}} = \frac{1}{2} \sum_i q_i \cdot \nu_{\mathsf{s}}(0)$$

$$= \sqrt{\frac{\alpha}{\pi}} \sum_i q_i^2.$$

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

$$\nu_{\text{sr}} = \sum_j \frac{q_j}{r} - \frac{q_j}{r} \operatorname{erf}\left(\sqrt{\alpha}r\right)$$

$$= \sum_j \frac{q_j}{r} \operatorname{erfc}\left(\sqrt{\alpha}r\right)$$

which gives the following energy term

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

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

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

we find that

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

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.

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

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

⚙ 5

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

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

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▶ 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.

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▶ 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 $\vec{c}\prime = \mathbf{H}\vec{c}$ should be known.

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

where the effective potential is given by

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

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

```python
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

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

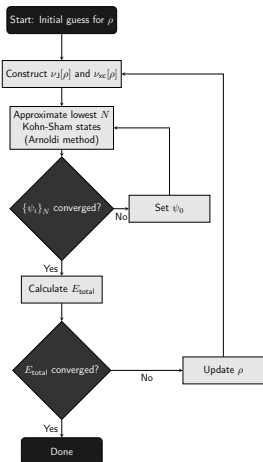The total electronic energy is then given by

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

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

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

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

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

- 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.

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- 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).
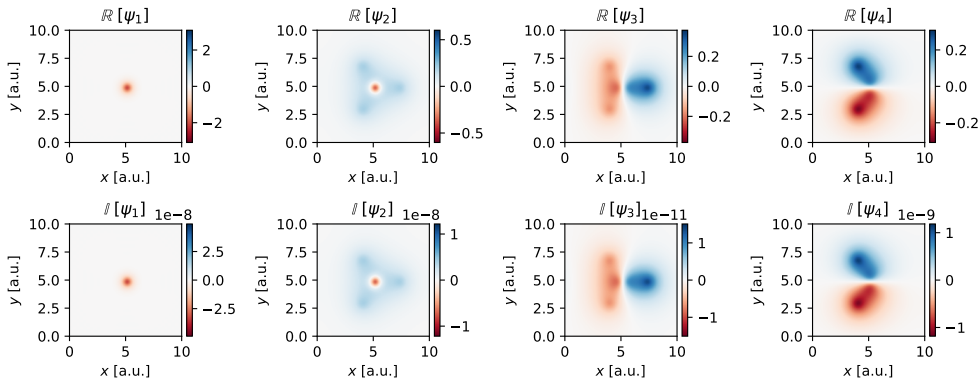
- Solutions are unique up to a phase factor, such that

$$\psi(\vec{r}) \prime \leftarrow \psi(\vec{r}) \cdot \exp\left(i\varphi\right)$$

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

$$\max_{\varphi} \left(\sum_i \mathbb{R}\left[\psi(\vec{r}_i) \cdot \exp\left(i\varphi\right)\right]^2 \right).$$
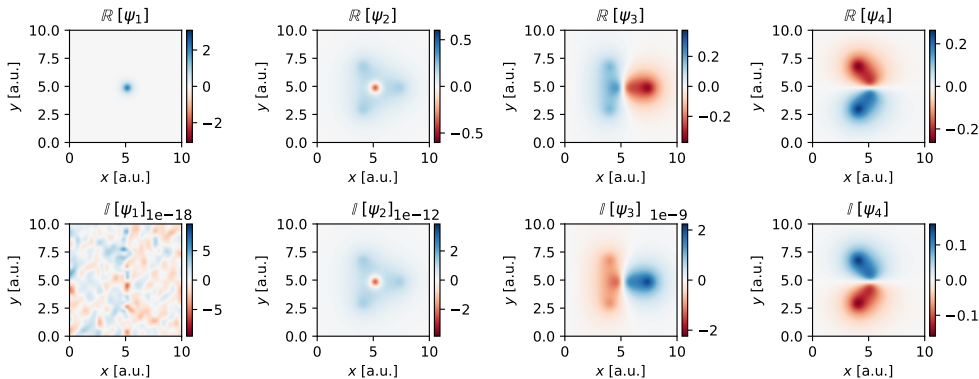
⚠ Note that ψ_4 has real and imaginary part of roughly equal size.

⚠ 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

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💬 Plane Wave Density Functional Theory from Scratch

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