

Plane Wave Density Functional Theory Exercises

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The electronic source code associated with these questions can be found at <https://github.com/ifilot/hsl-pwdf-t-exercises>. We recommend to use the Spyder IDE as provided as part of the Anaconda Software Suite. Installation instructions for Windows, MacOS and Linux can be found at <https://docs.anaconda.com/anaconda/install/>.

EXERCISE 1

The wave functions corresponding to the double degenerate 1π molecular orbitals of the CO molecule, henceforth referred to as ψ_5 and ψ_6 , are calculated at the HF/sto-3g level of theory. These wave functions are sampled in a $10 \times 10 \times 10$ a.u. cubic unit cell using 64 grid points per Cartesian direction. The corresponding scalar fields are stored as `mo5.npy` and `mo6.npy` and organized such that z is the slowest moving index and x the fastest moving index.

- a) Visualize the two molecular orbitals by producing a contour plot on the xy and xz planes for ψ_5 and ψ_6 , respectively.
- b) Show by means of Equation (1), corresponding to simple numerical integration,

$$I = \Delta V \sum_i |\psi(\vec{r}_i)|^2 \quad (1)$$

that the following properties hold:

- The two molecular orbitals are normalized in real-space.
 - The two molecular orbitals are orthogonal with respect to each other.
- c) Perform a Fourier transform on both molecular orbitals via

$$\tilde{\psi}(\vec{G}) = \mathcal{F}_{\text{pw}}[\psi(\vec{r}_i)] \quad (2)$$

and show that in reciprocal space, i.e. using the Fourier expansion coefficients, that the molecular orbitals remain orthonormal by means of Equation (3):

$$\langle \psi_i | \psi_j \rangle = \sum_{\vec{G}} \tilde{\psi}_i(\vec{G}) \cdot \tilde{\psi}_j^*(\vec{G}) \quad (3)$$

IMPORTANT Recall that the Fast Fourier Transform, such as implemented in Numpy, requires an additional ‘renormalization’ such that it complies with our expansion definition:

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

EXERCISE 2

Calculate the kinetic energy of the 1π molecular orbitals of the CO molecule in reciprocal space by means of Equation (4).

$$E_{\text{kin}} = \frac{1}{2} \sum_{\vec{G}} \tilde{\psi}(\vec{G}) \cdot \tilde{\psi}^*(\vec{G}) \cdot |\vec{G}|^2 \quad (4)$$

- Show that the result is approximately 2.0 Ht.
- Verify that both molecular orbitals yield the same kinetic energy.

IMPORTANT Ensure that the ordering of the \vec{G} -vectors in $\{\vec{G}\}$ is congruent with the definition of the specific FFT (here: `numpy.fft`) that you are using. Furthermore, similar to the scalar field in real-space, G_z should be the slowest moving index and G_x the fastest moving index. Both aspects can be achieved by first constructing the values for the \vec{G} -vectors for a given lattice vectors and then assembling these into the three-dimensional array. To construct the vector elements, one can use `numpy.fft.fftfreq`. To assemble them into a larger array, one can use `numpy.meshgrid`. Read the documentation of both these functions to ensure you understand how they work.

EXERCISE 3

Consider the normalized wave function centered at the origin as described by

$$\psi(\vec{r}) = \left(\frac{2}{\pi}\right)^{3/4} \exp(-|\vec{r}|^2). \quad (5)$$

This wave function will be sampled in a unit cell of $10 \times 10 \times 10$ a.u.

- Build a script that allows you to sample Equation (5) using a variable number of sampling points per Cartesian direction. The result should be a scalar field using the same convention as used in previous exercises (z being the slowest moving index and x the fastest moving index).
- Show that Equation (5) is indeed normalized by performing a numerical integration in real-space.
- Construct the electron density in real-space via

$$\rho(\vec{r}) = |\psi(\vec{r})|^2 \quad (6)$$

and determine its discretized Fourier transform via

$$\tilde{\rho}(\vec{G}) = \mathcal{F}[\rho(\vec{r})]. \quad (7)$$

No renormalization is required in this case.

d) Calculate the Hartree potential in reciprocal space by performing. Set $\tilde{\varphi}(\vec{G} = \vec{0}) = 0$. Appropriately handle or avoid the division by zero in Python.

$$\tilde{\varphi}(\vec{G}) = \frac{4\pi}{|\vec{G}|^2} \tilde{\rho}(\vec{G}), \quad \vec{G} \neq \vec{0} \quad (8)$$

e) Construct the Hartree potential in real-space by performing the inverse FFT

$$\varphi(\vec{r}) = \mathcal{F}^{-1} \left[\frac{4\pi}{|\vec{G}|^2} \tilde{\rho}(\vec{G}) \right]_{\vec{G} \neq \vec{0}} \quad (9)$$

and use the result to calculate the electron-electron repulsion energy in real-space via numerical integration

$$E_{e-e} = \Delta V \sum_i \varphi(\vec{r}_i) \rho(\vec{r}_i). \quad (10)$$

Compare your results to the analytical result of $2/\sqrt{\pi}$ and explore how well the procedure matches this result with increasing number of sampling points per Cartesian direction.

NOTE Please do not be disturbed if the value found is significantly different from $2/\sqrt{\pi}$, we are going to fix upon that in the next exercise. The reason for the difference is because the $\vec{G} = \vec{0}$ term is discarded.

EXERCISE 4

a) Construct the nuclear attraction potential, i.e. the external potential, due to a positive charge $Z = 1$ located at the center of a $10 \times 10 \times 10$ a.u. unitcell by means of solving the Poisson equation. Use the fact that the Fourier Transform of a point charge has an exact solution to your advantage by utilizing

$$\tilde{\rho}_{\text{nuc}}(\vec{G}) = \frac{1}{\sqrt{\Omega}} \exp(i\vec{G} \cdot \vec{R}) \quad (11)$$

where \vec{R} is the position of the point charge.

b) Calculate the sum of the electron-electron repulsion and the nuclear attraction of a Gaussian charge as provided by Equation (5) via

$$E = \Delta V \sum_i [\varphi(\vec{r}_i) + \nu_{\text{ext}}(\vec{r}_i)] \rho(\vec{r}_i). \quad (12)$$

and compare it to the analytical value of

$$E_{\text{analytical}} = \frac{2(1 - \sqrt{2})}{\sqrt{\pi}}. \quad (13)$$

EXERCISE 5

a) Produce the Ewald sum of a CO molecule positioned in a cubic unit cell with dimensions $10 \times 10 \times 10$ a.u. with the following coordinates for C and O:

$$\begin{aligned}\vec{r}_C &= (5.0000, 5.0000, 3.7097) \\ \vec{r}_O &= (5.0000, 5.0000, 5.9677)\end{aligned}$$

Show that the result is approximately -6 Ht. Please do not be disturbed that the result is negative. This is due to the exclusion of the divergent $\vec{G} = \vec{0}$ term in the long-range interaction.

b) Determine the effect of E_{cut} on the number of neighboring unit cells and the number of plane waves for the short-range and long-range sampling and consequently, the total computational time. At which value is the optimal computation time found and how does it compare to the “default” value of $E_{\text{cut}} = 2$? Test between $0.5 \leq E_{\text{cut}} \leq 6$ Ht.

EXERCISE 6

a) In the file `ch4_orbs.npy` the occupied molecular orbitals of CH_4 are stored using a plane wave basis set. These molecular orbitals are calculated using a $10 \times 10 \times 10$ a.u. unit cell using 32 sampling points per Cartesian direction. The atomic coordinates are listed below.

$$\begin{aligned}\vec{r}_C &= (5.0000, 5.0000, 3.7097) \\ \vec{r}_{\text{H}_1} &= (6.1958, 6.1958, 6.1958) \\ \vec{r}_{\text{H}_2} &= (3.8042, 3.8042, 6.1958) \\ \vec{r}_{\text{H}_3} &= (3.8042, 6.1958, 3.8042) \\ \vec{r}_{\text{H}_4} &= (6.1958, 3.8042, 3.8042)\end{aligned}$$

Calculate the total kinetic energy of the electrons in the CH_4 molecule and verify that it corresponds (approximately) to $E_{\text{kin}} = 31.9192$ Ht.

b) Construct the electron density ρ on the basis of the occupied molecular orbitals. Verify that the total number of electrons corresponds (within numerical approximation) to $N_{\text{elec}} = 10$ and calculate the electron-electron repulsion energy, the nuclear attraction energy and the exchange-correlation energy. Show that the energy terms correspond to $E_{e-e} = 19.0539$ Ht, $E_{\text{nuc}} = -81.7603$ Ht, and $E_{\text{xc}} = -6.4763$ Ht.

c) Calculate the nuclear-nuclear repulsion energy by means of the Ewald sum and add all energy terms together. Show that the total electronic energy corresponds to $E_{\text{tot}} = -37.7446$ Ht.

EXERCISE 7

The file `co_fock.npy` contains the Fock matrix for a localized-orbital calculation of the CO molecule. Calculate the molecular orbital energies for the occupied molecular orbitals of CO, i.e. its first 7 orbitals, using the Arnoldi method via the function `scipy.sparse.linalg.eigsh`. Compare the result with a full canonical matrix diagonalization using `numpy.linalg.eigh`.

NOTE For `scipy.sparse.linalg.eigsh`, ensure you set `which='SA'` and `k=7` to ensure that the algorithm searches for the 7 lowest eigenvalues.

EXERCISE 8

- a) Perform a plane wave density functional theory calculation of the BH_3 molecule using the program PyPWDFT. Visualize its molecular orbitals. Note that the molecular orbitals are complex scalar fields and you need to visualize both the real and the complex part.
- b) Perform a phase transformation such that the molecular orbitals become real-valued. Convince yourself the operation has not modified the kinetic energy of the molecular orbitals, nor has impaired upon the orthonormality of the Kohn-Sham states.