Quick introduction to quantum many-body problems via Analysis of Atomic Ground States

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Preface

This note was created to introduce the basics of mean-field theory and density functional theory. Although it was primarily prepared for students conducting their graduation research in the Sato Group at the Department of Physics, Graduate School of Science, Tohoku University, I hope it will be useful for anyone interested in quantum many-body problems. Using atoms as examples of many-electron systems, this note reviews perturbation theory and the variational method while explaining the foundations of quantum many-body theory for fermionic systems. Additionally, through the development of computational codes to investigate the ground states of quantum systems such as the hydrogen atom, helium atom, and heavier atoms, this note aims to deepen understanding of each theory and provide opportunities to review and practice fundamental skills in numerical computation and programming used in actual research. The content is designed to be accessible to those with basic knowledge of quantum mechanics, numerical computation, and programming.

Please note that the content covered in this note is limited to the very basics of quantum many-body theory and is not sufficient in scope or depth for conducting research at the graduate level or beyond. For those interested in research beyond the graduate level, it is recommended to study reputable textbooks and academic papers in detail.

This note is also a draft version and is subject to ongoing updates. Please refer to the latest version of the note at the URL below.

`https://shunsuke-sato.github.io/page/etc/lecture_notes/LectureNoteForAtomDFT_en.pdf`

1 Introduction: Atomic ground state energy and ionization potential

In this note, as an introduction to the quantum many-body problem, we address the ground state of atoms and explain several approximation methods and numerical analysis techniques. An atom is a quantum many-body system in which negatively charged electrons are bound to a positively charged nucleus. To rigorously consider the ground state of an atom, one must account not only for the motion of the electrons within the atom but also for the motion of the nucleus. However, in this note, the nucleus is treated as a fixed point charge located at a point in space. This treatment is justified by the fact that the mass of the nucleus is sufficiently larger than that of the electrons. Under this approximation, the problem of determining the ground state of an atom reduces to the problem of determining the ground state of a multi-electron system under the potential created by a point charge. Therefore, the quantum many-body system treated in this note is a quantum many-body system of electrons, which are fermions.

Before investigating the ground state of atoms, let us reconsider the energy of the atomic ground state. Consider the Hamiltonian of an atom given as follows:

$$H = \sum_{j}^{N} \left[\frac{\boldsymbol{p}_j^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r_j} \right] + \sum_{j>i} \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\boldsymbol{r}_j - \boldsymbol{r}_i|}, \tag{1}$$

where N is the number of electrons, $\boldsymbol{r}_j$ is the position, $\boldsymbol{p}_j$ is the momentum of the electron, and Z represents the atomic number of the nucleus. Let us denote the ground state energy of this Hamiltonian as $E_{\mathrm{gs}}(Z, N)$. In particular, for a neutral atom, we have $N = Z$.

Let us consider removing one electron from the ground state of a neutral atom with atomic number Z. After removing one electron, the original atom separates into two subsystems: a singly charged ion of the original atom and a single electron. If this operation is performed with the minimum necessary energy, each subsystem should attain its minimum possible energy. The minimum energy of the singly charged ion is the ground state energy of that electron many-body system, which can be expressed as $E_{\mathrm{gs}}(Z, Z-1)$ using the notation introduced earlier. The minimum energy of the separated electron is zero. Therefore, the minimum energy required to remove one electron from a neutral atom of atomic number Z is given by

$$\mathrm{IP}_{\mathrm{1st}} = E_{\mathrm{gs}}(Z, Z-1) - E_{\mathrm{gs}}(Z, Z). \tag{2}$$

At this point, $\mathrm{IP}_{\mathrm{1st}}$ is called the first ionization potential.

Similarly, the minimum energy required to further remove an electron from a singly charged ion is called the second ionization potential, and it is given by

$$\mathrm{IP}_{\mathrm{2nd}} = E_{\mathrm{gs}}(Z, Z-2) - E_{\mathrm{gs}}(Z, Z-1). \tag{3}$$

In general, the minimum energy required to remove an electron from an $(N-1)$-times charged ion is called the Nth ionization potential, and it is given by

$$\mathrm{IP}_{N\mathrm{th}} = E_{\mathrm{gs}}(Z, Z-N) - E_{\mathrm{gs}}(Z, Z-N+1). \tag{4}$$

Next, let us consider the process of removing electrons one by one from a neutral atom with atomic number Z, until all the electrons and the nucleus are separated. If a charge-neutral atom is decomposed into electrons and a bare nucleus with the minimum required energy, then the energy of each subsystem after the decomposition becomes zero, and the total energy of the whole system becomes zero. Corresponding to this operation, by considering the sum of the ionization potentials from the first to the Zth, we find the following relation:

$$\begin{aligned}
\mathrm{IP}_{\mathrm{1st}} + \mathrm{IP}_{\mathrm{2nd}} + \cdots + \mathrm{IP}_{Z\mathrm{th}} =& \left(E_{\mathrm{gs}}(Z, Z-1) - E_{\mathrm{gs}}(Z, Z)\right) \\
&+ \left(E_{\mathrm{gs}}(Z, Z-2) - E_{\mathrm{gs}}(Z, Z-1)\right) + \cdots \\
&+ \left(0 - E_{\mathrm{gs}}(Z, 1)\right) \\
=& - E_{\mathrm{gs}}(Z, Z).
\end{aligned} \tag{5}$$

Therefore, it is found that the sum of the ionization potentials from the first to the Zth is equal to the negative of the ground state energy of the neutral atom. In this way, the ground state energy of an atom can be experimentally determined by measuring its ionization potentials. Furthermore, from the above discussion, the negative of the ground state energy is equal to the minimum energy required to decompose the atom into electrons and nucleus, and is sometimes referred to as the *binding energy*.

In this note, we will investigate the ground state energy of electronic many-body systems in the situation where the nucleus with atomic number Z is fixed at the origin. As an advanced form of such a problem, the analysis of determining the ground state of an electronic many-body system under a given nuclear configuration, such as in molecules and solids, is one of the fundamental analytical methods for investigating the properties of matter around us and remains a highly important problem in the fields of condensed matter physics and quantum chemistry. Although this note mainly deals with electronic many-body systems, the methods explained here are also important in nuclear physics, which studies the motion of nucleons (protons and neutrons) within nuclei, where the spatial, temporal, and energy scales are vastly different.

2 Hydrogen atom

2.1 Analytical solution of hydrogen-like atoms

Before looking into the many-body problem, let us first review the Schrödinger equation for the one-body problem of hydrogen-like atoms[1]. Consider a system where a nucleus with atomic number Z is fixed at the origin, and a single electron moves around it. The Hamiltonian of this system is given by:

$$H = \frac{\boldsymbol{p}^2}{2m_e} - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r}. \tag{6}$$

The Schrödinger equation in coordinate representation corresponding to this Hamiltonian is

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r}\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}). \tag{7}$$

By expressing this Schrödinger equation in spherical coordinates, we obtain the following equation:

$$\begin{aligned}&\left[-\frac{\hbar^2}{2m_e}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}\right]\psi(r,\theta,\phi)\\ &= \left[-\frac{\hbar^2}{2m_e}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right\} + \frac{\boldsymbol{L}^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}\right]\psi(r,\theta,\phi) = E\psi(r,\theta,\phi). \end{aligned}\tag{8}$$

Here, the angular momentum operator $\boldsymbol{L}$ and its square are given by:

$$\boldsymbol{L} = \boldsymbol{r}\times\boldsymbol{p}, \tag{9}$$

$$\boldsymbol{L}^2 = \boldsymbol{L}\cdot\boldsymbol{L} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{10}$$

The spherical harmonics, $Y_{lm}(\theta,\phi)$, are eigenfunctions of $\boldsymbol{L}^2$ and satisfy the following equation:

$$\boldsymbol{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1)Y_{lm}(\theta,\phi). \tag{11}$$

Here, l is the azimuthal quantum number and is a non-negative integer.

Considering the separation of variables using the spherical harmonics $Y_{lm}(\theta,\phi)$,

$$\psi(r,\theta,\phi) = \frac{\chi_l(r)}{r}Y_{lm}(\theta,\phi). \tag{12}$$

Then, we find that the radial wave function $\chi_l(r)$ satisfies the following equation:

$$\left[-\frac{\hbar^2}{2m_e}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2m_e}\frac{1}{r^2} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}\right]\chi_l(r) = E\chi_l(r). \tag{13}$$

Furthermore, the radial wave function $\chi_l(r)$ satisfies the following boundary conditions:

$$\lim_{r\to 0}\chi_l(r) = \lim_{r\to\infty}\chi_l(r) = 0. \tag{14}$$

Eq. (13) for hydrogen-like atoms can be solved analytically. For example, the wave function of the ground state $1s$ orbital of a hydrogen-like atom can be written as

$$\phi_{1s}(\boldsymbol{r}) = \sqrt{\frac{Z^3}{a_0^3}}\cdot 2e^{-Zr/a_0}\frac{1}{\sqrt{4\pi}}. \tag{15}$$

Here, a_0 is the Bohr radius defined by

$$a_0 = \frac{4\pi\varepsilon_0}{e^2}\frac{\hbar^2}{m_e}. \tag{16}$$

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[1] This problem is explained in detail in standard quantum mechanics textbooks.

2.2 Numerical calculation of hydrogen-like atoms

Before investigating the ground state of atoms as quantum many-body systems, we will explain how to numerically solve the problem of hydrogen-like atoms as a one-body problem. The numerical methods discussed here are also used in the study of helium atoms and heavier atoms.

2.2.1 Non-dimensionalization of the equation and atomic units

Before proceeding to the actual numerical calculations, we derive a form of the equation suitable for numerical computations that does not explicitly include physical constants by non-dimensionalizing the equation to be solved. For this purpose, consider the following variable transformation applied to the Schrödinger equation for the hydrogen atom [Eq. (7)].

$$\boldsymbol{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = a_0 \begin{pmatrix} \xi \\ \eta \\ \zeta \end{pmatrix} = a_0 \boldsymbol{s}. \tag{17}$$

Here, a_0 is a quantity with the dimension of length, and its magnitude will be determined later. Also, $\boldsymbol{s}$ is a dimensionless quantity. For convenience later, we define the gradient and Laplacian with respect to the vector variable $\boldsymbol{s}$ as follows.

$$\boldsymbol{\nabla}_{\boldsymbol{s}} = \begin{pmatrix} \frac{\partial}{\partial \xi} \\ \frac{\partial}{\partial \eta} \\ \frac{\partial}{\partial \zeta} \end{pmatrix}, \tag{18}$$

$$\nabla_{\boldsymbol{s}}^2 = \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \zeta^2}. \tag{19}$$

By performing this type of variable transformation, the Schrödinger equation can be rewritten as follows:

$$\left[-\frac{\hbar^2}{2m_e} \frac{1}{a_0^2} \nabla_{\boldsymbol{s}}^2 - \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{a_0 |\boldsymbol{s}|} \right] \psi(\boldsymbol{s}) = E\psi(\boldsymbol{s}). \tag{20}$$

Furthermore, by dividing both sides by $\hbar^2/m_e a_0^2$, we obtain the following equation:

$$\left[-\frac{1}{2} \nabla_{\boldsymbol{s}}^2 - \frac{Ze^2}{4\pi\varepsilon_0} \frac{a_0 m_e}{\hbar^2} \frac{1}{|\boldsymbol{s}|} \right] \psi(\boldsymbol{s}) = \frac{m_e a_0^2}{\hbar^2} E\psi(\boldsymbol{s}). \tag{21}$$

Let us define a_0 as

$$a_0 = \frac{4\pi\varepsilon_0}{e^2} \frac{\hbar^2}{m_e}, \tag{22}$$

and furthermore, let us introduce a dimensionless quantity ε as follows:

$$E = \frac{\hbar^2}{m_e a_0^2} \varepsilon = \frac{m_e}{\hbar^2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 \varepsilon = E_H \varepsilon. \tag{23}$$

Here, a constant E_H with the dimension of energy is introduced as follows:

$$E_H = \frac{\hbar^2}{m_e a_0^2} = \frac{m_e}{\hbar^2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2. \tag{24}$$

By using such variables, Eq. (7) can be rewritten as follows:

$$\left[-\frac{1}{2} \nabla_{\boldsymbol{s}}^2 - \frac{Z}{|\boldsymbol{s}|} \right] \psi(\boldsymbol{s}) = \varepsilon \psi(\boldsymbol{s}). \tag{25}$$

Eq. (25) is a dimensionless equation that explicitly contains no physical constants, making it convenient for creating programs to perform numerical computations.

The quantity a_0 introduced through Eq. (22) during the process of nondimensionalization is nothing but the Bohr radius defined in Eq. (16). Furthermore, by multiplying the dimensionless eigenvalue ε by the constant E_H, one can obtain the energy eigenvalues of the Schrödinger equation. The quantity E_H, which has the dimension of energy, is called the Hartree energy unit and has a value of approximately $E_H \approx 27.2114$ eV. When analyzing dimensionless equations such as Eq. (25) numerically and comparing the obtained results with experiments, it is necessary to convert the results into quantities with dimensions and units comparable to experimental values by multiplying them by the Bohr radius a_0 or the Hartree energy unit E_H.

Similar to the nondimensionalization of equations as described above, another method for obtaining equations suitable for numerical computation that do not explicitly contain physical constants is to adopt the **atomic unit** system. Specifically, a unit system is adopted in which the magnitudes of the following physical constants are set to 1:

$$\hbar = 1 \text{ a.u.} \tag{26}$$

$$m_e = 1 \text{ a.u.} \tag{27}$$

$$e = 1 \text{ a.u.} \tag{28}$$

$$\frac{1}{4\pi\varepsilon_0} = 1 \text{ a.u.} \tag{29}$$

Here, a.u. represents atomic units and indicates appropriate dimensional units in the atomic unit system. For example, a length of 1 a.u. corresponds to the Bohr radius ($a_0 \approx 0.529$ Å). By adopting such a unit system, equation (7) can be expressed as follows:

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{|\boldsymbol{r}|}\right]\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r}). \tag{30}$$

Eq. (30) and Eq. (25) are equivalent except for the presence or absence of dimensions, and many software packages adopt this notation using the atomic unit system.

Also, when the radial Schrödinger equation [Eq. (13)] is expressed using the atomic unit system, the following equation is obtained:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2}\frac{1}{r^2} - \frac{Z}{r}\right]\chi_l(r) = E\chi_l(r). \tag{31}$$

In the following, we will explain how to numerically solve Eq. (31) using the atomic unit system.

2.2.2 Finite difference method

To numerically solve differential equations, let us utilize the finite difference approximation of a derivative. For a function $f(x)$ and a small quantity Δx, consider the following Taylor expansion:

$$f(x+\Delta x) = f(x) + \frac{df(x)}{dx}\Delta x + \frac{1}{2}\frac{d^2 f(x)}{dx^2}\Delta x^2 + \frac{1}{6}\frac{d^3 f(x)}{dx^3}\Delta x^3 + \mathcal{O}(\Delta x^4). \tag{32}$$

Here, $\mathcal{O}(\Delta x^4)$ denotes the terms of order Δx^4 and higher. From this Taylor expansion, we can derive the following relation:

$$\frac{f(x+\Delta x) - f(x)}{\Delta x} = \frac{df(x)}{dx} + \mathcal{O}(\Delta x) \tag{33}$$

From this, we can evaluate the derivative of the function $f(x)$ using the formula on the left-hand side, and the error is proportional to Δx. This kind of difference formula is called the forward difference formula.

Using Eq. (32), we can construct the following relation:

$$f(x+\Delta x) - f(x-\Delta x) = 2\frac{df(x)}{dx}\Delta x + \mathcal{O}(\Delta x^3). \tag{34}$$

Furthermore, by dividing both sides by $2\Delta x$, we can derive the following finite difference approximation formula:

$$\frac{f(x+\Delta x) - f(x-\Delta x)}{2\Delta x} = \frac{df(x)}{dx} + \mathcal{O}(\Delta x^2). \tag{35}$$

This type of difference formula is called the central difference formula, and its error is known to be proportional to Δx^2.

Whereas the error in the forward difference formula of Eq. (33) is proportional to Δx, the error in the central difference formula of Eq. (35) is proportional to Δx^2. Hence, the error of the central difference approximation approaches zero more rapidly in the limit as Δx becomes smaller.

By performing a similar analysis, we can construct the following difference formula for the second derivative:

$$\frac{f(x+\Delta x) - 2f(x) + f(x-\Delta x)}{\Delta x^2} = \frac{d^2 f(x)}{dx^2} + \mathcal{O}(\Delta x^2). \tag{36}$$

2.2.3 Shooting Method

We will discuss how to numerically solve the radial Schrödinger equation for hydrogen-like atoms [Eq. (31)] under the boundary conditions [Eq. (14)]. There are several numerical methods for solving such problems, but here we will explain the numerical solution using the shooting method. First, let us consider the discretization of the radial coordinate r with intervals of Δr. If the origin is taken as the 0-th point, the coordinate r_j of the j-th point is given by

$$r_j = \Delta r \times j. \tag{37}$$

Using these discretized coordinates r_j, we aim to rewrite the Schrödinger equation. Specifically, assuming that the width Δr is sufficiently small and using the finite difference formula of Eq. (36), Eq. (31) can be approximated as follows:

$$-\frac{1}{2}\frac{\chi(r_{j+1}) - 2\chi(r_j) + \chi(r_{j-1})}{\Delta r^2} + \left[\frac{l(l+1)}{2}\frac{1}{r_j^2} - \frac{Z}{r_j}\right]\chi_l(r_j) = E\chi_l(r_j). \tag{38}$$

Furthermore, this equation can be rewritten as:

$$\chi(r_{j+1}) = 2\chi(r_j) - \chi(r_{j-1}) - 2\Delta r^2\left[E - \frac{l(l+1)}{2}\frac{1}{r_j^2} + \frac{Z}{r_j}\right]\chi_l(r_j). \tag{39}$$

Here, the left-hand side represents the wave function $\chi_l(r_{j+1})$ at the $(j+1)$-th point, and the right-hand side involves only the wave functions $\chi_l(r_j)$ and $\chi_l(r_{j-1})$ at the j-th and $(j-1)$-th points. Therefore, it can be seen that this is a recurrence formula where the wave function values at successive points can be sequentially determined once the values at two neighboring points are known.

From the boundary condition [Eq. (14)], the wave function must be zero at the origin. That is, the wave function at the 0-th point ($r_0 = 0$) must satisfy $\chi_l(r_0) = 0$. Moreover, since multiplying the entire wave function by a constant does not change the represented quantum state, the value of the wave function at the 1st point ($r_1 = \Delta r$) can be chosen arbitrarily. For computational convenience, let us assign the values of the wave function at the 0-th and 1st points as follows:

$$\chi_l(r_0) = \chi_l(0) = 0, \tag{40}$$

$$\chi_l(r_1) = \chi_l(\Delta r) = \Delta r. \tag{41}$$

Once the wave function values at the 0-th and 1st points are specified, the recurrence formula [Eq. (39)] can be used to sequentially determine the wave function values at points from the 2nd onward.

To investigate the properties of the recurrence formula in Eq. (39), let us explicitly evaluate the recurrence starting from the initial values given in Eq. (40) and Eq. (41). Here, we will consider the s orbital of the hydrogen atom by setting $l = 0$ and $Z = 1$. Also, we set the step size Δr of the recurrence formula to 0.01 Bohr. We will evaluate the recurrence formula for four energy values in Eq. (39): -0.503, -0.501, -0.499, -0.497 Hartree.

To assist in writing your own program, a Python code evaluating the recurrence formula in Eq. (39) under the above settings is provided in Source Code 1.

`https://github.com/shunsuke-sato/python_qe/blob/develop/note_atom_dft/src/shooting_example.py`

Source code 1: Code to examine the shooting method

```python
import numpy as np
import matplotlib.pyplot as plt

# Define grid
radius = 20.0
num_grid = 2000
dr = radius / num_grid

rj = np.linspace(0.0, radius, num_grid)

# Define energy values
energy = np.array([-0.497, -0.499, -0.501, -0.503])
num_energy = energy.size

# Initialize chi array
chi = np.zeros((num_grid, num_energy))
chi[0, :] = 0.0
chi[1, :] = dr

# Compute wavefunction using finite difference method
factor = 2 * dr**2
for j in range(1, num_grid - 1):
    chi[j + 1, :] = (
        2 * chi[j, :]
        - chi[j - 1, :]
        - factor * (energy[:] + 1.0 / rj[j]) * chi[j, :]
    )

# Plot results
plt.figure(figsize=(8, 6))
for i, E in enumerate(energy):
    plt.plot(rj, chi[:, i], label=f"E={E:.3f}␣a.u.")

plt.xlim(0.0, 10.0)
plt.ylim(-1.5, 1.5)
plt.xlabel("Radius␣(Bohr)")
plt.ylabel(r"$\chi␣(r)$")
plt.title("Shooting␣Method␣Example")
plt.legend()
plt.grid()
plt.tight_layout()

# Save and show the figure
plt.savefig("shooting_example.pdf", dpi=300)
plt.show()
```

Figure 1 shows the wave function $\chi_l(r)$ obtained by explicitly evaluating the recurrence relation of Eq. (39), using the source code 1. When the energy E is set to -0.503 or -0.501 Hartree, it can be observed that the wave function diverges in the positive direction while remaining positive throughout the entire investigated range. In contrast, when the energy E is set to -0.499 or -0.497 Hartree, the wave function changes sign once and then diverges in the negative direction. From this, it can be expected that there is a point between $E = -0.499$ Hartree and $E = -0.501$ Hartree at which the number of sign changes in the wave function varies, and the sign of divergence switches.

The true eigenwave function to be found must satisfy the boundary condition [Eq. (14)], requiring it to approach zero at large distances ($r \to \infty$). From Fig. 1, it can be expected that the energy eigenvalue E of a wave function satisfying such a boundary condition lies between -0.499 Hartree and -0.501 Hartree. In fact, the ground state (1s state) energy the hydrogen atom is $E = -0.5$ Hartree. In this way, by varying the value of the energy E and searching for the wave function that satisfies the imposed boundary condition, the eigenvalue problem can be solved. This method is called the **shooting method**. The meaning of its name should be apparent from the process of finding the eigenvalue.

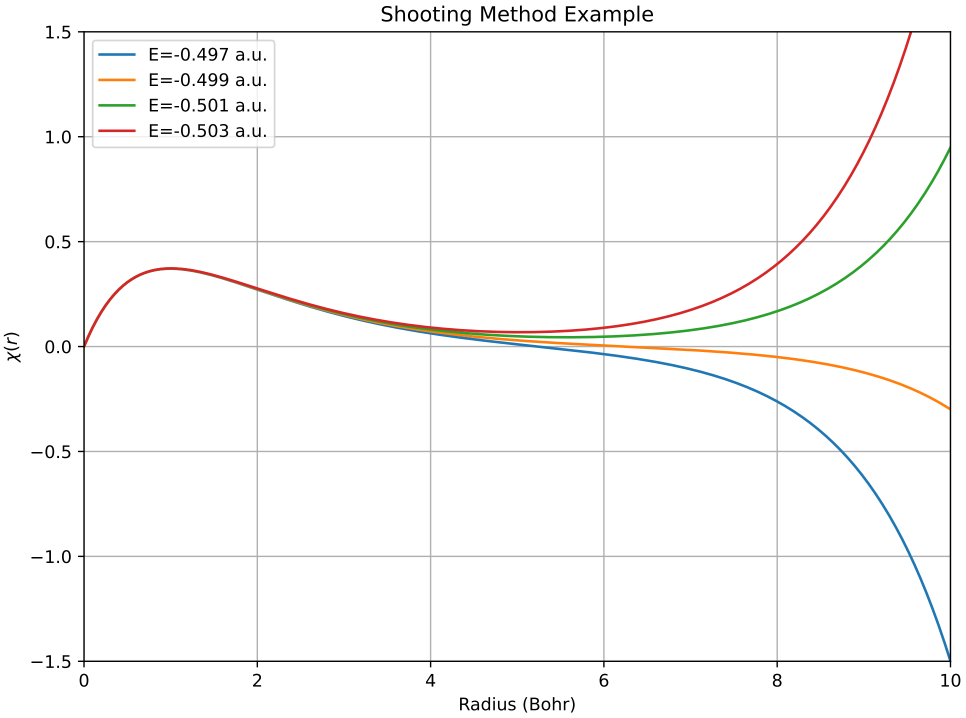

Figure 1: Process of determining the eigenvalue of the hydrogen atom ground state using the shooting method.

From here, we explain in detail how to solve the radial Schrödinger equation using the shooting method. The exact boundary condition for the eigenvalue problem to be solved [Eq. (14)] was that the wavefunction should vanish at infinity. However, it is not easy to handle infinity numerically. Therefore, we replace the point at infinity with a sufficiently distant point R_p and impose the boundary condition [$\chi_l(R_p) = 0$], meaning the wavefunction vanishes at distance R_p, instead of at infinity. Whether R_p is sufficiently large can be confirmed by checking that increasing R_p further does not change the results of numerical calculations (**convergence check**).

Moreover, it is actually not easy to directly find the energy eigenvalue E that satisfies the boundary condition [$\chi_l(R_p) = 0$] using the shooting method. This is because even a slight change in energy E can cause a significant change in the value of $\chi_l(R_p)$ obtained through the recurrence relation [Eq. (39)].

To avoid such problems, instead of focusing on the value of the wavefunction $\chi_l(R_p)$ at $r = R_p$, one can focus on the number of sign changes (nodes) of the wavefunction $\chi_l(r)$ in the region ($0 \leq r \leq R_p$). For example, from Fig. 1, the wavefunction changes sign 0 times for energy $E = -0.501$ Hartree, and 1 time for energy $E = -0.499$ Hartree. Therefore, we can see that the energy E for which the number of sign changes in the region ($0 \leq r \leq 10$ Bohr) changes lies in the range -0.501 a.u. $\leq E \leq -0.499$ a.u.. In this way, one can efficiently determine the energy eigenvalue by using methods such as bisection search to find the energy where the number of sign changes changes. The wavefunction belonging to the lowest eigenvalue has no nodes (no sign change), so the energy E where the number of nodes changes from 0 to 1 is the energy eigenvalue of that wavefunction. Similarly, the energy where the number of nodes changes from 1 to 2 corresponds to the energy eigenvalue of the first excited state, and the energy where the number of nodes changes from 2 to 3 corresponds to the energy eigenvalue of the second excited state.

While the wavefunction can be obtained using the method described above, it is often convenient to normalize the obtained wavefunction. The wavefunction in three-dimensional space satisfies the following normalization condition:

$$\begin{aligned}\int d\boldsymbol{r}\,\left|\phi(\boldsymbol{r})\right|^2 &= \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int^{2\pi} *0 d\phi \left|\frac{\chi_l(r)}{r} Y*lm(\theta,\phi)\right|^2 \\ &= \int_0^\infty dr \left|\chi_l(r)\right|^2 \int_0^\pi d\theta \sin\theta \int^{2\pi} *0 d\phi \left|Y*lm(\theta,\phi)\right|^2 \\ &= \int_0^\infty dr \left|\chi_l(r)\right|^2 \\ &= 1. \end{aligned} \tag{42}$$

Therefore, the radial wavefunction $\chi_l(r)$ must satisfy the following normalization condition:

$$\int_0^\infty dr \left|\chi_l(r)\right|^2 = 1. \tag{43}$$

Using the values of the wavefunction $\chi_l(r_j)$ on the discretized coordinates r_j, the normalization condition can be approximately evaluated by numerical integration:

$$\sum_{j=0}^{N} \left|\chi_l(r_j)\right|^2 \Delta r = 1. \tag{44}$$

Based on the above, the Python code for determining the eigenstates of hydrogen-like atoms is shown in Source Code 2.

`https://github.com/shunsuke-sato/python_qe/blob/develop/note_atom_dft/src/hydrogen.py`

Source code 2: Code for investigating hydrogen atom eigenstates using the shooting method

```python
import numpy as np
from matplotlib import pyplot as plt

def calc_radial_wavefunction(zval, l, dr, rmax, num_state):
    num_grid = int(rmax / dr) + 1
    rj = np.linspace(0.0, rmax, num_grid)

    chi = np.zeros((num_grid, num_state))
    energy = np.zeros(num_state)

    for jstate in range(num_state):
        chi[:, jstate], energy[jstate] = shooting_method(zval, l, dr, num_grid, rj, jstate)

    return rj, chi, energy


def shooting_method(zval, l, dr, num_grid, rj, jstate):
    chi_s = np.zeros(num_grid)
    ene_max = 0.1 * zval**2
    ene_min = -0.6 * zval**2

    for iter in range(100):
        ene_t = 0.5 * (ene_max + ene_min)

        chi_s, num_node = get_radial_wavefunction(zval, l, dr, num_grid, rj, jstate, ene_t)
```

```
        if num_node >= jstate+1:
            ene_max = ene_t
        else:
            ene_min = ene_t

        if ene_max - ene_min < 1e-6:
            break


    ene_t = ene_max
    chi_s, num_node = get_radial_wavefunction(zval, l, dr, num_grid, rj, jstate, ene_t)

# refine wavefunction
    num_node = 0
    for j in range(1, num_grid - 1):
        if chi_s[j + 1] == 0.0:
            num_node += 1
        elif chi_s[j + 1] * chi_s[j] < 0.0:
            num_node += 1

        if num_node == jstate+1:
            chi_s[j+1:] = 0.0
            break

    norm = np.sum(chi_s**2)*dr
    chi_s = chi_s / np.sqrt(norm)

    return chi_s, ene_t


def get_radial_wavefunction(zval, l, dr, num_grid, rj, jstate, energy):
    chi_s = np.zeros(num_grid)
    chi_s[0] = 0.0
    chi_s[1] = dr / zval
    factor = 2 * dr**2

    num_node = 0

    for j in range(1, num_grid - 1):
        chi_s[j + 1] = (
            2 * chi_s[j] - chi_s[j - 1]
            - factor * (energy - 0.5 * l * (l + 1) / rj[j]**2 + zval / rj[j]) * chi_s[j]
        )

        if chi_s[j+1] == 0.0:
            num_node += 1
        elif chi_s[j+1] * chi_s[j] < 0.0:
            num_node += 1

    return chi_s, num_node

zval = 1.0
num_state = 3
dr = 0.01
rmax = 100.0
l_angular = np.array([0, 1, 2])

for l in l_angular:
    rj, chi_l, energy = calc_radial_wavefunction(zval, l, dr, rmax, num_state)
    print(f"l␣=␣{l},␣Energy␣levels␣:␣{energy}")

    # Plot results
    plt.figure(figsize=(8, 6))
    for i in range(num_state):
        plt.plot(rj, chi_l[:, i], label=f"{i}-state")

    plt.xlim(0.0, 50.0)
    plt.ylim(-0.5, 0.8)
    plt.xlabel("Radius␣(Bohr)")
    plt.ylabel(r"$\chi␣(r)$")
    plt.title(f"Wavefunctions␣(l={l})")
    plt.legend()
    plt.grid()
    plt.tight_layout()

    plt.savefig(f"hydrogen_wf_l{l}.pdf", dpi=300)
```

The behavior of the radial wavefunction of the hydrogen atom eigenstates obtained by executing

Source Code 2 is shown in Fig. 2.

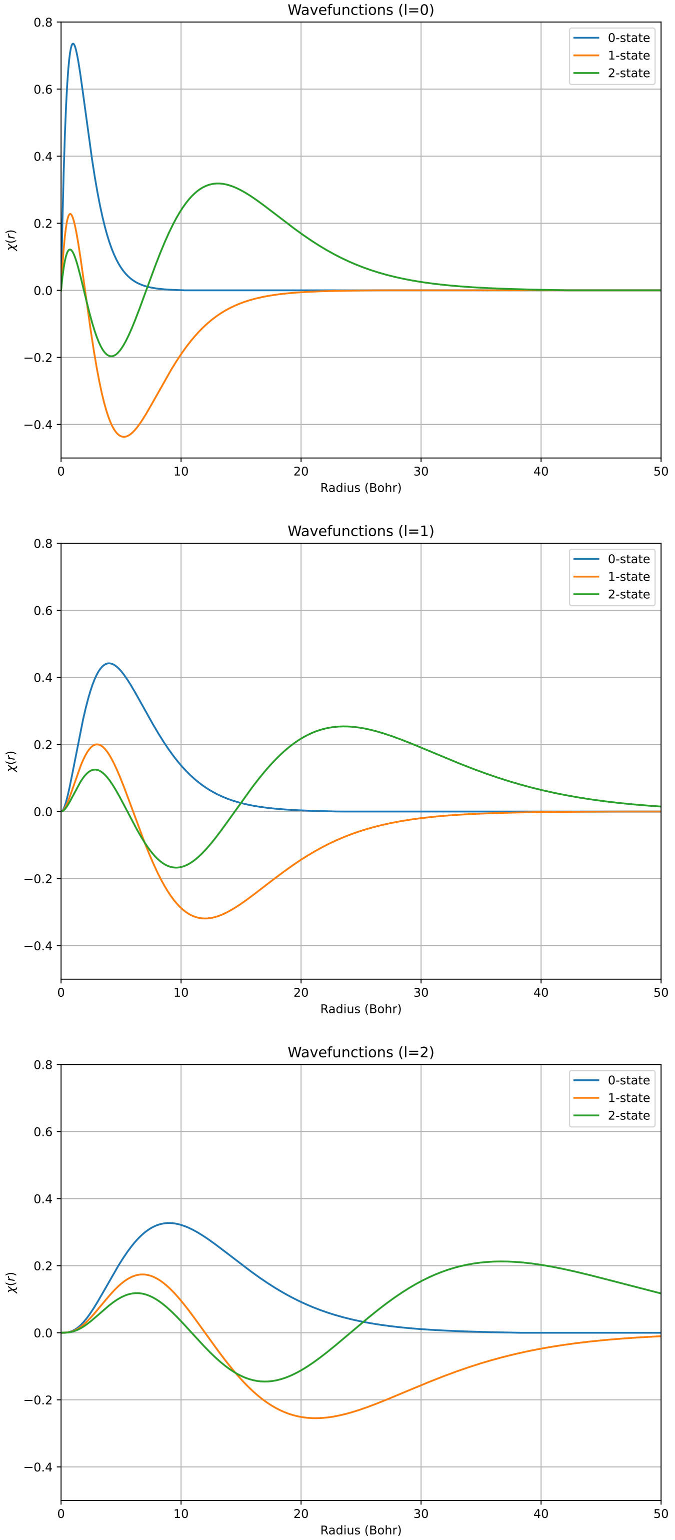

Figure 2: Process of determining the eigenvalues of the hydrogen atom ground state using the shooting method.

3 Helium atom

In this section, we will first revisit basic quantum mechanics topics such as perturbation theory and the variational method. Building on these fundamentals, we will further explain the mean-field approximation and the Hartree–Fock method through an analysis of the ground state of the helium atom.

3.1 Two-electron wavefunctions and spin

When investigating the eigenstates of single-electron systems such as the hydrogen atom, the spin degrees of freedom were not explicitly considered. However, in the study of multi-electron systems, the spin degrees of freedom of electrons play an important role. To represent this spin degree of freedom, let us denote the z-component of spin for each electron as $s_{z,1}$ and $s_{z,2}$, and express the two-electron wavefunction including the spin degree of freedom as $\Psi(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2})$. Here, $s_{z,j}$ takes the value $+\frac{1}{2}$ or $-\frac{1}{2}$, corresponding respectively to the states with $+\hbar/2$ or $-\hbar/2$ of spin angular momentum in the z-direction.

Since electrons are fermions, their wavefunction must be antisymmetric under particle exchange. In the case of a two-electron system, the wavefunction must satisfy the following antisymmetry:

$$\Psi(\boldsymbol{r}_2, s_{z,2}, \boldsymbol{r}_1, s_{z,1}) = -\Psi(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}). \tag{45}$$

For later convenience, we introduce the spin functions $\alpha(s_z)$ and $\beta(s_z)$ as follows:

$$\alpha(s_z) = \begin{cases} 1 & s_z = +\frac{1}{2} \\ 0 & s_z = -\frac{1}{2} \end{cases} \tag{46}$$

$$\beta(s_z) = \begin{cases} 0 & s_z = +\frac{1}{2} \\ 1 & s_z = -\frac{1}{2} \end{cases} \tag{47}$$

Here, $\alpha(s_z)$ and $\beta(s_z)$ are functions corresponding to the spin-up state ($s_z = 1/2$) and spin-down state ($s_z = -1/2$), respectively. Note also that any spin function $\chi(s_z)$ can be expressed as a linear combination of $\alpha(s_z)$ and $\beta(s_z)$.

As a concrete example using spin functions, let us consider the one-particle wavefunction for a spin-up electron occupying the $1s$ orbital of a hydrogen atom ($\phi_{1s}(\boldsymbol{r})$). The wavefunction for such a state can be written as follows:

$$\psi(\boldsymbol{r}, s_z) = \phi_{1s}(\boldsymbol{r})\alpha(s_z). \tag{48}$$

3.2 Schrödinger equation for helium-like atoms

Helium-like atoms are quantum many-body systems in which two electrons are bound to a nucleus with atomic number Z. In the case of a helium nucleus, $Z = 2$. For simplicity, we consider the nucleus as a fixed point charge located at the origin and treat the helium-like atom approximately as a two-electron system. The Schrödinger equation for such a two-electron system is given by:

$$\begin{aligned} &\left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r_1} - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r_2} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}\right]\Psi(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}) \\ &= E\Psi(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}). \end{aligned} \tag{49}$$

By finding the ground state of this Schrödinger equation, we can investigate the properties of the ground state of helium-like atoms. This problem is a quantum many-body problem and cannot be solved analytically like the hydrogen atom. In this section, we learn methods to approximately study the ground state of helium-like atoms.

3.3 Ground state analysis of the helium atom using first-order perturbation theory

First, let us examine the ground state of the helium atom using perturbation theory. To apply perturbation theory, we divide the Hamiltonian in Eq. (49) into the unperturbed term $\hat{H}_0$ and the perturbation term $\hat{V}$ as follows:

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r_1} - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r_2}, \tag{50}$$

$$\hat{V} = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}. \tag{51}$$

If there is no degeneracy in the ground state, the ground state energy, including the first-order perturbation, is given by evaluating the expectation value of the full Hamiltonian ($\hat{H} = \hat{H}_0 + \hat{V}$) using the ground state $|\Phi_0\rangle$ of the unperturbed Hamiltonian. Then, the approximate ground state energy to first order in perturbation theory is given by

$$E_0 \approx \tilde{E}_0^{(0)} + \tilde{E}_0^{(1)} = \frac{\langle\Phi_0|\hat{H}|\Phi_0\rangle}{\langle\Phi_0|\Phi_0\rangle} = \frac{\langle\Phi_0|\hat{H}_0|\Phi_0\rangle}{\langle\Phi_0|\Phi_0\rangle} + \frac{\langle\Phi_0|\hat{V}|\Phi_0\rangle}{\langle\Phi_0|\Phi_0\rangle}, \tag{52}$$

where $\tilde{E}_0^{(0)}$ is the zeroth-order perturbation energy, and $\tilde{E}_0^{(1)}$ is the first-order perturbation energy.

To explicitly evaluate this expression, let us first examine the ground state of the unperturbed Hamiltonian $\hat{H}_0$. The unperturbed Hamiltonian $\hat{H}_0$ given in Eq. (50) can be expressed as a sum of one-body Hamiltonians for each electron coordinate:

$$\hat{H}_0 = \hat{h}(\boldsymbol{r}_1) + \hat{h}(\boldsymbol{r}_2), \tag{53}$$

$$\hat{h}(\boldsymbol{r}_j) = -\frac{\hbar^2}{2m_e}\nabla_j^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r_j}. \tag{54}$$

Here, as a solution to the Schrödinger equation for the unperturbed Hamiltonian $\hat{H}_0$, consider a separable solution of the form $\tilde{\Phi}_0(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2})$:

$$\hat{H}_0\tilde{\Phi}_0(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}) = E^{(0)}\tilde{\Phi}_0(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}), \tag{55}$$

$$\tilde{\Phi}_0(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}) = \phi_1(\boldsymbol{r}_1, s_{z,1})\phi_2(\boldsymbol{r}_2, s_{z,2}). \tag{56}$$

Substituting Eq. (56) into Eq. (55), it can be seen that the single-particle wave functions $\phi_1(\boldsymbol{r}, s)$ and $\phi_2(\boldsymbol{r}, s)$ are eigenstates of the one-body Hamiltonian $\hat{h}(\boldsymbol{r})$ and satisfy the following equations:

$$\hat{h}(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_1, s_{z,1}) = \varepsilon_1\phi_1(\boldsymbol{r}_1, s_{z,1}), \tag{57}$$

$$\hat{h}(\boldsymbol{r}_2)\phi_2(\boldsymbol{r}_2, s_{z,2}) = \varepsilon_2\phi_2(\boldsymbol{r}_2, s_{z,2}), \tag{58}$$

$$E^{(0)} = \varepsilon_1 + \varepsilon_2. \tag{59}$$

Using the wave function $\phi_{1s}(\boldsymbol{r})$ from Eq. (15), the lowest energy solutions to Eq. (57) and Eq. (58) are written as

$$\phi_1(\boldsymbol{r}_1, s_{z,1}) = \phi_{1s}(\boldsymbol{r}_1)\chi_1(s_{z,1}) = \sqrt{\frac{Z^3}{a_0^3}} \cdot 2e^{-Zr/a_0}\frac{1}{\sqrt{4\pi}}\chi_1(s_{z,1}), \tag{60}$$

$$\phi_2(\boldsymbol{r}_2, s_{z,2}) = \phi_{1s}(\boldsymbol{r}_1)\chi_2(s_{z,2}) = \sqrt{\frac{Z^3}{a_0^3}} \cdot 2e^{-Zr/a_0}\frac{1}{\sqrt{4\pi}}\chi_2(s_{z,2}), \tag{61}$$

where $\chi_1(s_1)$ and $\chi_2(s_2)$ are arbitrary spin functions. Also, note that the energy eigenvalues of these single-particle wave functions are

$$\varepsilon_1 = \varepsilon_2 = -\frac{Z^2}{2}\frac{m_e}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = -\frac{\hbar^2}{2m_e}\left(\frac{Z}{a_0}\right)^2. \tag{62}$$

The wave function of a Fermi particle system must be antisymmetric with respect to particle exchange. However, a wave function given by Eq. (56), $\tilde{\Phi}_0(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2})$, does not generally satisfy antisymmetry. Therefore, let us consider explicit antisymmetrizing this wave function as follows:

$$\begin{aligned}\Phi_0(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}) &= \mathcal{N}\left[\tilde{\Phi}_0(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}) - \tilde{\Phi}_0(\boldsymbol{r}_2, s_{z,2}, \boldsymbol{r}_1, s_{z,1})\right] \\ &= \mathcal{N}\phi_{1s}(\boldsymbol{r}_1)\phi_{1s}(\boldsymbol{r}_2)\left[\chi_1(s_{z,1})\chi_2(s_{z,2}) - \chi_1(s_{z,2})\chi_2(s_{z,1})\right]. \qquad (63)\end{aligned}$$

Here, the constant $\mathcal{N}$ represents the normalization factor. This wave function indicates that both electron 1 and electron 2 occupy the $1s$ orbital spatially. Moreover, if electron 1 and electron 2 occupy the same spin state (for example, both in the spin-up state $\alpha(s_z)$), the spin part of the wave function becomes zero due to antisymmetrization. Therefore, it is clear that two electrons cannot occupy the same spatial orbital and spin. This is nothing but the **Pauli exclusion principle**.

Furthermore, when the spin functions $\chi_1(s_z)$ and $\chi_2(s_z)$ of electron 1 and electron 2 occupy different spin states, the wave function in Eq. (63) becomes a spin singlet state. This can be understood by expanding each spin function in terms of $\alpha(s_z)$ and $\beta(s_z)$ and choosing an appropriate normalization constant, which leads to the wave function in Eq. (63) being expressed as

$$\Phi_0(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}) = \phi_{1s}(\boldsymbol{r}_1)\phi_{1s}(\boldsymbol{r}_2)\frac{1}{\sqrt{2}}\left[\alpha(s_{z,1})\beta(s_{z,2}) - \alpha(s_{z,2})\beta(s_{z,1})\right]. \qquad (64)$$

The wave function in Eq. (64) is an eigenstate of the unperturbed Hamiltonian, and the zeroth-order energy $\tilde{E}_0^{(0)}$ is given by

$$\tilde{E}_0^{(0)} = -2 \times \frac{Z^2}{2}\frac{m_e}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = -Z^2\frac{m_e}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = -Z^2 E_H. \qquad (65)$$

Here, E_H is the Hartree energy unit defined in Eq. (24).

Furthermore, let us evaluate the first-order perturbation energy $\tilde{E}_0^{(1)}$ using equation (52) as follows:

$$\begin{aligned}\tilde{E}_0^{(1)} = \frac{\langle\Phi_0|\hat{V}|\Phi_0\rangle}{\langle\Phi_0|\Phi_0\rangle} &= \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}\left|\phi_{1s}(\boldsymbol{r}_1)\right|^2\left|\phi_{1s}(\boldsymbol{r}_2)\right|^2 \\ &= \frac{5}{8}\frac{e^2}{4\pi\varepsilon_0}\frac{Z}{a_0} = \frac{5}{8}ZE_H. \qquad (66)\end{aligned}$$

This energy is nothing but the Coulomb energy between the charge densities $e\left|\phi_{1s}(\boldsymbol{r}_1)\right|^2$ and $e\left|\phi_{1s}(\boldsymbol{r}_2)\right|^2$ of the $1s$ orbital electrons.

By performing such a calculation, the ground state energy of helium-like atoms can be evaluated by considering the first-order term of the electron-electron interaction as follows:

$$E_{gs} \approx \tilde{E}_0^{(0)} + \tilde{E}_0^{(1)} = \left(-Z^2 + \frac{5}{8}Z\right)E_H. \qquad (67)$$

Specifically, evaluating this for the helium atom ($Z = 2$), the ground state energy using first-order perturbation theory is $E_{gs} = \left(-4 + \frac{10}{8}\right)E_H = -2.75$ Hartree ≈ -74.83 eV. The experimentally measured binding energy of the helium atom is -2.9033 Hartree ≈ -79.00 eV, indicating that using first-order perturbation theory yields a result with an error of approximately 5%.

3.4 Ground state analysis of the helium atom using the variational method

3.4.1 Revisit of the variational method

Let us investigate the ground state of the helium atom using the variational method. First, we revisit the variational method.

We introduce the eigenstates and eigenenergies for a given Hamiltonian $\hat{H}$ as follows:

$$\hat{H}|\Phi_n\rangle = E_n|\Phi_n\rangle. \tag{68}$$

Here, we assume that the eigenstates $|\phi_n\rangle$ form an orthonormal set.

Furthermore, consider evaluating the energy expectation value E using a given wavefunction $|\Psi\rangle$:

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{69}$$

Here, expand the wavefunction $|\Psi\rangle$ in terms of the eigenstates $|\Phi_n\rangle$ as follows:

$$|\Psi\rangle = \sum_n c_n|\Phi_n\rangle. \tag{70}$$

Using the expansion in Eq. (70), the energy expectation value can be evaluated as follows:

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\sum_n E_n|c_n|^2}{\sum_n |c_n|^2} \geq \frac{\sum_n E_{gs}|c_n|^2}{\sum_n |c_n|^2} = E_{\mathrm{gs}}. \tag{71}$$

Here, E_{gs} represents the ground state energy, and we used the fact that $E_n \geq E_{\mathrm{gs}}$ for any eigenvalue.

From this discussion, we obtain

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_{\mathrm{gs}}, \tag{72}$$

which indicates that the expected energy value evaluated using any wavefunction is never smaller than the ground state energy, and its minimum value is E_{gs}. This is called the **variational principle**.

The method of ground state analysis using the variational principle is called the **variational method**. Since the variational principle [Eq. (72)] guarantees that the minimum of the expected energy value is the ground state energy, finding a wavefunction that minimizes the energy as much as possible can be regarded as a better approximate wavefunction for the ground state.

Variational method exercise 1: Harmonic oscillator and Gaussian function

As an exercise in the variational method, let us analyze the ground state of a harmonic oscillator using a Gaussian function as the trial wavefunction. Consider the harmonic oscillator Hamiltonian $\hat{H}$ given by:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m}{2}\omega^2 x^2. \tag{73}$$

Furthermore, consider a Gaussian-type trial wavefunction as

$$\psi(x) = e^{-ax^2}. \tag{74}$$

Here, a is an arbitrary constant, determined such that the expectation value of the energy is minimized. Such a parameter is called a **variational parameter**. Using this Gaussian-type trial wavefunction, calculate the expectation value of the harmonic oscillator Hamiltonian and determine the value of a that minimizes this expectation value. Also, compare the resulting ground state energy and wavefunction with the exact ground state energy and wavefunction of the harmonic oscillator.

Variational method exercise 2: Harmonic oscillator and quadratic function

Investigate the ground state of the harmonic oscillator given by Eq. (73) using the variational method with the following trial wavefunction:

$$\psi(x) = \begin{cases} (x+a)(x-a) & -a \le x \le a \\ 0 & \text{otherwise} \end{cases} \tag{75}$$

3.4.2 Analysis of the helium ground state using the variational method

Here, we approximately examine the ground state of helium-like atoms using the variational method. As described in Section 3.3, the ground state of a helium-like atom in the absence of electron-electron interactions is expressed as the product of $1s$ orbital wavefunctions of hydrogen-like atoms. Therefore, we consider the following trial wavefunction, using the nuclear charge Z that appears in the $1s$ orbital wavefunction as a variational parameter:

$$\Phi_0(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}) = \frac{1}{\pi}\frac{\tilde{Z}^3}{a_0^3} \cdot \exp\left[-\frac{\tilde{Z}r_1}{a_0}\right] \exp\left[-\frac{\tilde{Z}r_2}{a_0}\right] \times \frac{1}{\sqrt{2}}\left[\alpha(s_{z,1})\beta(s_{z,2}) - \alpha(s_{z,2})\beta(s_{z,1})\right]. \tag{76}$$

Here, $\tilde{Z}$ is the variational parameter and represents the effective nuclear charge felt by the electrons. Using this trial wavefunction, evaluating the expectation value of the Hamiltonian in Eq. (49) yields the following expression as a function of $\tilde{Z}$:

$$\begin{aligned} E(\tilde{Z}) &= 2 \cdot \frac{\hbar^2}{2m}\frac{\tilde{Z}^2}{a_0^2} - 2 \cdot \frac{Ze^2}{4\pi\varepsilon_0}\frac{\tilde{Z}}{a_0} + \frac{5}{8}\frac{e^2}{4\pi\varepsilon_0}\frac{\tilde{Z}}{a_0} \\ &= \tilde{Z}^2 E_H - 2Z\tilde{Z}E_H + \frac{5}{8}\tilde{Z}E_H \\ &= \left[\left\{\tilde{Z} - \left(Z - \frac{5}{16}\right)\right\}^2 - \left(Z - \frac{5}{16}\right)^2\right] E_H. \end{aligned} \tag{77}$$

The effective nuclear charge that minimizes this energy expectation value is

$$\tilde{Z} = Z - 5/16 \tag{78}$$

and the corresponding energy expectation value is

$$E(\tilde{Z}) = -\left(Z - \frac{5}{16}\right)^2 E_H. \tag{79}$$

This can be interpreted as the Coulomb attraction felt by an electron from the nucleus being effectively reduced by 5/16 of the nuclear charge Z due to the screening effect of the other electron.

At this point, the ground state energy of the helium atom ($Z = 2$) obtained via the variational method is

$$E_{\text{gs}} \approx -\left(\frac{27}{16}\right)^2 E_H \approx 77.49 \text{ eV} \tag{80}$$

The experimentally measured binding energy of the helium atom is -2.9033 Hartree ≈ -79.00 eV, indicating that the variational method yields a value with an error of about 2%.

3.5 Hartree–Fock equation for two-electron systems

As we have seen so far, the accuracy of the variational methods strongly depends on the trial wavefunction. In general, using a trial wavefunction that allows exploration of a wider range of the wavefunction space enables a more accurate analysis of the ground state. In the previous section, we introduced a trial wavefunction as a product of the $1s$ orbitals of hydrogen-like atoms. At that time, the effective nuclear charge $\tilde{Z}$ was the variational parameter. Here, in order to expand the variational space in the variational method, we introduce a two-electron wavefunction that can be written in the following form:

$$\begin{aligned}\Phi_0(\boldsymbol{r}_1, s_{z,1}, \boldsymbol{r}_2, s_{z,2}) &= \phi(\boldsymbol{r}_1)\phi(\boldsymbol{r}_2)\frac{1}{\sqrt{2}}\left[\alpha(s_{z,1})\beta(s_{z,2}) - \alpha(s_{z,2})\beta(s_{z,1})\right] \\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\phi(\boldsymbol{r}_1)\alpha(s_{z,1}) & \phi(\boldsymbol{r}_2)\alpha(s_{z,2}) \\ \phi(\boldsymbol{r}_1)\beta(s_{z,1}) & \phi(\boldsymbol{r}_2)\beta(s_{z,2})\end{vmatrix}. \end{aligned} \tag{81}$$

This is nothing more than replacing the spatial part of the trial wavefunction in Eq. (76) with a general one-particle wavefunction $\phi(\boldsymbol{r})$. Also, in the trial wavefunction of Eq. (76), the effective nuclear charge $\tilde{Z}$ was the single variational parameter, whereas here, we aim to minimize the energy expectation value by optimizing the one-particle wavefunction $\phi(\boldsymbol{r})$ itself.

Using the trial wavefunction in Eq. (81), we calculate the energy expectation value of the Hamiltonian in Eq. (49), obtaining the following expression:

$$E\left[\phi(\boldsymbol{r})\right] = \frac{2\int d\boldsymbol{r}\phi^*(\boldsymbol{r})\hat{h}(\boldsymbol{r})\phi(\boldsymbol{r})}{\int d\boldsymbol{r}\left|\phi(\boldsymbol{r})\right|^2} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{\left(\int d\boldsymbol{r}\left|\phi(\boldsymbol{r})\right|^2\right)^2}\int d\boldsymbol{r}d\boldsymbol{r}'\frac{\left|\phi(\boldsymbol{r})\right|^2\left|\phi(\boldsymbol{r}')\right|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}. \tag{82}$$

Here, the one-body Hamiltonian $\hat{h}(\boldsymbol{r})$ is defined by Eq. (54). Also, the energy expectation value is denoted as $E\left[\phi(\boldsymbol{r})\right]$, explicitly indicating that a specific value is determined for a given function $\phi(\boldsymbol{r})$. A function returns a value for a given input x, i.e., $f(x)$, but something that returns a value for a given function $\phi(\boldsymbol{r})$, like the energy expectation value $E\left[\phi(\boldsymbol{r})\right]$ in Eq. (82), is called a **functional**. Functionals will be revisited in Sec. 3.6.

To approximately study the ground state of a helium-like atom, we seek the single-particle wavefunction $\phi(\boldsymbol{r})$ that minimizes the energy expectation value given by Eq. (82). To do this, we consider a small deviation $\phi(\boldsymbol{r}) + \delta\phi(\boldsymbol{r})$ from the wavefunction $\phi(\boldsymbol{r})$ that minimizes the energy expectation value, and examine how the energy expectation value changes due to this infinitesimal variation:

$$\delta E = E\left[\phi(\boldsymbol{r}) + \delta\phi(\boldsymbol{r})\right] - E\left[\phi(\boldsymbol{r})\right]. \tag{83}$$

If the single-particle wavefunction $\phi(\boldsymbol{r})$ minimizes the energy expectation value $E\left[\phi(\boldsymbol{r})\right]$, then for any change $\delta\phi(\boldsymbol{r})$, the following inequality must hold:

$$E\left[\phi(\boldsymbol{r}) + \delta\phi(\boldsymbol{r})\right] \geq E\left[\phi(\boldsymbol{r})\right]. \tag{84}$$

Therefore, we find that $\delta E \geq 0$. Hence, if $\phi(\boldsymbol{r})$ minimizes $E\left[\phi(\boldsymbol{r})\right]$, the first-order contribution of $\delta\phi(\boldsymbol{r})$ to δE must vanish.

By using this condition, we can derive the equation that $\phi(\boldsymbol{r})$ must satisfy. Consider expanding δE in terms of $\delta\phi(\boldsymbol{r})$. The first-order contribution of $\delta\phi(\boldsymbol{r})$ to δE, denoted as $\delta E^{(1)}$, is given by:

$$\begin{aligned}\delta E^{(1)} =& \frac{2}{\int d\boldsymbol{r}\ \left|\phi(\boldsymbol{r})\right|^2}\left[\int d\boldsymbol{r}\delta\phi^*(\boldsymbol{r})\left\{\hat{h}(\boldsymbol{r}) + \frac{e^2}{4\pi\varepsilon_0}\int d\boldsymbol{r}'\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} - \varepsilon\right\}\phi(\boldsymbol{r})\right] \\ &+ \frac{2}{\int d\boldsymbol{r}\ \left|\phi(\boldsymbol{r})\right|^2}\left[\int d\boldsymbol{r}\phi^*(\boldsymbol{r})\left\{\hat{h}(\boldsymbol{r}) + \frac{e^2}{4\pi\varepsilon_0}\int d\boldsymbol{r}'\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} - \varepsilon\right\}\delta\phi(\boldsymbol{r})\right]. \end{aligned} \tag{85}$$

Here, $\rho(\boldsymbol{r})$ and ε are defined as follows:

$$\rho(\boldsymbol{r}) = \frac{1}{\int d\boldsymbol{r}\left|\phi(\boldsymbol{r})\right|^2}\left|\phi(\boldsymbol{r})\right|^2, \tag{86}$$

$$\varepsilon = \frac{1}{\int d\boldsymbol{r}\left|\phi(\boldsymbol{r})\right|^2}\left[\int d\boldsymbol{r}\phi^*(\boldsymbol{r})\left\{\hat{h}(\boldsymbol{r}) + \frac{e^2}{4\pi\varepsilon_0}\int d\boldsymbol{r}'\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\right\}\phi(\boldsymbol{r})\right]. \tag{87}$$

If $\phi(\boldsymbol{r})$ minimizes $E\left[\phi(\boldsymbol{r})\right]$, then based on the above argument, $\delta E^{(1)}$ in Eq. (85) must vanish for any $\delta\phi(\boldsymbol{r})$. To achieve this, noting that the two terms on the right-hand side of Eq. (85) are complex conjugates of each other, it is sufficient that the integrand in the first term, excluding $\delta\phi(\boldsymbol{r})$, vanishes. This leads to the following equation that must be satisfied:

$$\left[\hat{h}(\boldsymbol{r}) + \frac{e^2}{4\pi\varepsilon_0}\int d\boldsymbol{r}'\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\right]\phi(\boldsymbol{r}) = \varepsilon\phi(\boldsymbol{r}). \tag{88}$$

One sees that Eq. (88) takes a similar form to a Schrödinger equation for a single electron. The potential consists of the Coulomb attraction from the nucleus and the Coulomb repulsion from the charge density, $-e\rho(\boldsymbol{r})$, of the other electron. The original problem of a helium-like atom involves two electrons moving complexly in a six-dimensional space under mutual influence. However, Eq. (88) is a three-dimensional equation for a single electron, where the effective Hamiltonian includes a Coulomb potential averaged over the probability density of the other electron. This type of approximation is called the **mean-field approximation** or **mean-field picture**. Furthermore, Eq. (88) is the Hartree–Fock equation applied to the two-electron problem of the helium atom. More general expression of the Hartree–Fock equation is discussed in Sec. 3.8.

3.6 Functionals and functional derivatives

For convenience later on, let us briefly touch on the concept of a functional. A conventional function is a mapping from one value to another. For example, a function $f(x)$ maps a given value x_1 to the value $f(x_1)$. A functional, often described as a "function of a function," represents a mapping from a function to a value. For instance, given a function $f(x)$, a functional that returns a value is written as $F\left[f(x)\right]$. A simple example of a functional is the following definite integral:

$$F\left[f(x)\right] = \int_0^1 dx\ f(x). \tag{89}$$

This definite integral acts as a functional that returns a value $F\left[f(x)\right]$ when a function $f(x)$ is given.

Next, we address the concept of the derivative of a functional. Consider a functional $F\left[f(x)\right]$ that depends on a function $f(x)$ defined over the domain $[x_i, x_f]$. Let us evaluate the infinitesimal change in the functional when $f(x)$ is slightly changed to $f(x) + \delta f(x)$.

$$\delta F = F\left[f(x) + \delta f(x)\right] - F\left[f(x)\right]. \tag{90}$$

If $\delta f(x)$ is sufficiently small such that higher-order contributions can be ignored, then δF can be evaluated as follows (the reason will be explained later):

$$\delta F \approx \int_{x_i}^{x_f} dx\ \delta f(x) G(x). \tag{91}$$

In this expression, $G(x)$ is called the functional derivative of $F[f(x)]$ with respect to $f(x)$ and is expressed as:

$$\frac{\delta F}{\delta f(x)} = G(x). \tag{92}$$

We previously derived the Hartree—Fock equation for a two-electron system from Eq. (85). By using the expression for functional derivatives, this is equivalent to examining the condition under which the functional derivative vanishes:

$$\frac{\delta E}{\delta\phi^*(\boldsymbol{r})} = \left[\hat{h}(\boldsymbol{r}) + \frac{e^2}{4\pi\varepsilon_0}\int d\boldsymbol{r}'\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} - \varepsilon\right]\phi(\boldsymbol{r}) = 0. \tag{93}$$

Now, let us consider how to understand the expression in Eq. (91). Suppose the functional $F[f(x)]$ is a functional of a function $f(x)$ defined over the domain $[x_i, x_f]$. Let us divide the domain into N equal parts and define the N coordinates as follows:

$$x_j = j \times \Delta x + x_i, \tag{94}$$

$$\Delta x = \frac{x_f - x_i}{N}. \tag{95}$$

Here, j is an integer from 0 to $N-1$. Let us denote the value of the function $f(x)$ evaluated at each x_j as f_j, i.e., let $f_j = f(x_j)$.

Consider a multivariable function $F_N(f_0, \cdots, f_{N-1})$ that depends on these N variables. Suppose each value f_j is changed to $f_j + \delta f_j$. If the variations δf_j are sufficiently small and higher-order contributions are negligible, the change in the function can be described using a first-order Taylor expansion:

$$F_N(f_0 + \delta f_0, \cdots, f_{N-1} + \delta f_{N-1}) \approx F_N(f_0, \cdots, f_{N-1}) + \sum_{j=0}^{N-1} \frac{\partial}{\partial f_j} F_N(f_0, \cdots, f_{N-1}) \delta f_j \tag{96}$$

Therefore, the variation δF_N of the multivariable function can be evaluated as follows:

$$\begin{aligned}
\delta F_N &= F_N(f_0 + \delta f_0, \cdots, f_{N-1} + \delta f_{N-1}) - F_N(f_0, \cdots, f_{N-1}) \\
&\approx \sum_{j=0}^{N-1} \frac{\partial F_N(f_0, \cdots, f_{N-1})}{\partial f_j} \delta f_j \\
&= \sum_{j=0}^{N-1} \Delta x \frac{1}{\Delta x} \frac{\partial F_N(f_0, \cdots, f_{N-1})}{\partial f_j} \delta f_j && (97) \\
&= \sum_{j=0}^{N-1} \Delta x G_j \delta f_j. && (98)
\end{aligned}$$

Here, we define:

$$G_j = \frac{1}{\Delta x} \frac{\partial}{\partial f_j} F_N(f_0, \cdots, f_{N-1}) \tag{99}$$

The functional $F[f(x)]$ depends on the value of the function $f(x)$ at every point in its domain. This kind of dependence is realized in the limit as $N \to \infty$ of the N-variable function discussed above. Thus, by identifying such a multivariable function with a functional, the infinitesimal variation of the functional $F[f(x)]$ can be evaluated as:

$$\delta F = \lim_{N\to\infty} \delta F_N = \lim_{N\to\infty} \sum_{j=0}^{N-1} \Delta x G_j \delta f_j = \int_{x_i}^{x_f} dx G(x) \delta f(x). \tag{100}$$

In this way, we obtain an expression like Eq. (91).

3.7 Numerical solution of the Hartree–Fock equation for helium-like atoms

Here, we describe how to numerically solve the Hartree–Fock equation given by Eq. (88). First, let us focus on the nonlinearity of this equation. The Schrödinger equation is linear with respect to the wavefunction, whereas Eq. (88) is a nonlinear equation with respect to the single-particle orbital $\phi(\boldsymbol{r})$. Due to this nonlinearity, even if we attempt to solve Eq. (88) as an eigenvalue problem for a Hamiltonian similar to the ordinary Schrödinger equation, we would need to know $\phi(\boldsymbol{r})$ in advance to construct such a Hamiltonian. Therefore, in order to solve Eq. (88), some additional techniques are required beyond the usual solution methods for the Schrödinger equation.

Here, we explain the commonly used **self-consistent field (SCF) iteration method**. The general procedure is as follows: first, using an initial density $\rho(\boldsymbol{r})$, the potential on the left-hand side of Eq. (88) is evaluated, and an effective Hamiltonian is constructed. Then, the ground state of this effective Hamiltonian is determined. From the wavefunction of the obtained ground state, a new density $\rho(\boldsymbol{r})$ is evaluated, and the potential and Hamiltonian are updated to again find the ground state. By repeating this process, if the density used to construct the Hamiltonian becomes equal to the density produced by the ground state of that Hamiltonian, then the nonlinear equation is consistently solved.

Specifically, this is done through an iterative method as follows:

1. Set an initial electron density $\rho^{(0)}(\boldsymbol{r})$ arbitrarily.
2. Given the electron density $\rho^{(n)}(\boldsymbol{r})$, evaluate the potential term of the Hartree–Fock equation, Eq. (88), as $\int d\boldsymbol{r}' \frac{\rho^{(n)}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$. Here, n is an integer, initially set to $n = 0$.
3. Solve the Hartree–Fock equation [Eq. (88)] with the given potential term, and denote the resulting wavefunction as $\phi^{(n+1)}(\boldsymbol{r})$.
4. If the density $\rho^{(n+1)}(\boldsymbol{r})$ obtained from the solved wavefunction $\phi^{(n+1)}(\boldsymbol{r})$ matches the density $\rho^{(n)}(\boldsymbol{r})$ used to construct the potential, then the nonlinear equation is solved. If not, return to step 2 using the new density $\rho^{(n+1)}(\boldsymbol{r})$.

Furthermore, in order to perform concrete numerical calculations, we assume spherical symmetry of the wavefunction and derive the radial equation. As with the numerical solution of hydrogen-like atoms, we assume a spherically symmetric solution of the form:

$$\phi(\boldsymbol{r}) = \phi(r) = \frac{1}{\sqrt{4\pi}}\frac{\chi(r)}{r}. \tag{101}$$

Substituting this spherically symmetric solution into Eq. (88), we can derive the following radial equation:

$$\left[-\frac{\hbar^2}{2m_e}\frac{d^2}{dr^2} - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r} + V_{HF}(r)\right]\chi(r) = \varepsilon\chi(r). \tag{102}$$

Here, the potential $V_{HF}(r)$ is defined assuming spherical symmetry of the density ($\rho(\boldsymbol{r}) = \rho(r) = |\phi(\boldsymbol{r})|^2$) as follows:

$$V_{HF}(r) = \frac{e^2}{4\pi\varepsilon_0}\int d\boldsymbol{r}' \frac{\rho(|\boldsymbol{r}'|)}{|\boldsymbol{r}-\boldsymbol{r}'|} = \frac{e^2}{4\pi\varepsilon_0}\left[\frac{4\pi}{r}\int_0^r dr' r'^2 \rho(r') + 4\pi\int_r^\infty dr' r' \rho(r')\right]. \tag{103}$$

The right-hand side of Eq. (103) is obtained by performing the angular integration of the 3D integral using the spherical symmetry of $\rho(r)$.

Moreover, by using the energy eigenvalue ε of the Hartree–Fock equation (88), the ground state energy [Eq. (82)] can be rewritten as:

$$E = 2\varepsilon - 4\pi\int_0^\infty dr r^2 \rho(r) V_{HF}(r). \tag{104}$$

With the above discussion, we are now ready to construct a computational code to investigate the ground state of helium-like atoms using the Hartree–Fock method. Let us actually create such a code and examine the accuracy of ground state calculations by the Hartree–Fock method.

For reference, the source code 3 shows an example of a calculation code for the Hartree–Fock method applied to the helium atom.

`https://github.com/shunsuke-sato/python_qe/blob/develop/note_atom_dft/src/helium.py`

Source code 3: Example code for Hartree–Fock method calculation for the helium atom

```python
import numpy as np
from matplotlib import pyplot as plt

def calc_hf_method(nscf, rmax, dr, zval):

    num_grid = int(rmax/dr)+1
    rj = np.linspace(0.0, rmax, num_grid)

    phi = np.zeros(num_grid)

    for iscf in range(nscf):

        rho = phi**2
        vhf = calc_potential(rho, rj, dr, num_grid)
        phi, epsilon_s = calc_wavefunction(rj, dr, num_grid, vhf, zval)

        total_energy = 2*epsilon_s - 4.0*np.pi*np.sum(rj**2*rho*vhf)*dr

        print("iscf,␣energy␣=",iscf, total_energy)

    return rj, phi, total_energy

def calc_potential(rho, rj, dr, num_grid):

    vhf = np.zeros(num_grid)

    for i in range(num_grid):

        v1 = 0.0
        for j in range(i):
            v1 = v1 + rj[j]**2*rho[j]*dr

        v1 = v1 + 0.5*rj[i]**2*rho[i]*dr
        if(i == 0):
            v1 = 0.0
        else:
            v1 = 4.0*np.pi*v1/rj[i]


        v2 = 0.5*rj[i]*rho[i]*dr
        for j in range(i+1, num_grid):
            v2 = v2 + rj[j]*rho[j]*dr

        v2 = 4.0*np.pi*v2

        vhf[i] = v1 + v2

    return vhf

def calc_wavefunction(rj, dr, num_grid, vhf, zval):

    ene_max = 0.0 * zval
    ene_min = -0.6 * zval**2


    for iter in range(100):
        ene_t = 0.5 * (ene_max + ene_min)

        chi, num_node = get_wavefunction(rj, dr, num_grid, vhf, zval, ene_t)

        if num_node >= 1:
            ene_max = ene_t
        else:
            ene_min = ene_t

        if ene_max - ene_min < 1e-6:
            break

    ene_t = ene_max
    chi, num_node = get_wavefunction(rj, dr, num_grid, vhf, zval, ene_t)

    # refine wavefunction
    num_node = 0
    for j in range(1, num_grid - 1):
        if chi[j + 1] == 0.0:
            num_node += 1
        elif chi[j + 1] * chi[j] < 0.0:
            num_node += 1
```

```python

        if num_node == 1:
            chi[j+1:] = 0.0
            break

    norm = np.sum(chi**2)*dr
    chi = chi/np.sqrt(norm)

    phi = np.zeros(num_grid)
    phi[1:num_grid-1] = chi[1:num_grid-1]/rj[1:num_grid-1]
    phi[0] = 2*phi[1] - phi[2]
    phi = phi/(np.sqrt(4.0*np.pi))


    return phi, ene_t

def get_wavefunction(rj, dr, num_grid, vhf, zval, energy):

    chi = np.zeros(num_grid)
    num_node = 0

    chi[0] = 0.0
    chi[1] = dr / zval

    factor = 2 * dr**2
    for j in range(1, num_grid - 1):
        chi[j + 1] = (
            2 * chi[j] - chi[j - 1]
            - factor * (energy + zval / rj[j] - vhf[j]) * chi[j]
        )

        if chi[j+1] == 0.0:
            num_node += 1
        elif chi[j+1] * chi[j] < 0.0:
            num_node += 1

    return chi, num_node

zval = 2.0
nscf = 10
rmax = 20.0
dr = 0.005


rj, phi, total_energy = calc_hf_method(nscf, rmax, dr, zval)


chi = rj*phi
plt.figure(figsize=(8, 6))
plt.plot(rj, chi)
plt.xlim(0.0, 8.0)
plt.ylim(-0.1, 0.3)
plt.xlabel("Radius (Bohr)")
plt.ylabel(r"$\chi (r)$")
plt.title(f"Wavefunctions")
plt.grid()
plt.tight_layout()

plt.savefig("helium_hf_wavefunction.pdf", dpi=300)
```

In the above calculation using the Hartree-Fock approximation, the ground state energy of the helium atom is obtained as -2.8617 Hartree (≈ -77.87 eV). This corresponds to an accuracy of about 99.85 % compared to the experimental value of the ground state energy (binding energy) of the helium atom, -2.9033 Hartree (≈ -79.00 eV). As we have seen so far, in the approximate calculation using first-order perturbation theory, the approximate value of the ground state energy is $E_{1st} = -2.75$ Hartree ≈ -74.73 eV, which has an error of about 5% compared to the experimental value. Also, in the variational method using an exponential-type trial wave function, the approximate value of the ground state energy is $E_{val} \approx -2.85$ Hartree ≈ -77.49 eV, with an error of about 2% compared to the experimental value.

Looking at the numerical values presented here, the Hartree–Fock method appears to be a highly accurate computational method. However, in practical applications, the calculation accuracy may sometimes be insufficient. In such cases, more accurate computational methods are required. Nevertheless, even when considering more advanced computational methods, the

Hartree–Fock method is often a very important theory that serves as their foundation.

3.8 Slater determinant and the Hartree–Fock equation for an N-particle system

In the previous section, we discussed the case where the number of particles N is fixed at 2. Here, we introduce the Slater determinant for a general number of particles N and describe its properties. We also discuss the Hartree–Fock equation derived using the variational method with the Slater determinant as a trial function.

3.8.1 Properties of the Slater Determinant

Here, we consider the wavefunction of a quantum many-body system of N fermions. Let the wavefunction be denoted by $\Psi(x_1, \cdots, x_N)$. Here, x_j represents the general coordinate of the j-th particle. For example, x_j may be a coordinate combining the three-dimensional space and spin, such as $x_j = (\boldsymbol{r}_j, s_{z,j})$.

First, as a wavefunction that satisfies the antisymmetry required for a fermionic system, we introduce the Slater determinant as follows:

$$\Phi(x_1, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \cdots & \phi_1(x_N) \\ \vdots & \ddots & \vdots \\ \phi_N(x_1) & \cdots & \phi_N(x_N) \end{vmatrix} = \frac{1}{\sqrt{N!}} \sum_{\sigma} \mathrm{sgn}(\sigma) \prod_{j}^{N} \phi_{\sigma(j)}(x_j) \tag{105}$$

Here, $\{\phi_1(x), \cdots, \phi_N(x)\}$ represents N orthonormal single-particle orbitals, and the sum is taken over all possible permutations σ. From the property of determinants that changes the sign with column exchanges, it is immediately evident that the Slater determinant is antisymmetric under particle exchange. Also, if two orbitals are the same (e.g., $\phi_i(x) = \phi_j(x)$), the Slater determinant becomes zero due to the properties of determinants. This expresses the **Pauli exclusion principle**, which states that two fermions cannot occupy the same quantum state. Furthermore, when the number of particles is $N = 2$, it can be seen that the Slater determinant in Eq. (105) coincides with Eq. (81).

Here, we examine several properties of the Slater determinant.

Normalization

The Slater determinant expressed in Eq. (105) is normalized. This can be demonstrated as follows:

$$\begin{aligned} &\int dx_1 \cdots dx_N \ \Phi^*(x_1, \cdots, x_N)\Phi(x_1, \cdots, x_N) \\ &= \frac{1}{N!} \sum_{\sigma\tau} \mathrm{sgn}(\sigma)\mathrm{sgn}(\tau) \prod_{j}^{N} \left(\int dx_j \phi^*_{\sigma(j)}(x_j)\phi_{\tau(j)}(x_j) \right) \\ &= \frac{1}{N!} \sum_{\sigma\tau} \mathrm{sgn}(\sigma)\mathrm{sgn}(\tau) \prod_{j}^{N} \delta_{\tau(j),\sigma(j)} \\ &= \frac{1}{N!} \sum_{\sigma\tau} \mathrm{sgn}(\sigma)\mathrm{sgn}(\tau)\delta_{\tau,\sigma} \\ &= \frac{1}{N!} \sum_{\sigma} \mathrm{sgn}^2(\sigma) \\ &= \frac{1}{N!} N! \\ &= 1. \end{aligned} \tag{106}$$

Eigenstates of a non-interacting system

The Hamiltonian of a non-interacting particle system is expressed as the sum of single-particle Hamiltonians $\hat{h}(x)$ for each particle, as follows:

$$\hat{H} = \sum_{j=1}^{N} \hat{h}(x_j). \tag{107}$$

Here, we introduce the orthonormal eigenstates of the single-particle Hamiltonian as follows:

$$\hat{h}(x)\phi_j(x) = \varepsilon_j \phi_j(x). \tag{108}$$

In this case, the Slater determinant composed of the eigenstates $\phi_j(x)$ becomes an eigenstate of the many-body Hamiltonian $\hat{H}$. This can be demonstrated as follows:

$$\begin{aligned}
\hat{H}\Phi(x_1, \cdots, x_N) &= \sum_{j=1}^{N} \hat{h}(x_j) \frac{1}{\sqrt{N!}} \sum_{\sigma} \mathrm{sgn}(\sigma) \prod_{k}^{N} \phi_{\sigma(k)}(x_k) \\
&= \frac{1}{\sqrt{N!}} \sum_{\sigma} \mathrm{sgn}(\sigma) \left(\sum_{j=1}^{N} \hat{h}(x_j) \right) \prod_{k}^{N} \phi_{\sigma(k)}(x_k) \\
&= \frac{1}{\sqrt{N!}} \sum_{\sigma} \mathrm{sgn}(\sigma) \left(\sum_{j=1}^{N} \hat{\varepsilon}_{\sigma(j)} \right) \prod_{k}^{N} \phi_{\sigma(k)}(x_k) \\
&= \frac{1}{\sqrt{N!}} \sum_{\sigma} \mathrm{sgn}(\sigma) \left(\sum_{j=1}^{N} \hat{\varepsilon}_{j} \right) \prod_{k}^{N} \phi_{\sigma(k)}(x_k) \\
&= \sum_{j=1}^{N} \varepsilon_j \frac{1}{\sqrt{N!}} \sum_{\sigma} \mathrm{sgn}(\sigma) \prod_{k}^{N} \phi_{\sigma(k)}(x_k) \\
&= \left(\sum_{j=1}^{N} \varepsilon_j \right) \Phi(x_1, \cdots, x_N) \\
&= E\Phi(x_1, \cdots, x_N).
\end{aligned} \tag{109}$$

Here, we have defined $E = \sum_{j=1}^{N} \varepsilon_j$. In this way, the eigenstates of a non-interacting system can be represented by a single Slater determinant, and each orbital forming the Slater determinant is an eigenstate of the single-particle Hamiltonian. Additionally, the energy eigenvalue of the entire system is the sum of the energy eigenvalues of each orbital.

Expectation value of one-body operators

Hamiltonians of non-interacting particle systems, such as $\hat{H} = \sum_j \hat{h}(x_j)$, and the total momentum of the system, $\hat{\boldsymbol{P}} = \sum_j \hat{\boldsymbol{p}}_j$, are expressed as sums of operators (such as $\hat{h}(x)$ and $\hat{\boldsymbol{p}}$) that involve only the degrees of freedom of a single particle. These types of operators are called one-body operators. In general, a one-body operator $\hat{A}$ for an N-particle system can be written in the following form:

$$\hat{A} = \sum_{j=1}^{N} \hat{a}(x_j). \tag{110}$$

Here, $\hat{a}(x_j)$ is an operator that acts only on the degrees of freedom of the j-th particle.

When evaluating the expectation value of such a one-body operator using a Slater determinant, the following relation is obtained:

$$
\begin{aligned}
&\int dx_1 \cdots dx_N \Phi^*(x_1, \cdots, x_N)\hat{A}\Phi(x_1, \cdots, x_N) \\
&= \sum_{l=1}^{N} \int dx_1 \cdots dx_N \Phi^*(x_1, \cdots, x_N)\hat{a}(x_l)\Phi(x_1, \cdots, x_N) \\
&= N \int dx_1 \cdots dx_N \Phi^*(x_1, \cdots, x_N)\hat{a}(x_1)\Phi(x_1, \cdots, x_N) \\
&= \frac{1}{N!} N \sum_{\sigma,\tau} \mathrm{sgn}(\sigma)\mathrm{sgn}(\tau) \int dx_1 \cdots dx_N \prod_{j=1}^{N} \phi^*_{\tau(j)}(x_j)\hat{a}(x_1) \prod_{k=1}^{N} \phi_{\sigma(k)}(x_k) \\
&= \frac{1}{N!} N \sum_{\sigma,\tau} \mathrm{sgn}(\sigma)\mathrm{sgn}(\tau) \int dx_1 \phi^*_{\tau(1)}(x_1)\hat{a}(x_1)\phi_{\sigma(1)}(x_1) \prod_{j=2}^{N} \left(\int dx_j \phi^*_{\tau(j)}(x_j)\phi_{\sigma(j)}(x_j) \right) \\
&= \sum_{j=1}^{N} \int dx \phi^*_j(x)\hat{a}(x)\phi_j(x). \qquad (111)
\end{aligned}
$$

Therefore, when the expectation value of a one-body operator is calculated using a Slater determinant, the value is equal to the sum of the expectation values of the corresponding one-body operator for each orbital.

Expectation value of two-body interaction operators

Consider the following two-body interaction potential:

$$
\hat{W} = \frac{1}{2} \sum_{i \neq j}^{N} W(x_i, x_j). \qquad (112)
$$

Here, the interaction potential $W(x_i, x_j)$ is assumed to satisfy $W(x_i, x_j) = W(x_j, x_i)$.

Using a Slater determinant, the expectation value of $\hat{W}$ can be evaluated as follows:

$$
\begin{aligned}
\langle W \rangle &= \int dx_1 \cdots dx_N \ \Phi^*(x_1, \cdots, x_N)\hat{W}\Phi(x_1, \cdots, x_N) \\
&= \frac{1}{2} \sum_{l \neq m} \int dx_1 \cdots dx_N \Phi^*(x_1, \cdots, x_N) W(x_l, x_m)\Phi(x_1, \cdots, x_N) \\
&= \frac{N(N-1)}{2} \int dx_1 \cdots dx_N \Phi^*(x_1, \cdots, x_N) W(x_1, x_2)\Phi(x_1, \cdots, x_N) \\
&= \frac{N(N-1)}{N!} \sum_{\sigma,\tau} \mathrm{sgn}(\sigma)\mathrm{sgn}(\tau) \int dx_1 \int dx_2 \ \phi^*_{\tau(1)}(x_1)\phi^*_{\tau(2)}(x_2) W(x_1, x_2)\phi_{\sigma(1)}(x_1)\phi_{\sigma(2)}(x_2) \\
&\times \int dx_3 \cdots dx_N \prod_{j=3}^{N} \phi^*_{\tau(j)}(x_j)\phi_{\sigma(j)}(x_j) \\
&= \frac{1}{2} \sum_{jk} \int dx dx' \left|\phi_j(x)\right|^2 \left|\phi_k(x')\right|^2 W(x, x') - \frac{1}{2} \sum_{jk} \int dx dx' \phi^*_j(x)\phi^*_k(x') W(x, x')\phi_k(x)\phi_j(x') \\
&= \frac{1}{2} \int dx dx' \rho(x)\rho(x') W(x, x') - \frac{1}{2} \int dx dx' \rho(x, x')\rho(x', x) W(x, x'). \qquad (113)
\end{aligned}
$$

Here, the one-body density $\rho(x)$ and the one-body reduced density matrix $\rho(x, x')$ are defined as follows:

$$\rho(x) = \frac{N\int dx_2 \cdots dx_N |\Phi(x, x_2, \cdots, x_N)|^2}{\int dx_1 \cdots dx_N |\Phi(x_1, x_2, \cdots, x_N)|^2} = \sum_{j=1}^{N} |\phi_j(x)|^2 , \tag{114}$$

$$\rho(x, x') = \frac{N\int dx_2 \cdots dx_N \Phi(x, x_2, \cdots, x_N)\Phi^*(x', x_2, \cdots, x_N)}{\int dx_1 \cdots dx_N |\Phi(x_1, x_2, \cdots, x_N)|^2} = \sum_{j=1}^{N} \phi_j(x)\phi_j^*(x'). \tag{115}$$

Regarding the expectation value of the two-body interaction calculated using the Slater determinant, the first term on the right-hand side of Eq. (113) is called the direct term or Hartree energy. The second term is called the exchange term or exchange energy.

3.8.2 Hartree–Fock equation

Let us consider minimizing the expectation value of the energy of a many-body system using the variational method, with the Slater determinant as the trial wavefunction. For a concrete calculation, let us consider the Hamiltonian of a many-body system as follows:

$$\hat{H} = \sum_{j=1}^{N} \hat{h}(x_j) + \frac{1}{2}\sum_{i \neq j}^{N} W(x_i, x_j). \tag{116}$$

Here, the interaction potential $W(x_i, x_j)$ is assumed to satisfy $W(x_i, x_j) = W(x_j, x_i)$.

Evaluating the expectation value of the Hamiltonian in Eq. (116) using the Slater determinant $\Phi(x_1, \cdots, x_N)$ composed of N orthonormal single-particle orbitals $\{\phi_j(x)\}$ yields the following:

$$\begin{aligned} E &= \frac{\int dx_1 \cdots dx_N \Phi^*(x_1, \cdots, x_N)\hat{H}\Phi(x_1, \cdots, x_N)}{\int dx_1 \cdots dx_N \Phi^*(x_1, \cdots, x_N)\Phi(x_1, \cdots, x_N)} \\ &= \sum_{j}^{N} \int dx \phi_j^*(x)\hat{h}(x)\phi_j(x) + \frac{1}{2}\int dx dx' \rho(x)\rho(x')W(x, x') - \frac{1}{2}\int dx dx' \rho(x, x')\rho(x', x)W(x, x'). \end{aligned} \tag{117}$$

When the Slater determinant $\Phi(x_1, \cdots, x_N)$ minimizes the energy in Eq. (117), the first-order term of the energy variation δE must vanish when a small change is made to each single-particle orbital. For example, when the k-th orbital $\phi_k(x)$ is varied as $\phi_k(x) + \delta\phi_k(x)$, the first-order term in $\delta\phi_k(x)$ in the variation of the energy expectation value must be zero. Based on this requirement, one can derive the equations that each orbital must satisfy. However, note that the expression in Eq. (117) assumes that each orbital is normalized and orthogonal to the others, so the orbitals $\{\phi_k(x)\}$ cannot be varied freely. For such a constrained minimization problem, one can use the method of Lagrange multipliers[2]. Instead of minimizing the energy expectation value E, we consider minimizing the following quantity:

$$\begin{aligned} L = E &- \sum_{m=1}^{N} \varepsilon_{mm} \left(\int dx |\phi_m(x)|^2 - 1 \right) \\ &- \sum_{m=1}^{N} \sum_{n=1}^{m-1} \varepsilon_{mn}^{\mathrm{R}} \int dx \left[\phi_m^*(x)\phi_n(x) + \phi_m(x)\phi_n^*(x) \right] \\ &- \sum_{m=1}^{N} \sum_{n=1}^{m-1} i\varepsilon_{mn}^{\mathrm{I}} \int dx \left[\phi_m^*(x)\phi_n(x) - \phi_m(x)\phi^* * n(x) \right]. \end{aligned} \tag{118}$$

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[2] When deriving the Hartree–Fock equation in Eq. (88), the normalization factors were treated explicitly, so the equation was derived without using constraint conditions. In this case as well, one could treat the normalization factors explicitly and avoid constrained minimization, but using the method of Lagrange multipliers gives better clarity because the calculations would otherwise become complicated.

Here, ε_{mm}, $\varepsilon^{\mathrm{R}}_{mn}$, and $\varepsilon^{\mathrm{I}}_{mn}$ are Lagrange multipliers, which are real numbers introduced to satisfy the orthonormality conditions of the orbitals. Also note that constraint conditions are imposed on both the real and imaginary parts of the inner products of the orbitals.

The equation that each orbital must satisfy is derived from the condition that the functional derivative of L with respect to each orbital $\{\phi_k(x)\}$ vanishes. Evaluating the functional derivative with respect to the k-th orbital $\phi_k(x)$ gives the following expression:

$$\begin{aligned}\frac{\delta L}{\delta\phi^*_k(x)} &= \frac{\delta E}{\delta\phi^*_k(x)} - \varepsilon_{kk}\phi_k(x)\\ &\quad - \sum_{n=1}^{k-1}\varepsilon^{\mathrm{R}}_{kn}\phi_n(x) - \sum_{m=k+1}^{N}\varepsilon^{\mathrm{R}}_{mk}\phi_m(x) - \sum_{n=1}^{k-1} i\varepsilon^{\mathrm{I}}_{kn}\phi_n(x) + \sum_{m=k+1}^{N} i\varepsilon^{\mathrm{I}}_{mk}\phi_m(x). \end{aligned} \tag{119}$$

Now, the Lagrange multipliers $\varepsilon^{\mathrm{R}}_{mn}$ and $\varepsilon^{\mathrm{I}}_{mn}$ were defined only for $m > n$. For the case where $m < n$, let us introduce the following new notation:

$$\varepsilon^{\mathrm{R}}_{mn} = \varepsilon^{\mathrm{R}}_{nm}, \tag{120}$$

$$\varepsilon^{\mathrm{I}}_{mn} = -\varepsilon^{\mathrm{I}}_{nm}. \tag{121}$$

Furthermore, let us introduce the following complex number ε_{mn}:

$$\varepsilon_{mn} = \varepsilon^{\mathrm{R}}_{mn} + i\varepsilon^{\mathrm{I}}_{mn}. \tag{122}$$

From the definition, it is clear that $\varepsilon^*_{mn} = \varepsilon_{nm}$ holds.

By introducing the complex constants ε_{mn} in this way, we can rewrite Eq. (119) and express the functional derivative of L as follows:

$$\begin{aligned}\frac{\delta L}{\delta\phi^*_k(x)} &= \frac{\delta E}{\delta\phi^*_k(x)} - \sum_{m=1}^{N}\varepsilon_{km}\phi_m(x)\\ &= \left[\hat{h}(x) + \int dx'\rho(x')W(x,x') + \hat{V}_F\right]\phi_k(x) - \sum_{m=1}^{N}\varepsilon_{km}\phi_m(x). \end{aligned} \tag{123}$$

Here, the operator $\hat{V}_F$ is called the Fock operator, and is defined as follows:

$$\hat{V}_F\phi(x) = -\int dx'\rho(x,x')W(x,x')\phi(x'). \tag{124}$$

Ultimately, from the condition that Eq. (123) vanishes, the equation that $\phi_k(x)$ must satisfy is given as follows:

$$\left[\hat{h}(x) + \int dx'\rho(x')W(x,x') + \hat{V}_F\right]\phi_k(x) = \sum_{m=1}^{N}\varepsilon_{km}\phi_m(x). \tag{125}$$

The Slater determinant remains invariant under the following arbitrary unitary transformation:

$$\phi_k(x) = \sum_{m=1}^{N} U_{km}\tilde{\phi}_m(x). \tag{126}$$

Here, U_{km} is the (k,m) matrix element of an arbitrary unitary matrix U. Let us consider using this arbitrariness to rewrite the equation in a more convenient form.

Let the (n,k) matrix element of the inverse of the unitary matrix U be denoted by $\left(U^{-1}\right)_{nk}$, and consider multiplying both sides of Eq. (125) by $\left(U^{-1}\right)_{nk}$ and summing over k. This yields the following equation:

$$\sum_{k=1}^{N}\left(U^{-1}\right)_{nk}\left[\hat{h}(x) + \int dx'\rho(x')V(x,x') + \hat{V}_F\right]\phi_k(x) = \sum_{k=1}^{N}\left(U^{-1}\right)_{nk}\sum_{m=1}^{N}\varepsilon_{km}\phi_m(x). \tag{127}$$

Furthermore, by substituting the unitary transformation of Eq. (126), we obtain:

$$\left[\hat{h}(x) + \int dx' \rho(x') V(x,x') + \hat{V}_F\right] \tilde{\phi}_n(x) = \sum_{k=1}^{N} \left(U^{-1}\right)_{nk} \sum_{m=1}^{N} \varepsilon_{km} \sum_{l=1}^{N} U_{ml} \tilde{\phi}_l. \tag{128}$$

Since the Slater determinant is invariant under any unitary transformation such as Eq. (126), the unitary matrix U can be chosen freely without affecting the result. Therefore, we choose the unitary matrix U so that it diagonalizes the Hermitian matrix K, whose matrix elements are ε_{mn}. That is,

$$U^{-1} K U = \begin{pmatrix} \varepsilon_1 & & & & \\ & \varepsilon_2 & & \text{\huge 0} & \\ & & \ddots & & \\ & \text{\huge 0} & & \ddots & \\ & & & & \varepsilon_N \end{pmatrix} \tag{129}$$

so that U is chosen accordingly. Here, ε_k are the eigenvalues of the Hermitian matrix K.

By rewriting $\tilde{\phi}_k(x)$ as $\phi_k(x)$, we ultimately arrive at the following equation that the single-particle orbital $\phi_k(x)$ must satisfy:

$$\left[\hat{h}(x) + \int dx' \rho(x') V(x,x') + \hat{V}_F\right] \phi_k(x) = \varepsilon_k \phi_k(x). \tag{130}$$

This equation is known as the Hartree–Fock equation. While originally dealing with a many-body problem, Eq. (130) takes a form similar to a single-particle Schrödinger equation. At this point, the Hamiltonian governing the motion of a single-particle orbital consists of the original one-body Hamiltonian $\hat{h}(x)$, along with the classical potential (Hartree potential) created by the particle density $\rho(x)$,

$$\int dx' \rho(x') V(x,x'), \tag{131}$$

and the Fock operator $\hat{V}_F$ arising from the antisymmetry of fermions, which are included as potentials. In this way, the effects of other particles are incorporated as an "average one-body potential," and such an approximation is sometimes referred to as the **mean-field approximation**.

4 Heavier atoms

In this section, we investigate the ground states of atoms heavier than the helium atom. Although such problems can also be studied using the Hartree–Fock equations discussed in the previous section, here we examine atomic ground states using density functional theory (DFT), which is widely used in recent condensed matter physics property calculations.

4.1 Density functional theory

Before specifically examining atomic ground states, let us explain the basics of DFT.

4.1.1 Kato's Theorem

Before considering DFT, let us examine an N-electron system under the influence of the Coulomb potential from atomic nuclei. Such an N-electron system is described by the following Hamiltonian:

$$\hat{H} = \sum_{j=1}^{N}\left[\frac{\boldsymbol{p}_j^2}{2m_e} - \sum_a \frac{e^2}{4\pi\varepsilon_0}\frac{Z_a}{|\boldsymbol{r}_j - \boldsymbol{R}_a|}\right] + \frac{1}{2}\sum_{i\neq j}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \frac{1}{2}\sum_{a\neq b}\frac{1}{4\pi\varepsilon_0}\frac{e^2 Z_a Z_b}{|\boldsymbol{R}_a - \boldsymbol{R}_b|}, \qquad (132)$$

where Z_a and $\boldsymbol{R}_a$ represent the charge and position of the a-th nucleus.

Given the number of electrons N and the charges and positions of the nuclei $\{Z_a, \boldsymbol{R}_a\}$, the Hamiltonian of the multi-electron system is determined. Furthermore, by solving the Schrödinger equation for that Hamiltonian, we can obtain the ground state wave function $\Psi_{\mathrm{gs}}(\boldsymbol{r}_1, s_{z,1}, \cdots, \boldsymbol{r}_N, s_{z,N})$, from which the electron density can be obtained as follows:

$$\rho(\boldsymbol{r}) = N \sum_{s_{z,1},\cdots,s_{z,N}} \int d\boldsymbol{r}_2 \cdots \boldsymbol{r}_N \left|\Psi_{\mathrm{gs}}(\boldsymbol{r}, s_{z,1}, \cdots, \boldsymbol{r}_N, s_{z,N})\right|^2. \qquad (133)$$

Therefore, given the number of electrons N and the nuclear charges and positions $\{Z_a, \boldsymbol{R}_a\}$, the ground state electron density $\rho(\boldsymbol{r})$ is determined.

Now, for a given electronic system, if the ground state electron density $\rho(\boldsymbol{r})$ is provided, is it possible to determine the number of electrons N and the nuclear charges and positions $\{Z_a, \boldsymbol{R}_a\}$ from just the information in $\rho(\boldsymbol{r})$? This is indeed possible and is known as **Kato's theorem** [5]. Let us now see specifically how to extract the number of electrons N and the nuclear charges and positions $\{Z_a, \boldsymbol{R}_a\}$ from the information in $\rho(\boldsymbol{r})$.

The simplest quantity is the number of electrons N, which can be obtained by integrating the given electron density $\rho(\boldsymbol{r})$ over all space:

$$N = \int d\boldsymbol{r}\rho(\boldsymbol{r}). \qquad (134)$$

Next, to determine the positions of the atomic nuclei $\boldsymbol{R}_a$ from the electron density, let us revisit the wave function of the hydrogen $1s$ orbital. The wave function of the hydrogen $1s$ orbital, such as in Eq. (15), is known to have a sharp structure (cusp) at the position of the nucleus. When the kinetic energy operator acts on such a wave function with a cusp, it exhibits a divergence at the cusp point. This positive divergence from the kinetic energy operator is canceled by the divergence of the Coulomb potential at the position of the nucleus, resulting in the $1s$ orbital wave function being an eigenstate of the Schrödinger equation for the hydrogen atom. Thus, since the Coulomb potential diverges at the positions of the nuclei, the wave function has a cusp to cancel this divergence, and such a sharp structure also appears in the electron density. Therefore, by exploring the positions of the cusps in the electron density, one can determine the positions of the nuclei $\boldsymbol{R}_a$ in the system.

Furthermore, the sharpness of the electron density at a point allows us to determine the nuclear charge at that point. Specifically, the following relation holds:

$$\frac{Z_a}{a_0} = -\frac{1}{2\rho(\boldsymbol{r})}\frac{d\rho(\boldsymbol{r})}{dr}\Big|_{\boldsymbol{r}\to\boldsymbol{R}_a}. \qquad (135)$$

Therefore, if the ground-state electron density $\rho(\boldsymbol{r})$ is known, the number of electrons N and the positions and charges of the nuclei $\boldsymbol{R}_a, Z_a$ can be determined. Furthermore, using this information, the Hamiltonian in Eq. (132) can be specified, and by solving the Schrödinger equation, the ground-state wave function can be obtained. In an N-electron many-body system composed of nuclei and electrons, the ground-state wave function is a functional of the ground-state electron density: $\Psi_{\mathrm{gs}}\left[\rho(\boldsymbol{r}')\right](\boldsymbol{r}_1, s_{z,1}, \cdots, \boldsymbol{r}_N, s_{z,N})$. This implies that the expectation value of any physical quantity in the ground state is a functional of the ground-state electron density.

4.1.2 The First Hohenberg–Kohn theorem

In the previous section, we discussed the motion of electrons confined by the Coulomb potential created by atomic nuclei. Here, we consider a more general case of many-particle systems under the influence of a one-body potential. Specifically, let us consider the following Hamiltonian:

$$\hat{H} = \sum_{j=1}^{N}\left[\frac{\boldsymbol{p}_j^2}{2m_e} + v(\boldsymbol{r}_j)\right] + \frac{1}{2}\sum_{i\neq j} w(|\boldsymbol{r}_i - \boldsymbol{r}_j|), \tag{136}$$

where $v(\boldsymbol{r})$ is a one-body potential, and $w(|\boldsymbol{r}|)$ is a two-particle interaction potential.

Here, we consider a many-particle system with a given interaction potential $w(|\boldsymbol{r}|)$. When a one-body potential $v(\boldsymbol{r})$ is given, we can solve the Schrödinger equation corresponding to the Hamiltonian in Eq. (136) to obtain the ground-state wave function $\Psi_{\mathrm{gs}}(\boldsymbol{r}_1, s_{z,1}, \cdots, \boldsymbol{r}_N, s_{z,N})$ and the ground-state particle density $n(\boldsymbol{r})$. Now, if the ground-state particle density $n(\boldsymbol{r})$ is given, can we uniquely determine the one-body potential $v(\boldsymbol{r})$ that yields that ground state? The answer to this question is given by the **first Hohenberg–Kohn theorem**.

The first Hohenberg–Kohn theorem states that, for the Hamiltonian in Eq. (136), there is a one-to-one correspondence between the one-body potential $v(\boldsymbol{r})$ and the ground-state particle density $n(\boldsymbol{r})$. However, potentials that differ only by an additive constant c are physically equivalent, as they merely shift the reference point of the energy, and are therefore considered the same potential.

To consider the one-to-one correspondence between the one-body potential $v(\boldsymbol{r})$ and the ground-state particle density $n(\boldsymbol{r})$, let us examine the mapping $f : v(\boldsymbol{r}) \to n(\boldsymbol{r})$. This mapping f assigns a specific $n(\boldsymbol{r})$ to each given one-body potential $v(\boldsymbol{r})$. This mapping can be realized by solving the Schrödinger equation with the Hamiltonian (Eq. 136) that includes the potential $v(\boldsymbol{r})$, and then evaluating the resulting density. Thus, the nontrivial aspect of the one-to-one correspondence lies in whether the inverse mapping $f^{-1} : v(\boldsymbol{r}) \leftarrow n(\boldsymbol{r})$ exists. Hohenberg and Kohn assumed that the ground state of the Hamiltonian in Eq. (136) is non-degenerate and demonstrated the existence of this inverse mapping as follows.

Here, we use proof by contradiction to show that "given a ground-state density $n(\boldsymbol{r})$, there is a unique one-body potential $v(\boldsymbol{r})$." For this, let us assume that "there exist different potentials $v(\boldsymbol{r})$ and $v'(\boldsymbol{r})$ that yield the same ground-state density $n(\boldsymbol{r})$." Furthermore, let us denote the Hamiltonian constructed from $v(\boldsymbol{r})$ as $\hat{H}$, and that from $v'(\boldsymbol{r})$ as $\hat{H}'$. Let the ground-state wave function and energy of $\hat{H}$ be $|\Psi\rangle$ and E, and those of $\hat{H}'$ be $|\Psi'\rangle$ and E'.

At this point, the variational principle gives the following relation:

$$E = \langle\Psi|\hat{H}|\Psi\rangle < \langle\Psi'|\hat{H}|\Psi'\rangle = \langle\Psi'|\hat{H}'|\Psi'\rangle + \langle\Psi'|\hat{H} - \hat{H}'|\Psi'\rangle = E' + \int d\boldsymbol{r}\, n(\boldsymbol{r})\left[v(\boldsymbol{r}) - v'(\boldsymbol{r})\right]. \tag{137}$$

Furthermore, the variational principle also gives the following relation:

$$E' = \langle\Psi'|\hat{H}'|\Psi'\rangle < \langle\Psi|\hat{H}'|\Psi\rangle = \langle\Psi|\hat{H}|\Psi\rangle + \langle\Psi|\hat{H}' - \hat{H}|\Psi\rangle = E + \int d\boldsymbol{r}\, n(\boldsymbol{r})\left[v'(\boldsymbol{r}) - v(\boldsymbol{r})\right]. \tag{138}$$

Here, adding both sides of Eq. (137) and Eq. (138) gives the following relation:

$$E + E' < E + E'. \tag{139}$$

This is clearly a contradiction. Therefore, the assumption that "there exist different potentials $v(\boldsymbol{r})$ and $v'(\boldsymbol{r})$ that yield the same ground state density $n(\boldsymbol{r})$" must be incorrect. In other words, it has been shown that "when a ground state density $n(\boldsymbol{r})$ is given, the external potential $v(\boldsymbol{r})$ is uniquely determined."

4.1.3 The Second Hohenberg–Kohn Theorem

In the previous section, we discussed the first Hohenberg–Kohn theorem, which states that there is a one-to-one correspondence between the external potential $v(\boldsymbol{r})$ and the ground-state density $n(\boldsymbol{r})$. This theorem tells us that if the ground-state density $n(\boldsymbol{r})$ is given, then the external potential $v(\boldsymbol{r})$ is uniquely determined. Therefore, it follows that the external potential $v(\boldsymbol{r})$ is a functional of the ground-state density: $v[n(\boldsymbol{r}')](\boldsymbol{r})$. Furthermore, since the ground state can be obtained by solving the Schrödinger equation for the Hamiltonian with this external potential $v[n(\boldsymbol{r}')](\boldsymbol{r})$, the ground-state wave function $|\Psi_{gs}[n(\boldsymbol{r})]\rangle$ and the energy $E[n(\boldsymbol{r})]$ are also functionals of the ground-state density $n(\boldsymbol{r})$. Hence, all physical quantities of the system are functionals of the ground-state density of the system.

Then, we consider the Hamiltonian $\hat{H}$ of Eq. (136) with a certain external potential $v(\boldsymbol{r})$, and the corresponding ground-state wave function $|\Psi_{gs}\rangle$, energy E_{gs}, and density $n(\boldsymbol{r})$. Also, let $\rho(\boldsymbol{r})$ be the ground-state density obtained using certain external potential $\tilde{v}(\boldsymbol{r})$ in Eq. (136). Here, $\tilde{v}(\boldsymbol{r})$ and $\rho(\boldsymbol{r})$ may or may not coincide with $v(\boldsymbol{r})$ and $n(\boldsymbol{r})$. Furthermore, according to the above discussion, the wave function that has $\rho(\boldsymbol{r})$ as its ground-state density can be expressed as a functional of $\rho(\boldsymbol{r})$, namely $|\tilde{\Psi}_{gs}\,[\rho(\boldsymbol{r})]\rangle$.

Here, by explicitly indicating the dependence on the external potential $v(\boldsymbol{r})$, we introduce the following energy functional:

$$E_v[\rho(\boldsymbol{r})] = \langle\tilde{\Psi}_{gs}\,[\rho(\boldsymbol{r})]\,|\hat{H}|\tilde{\Psi}_{gs}\,[\rho(\boldsymbol{r})]\rangle. \tag{140}$$

By the variational principle applied to the wavefunction, the following **second Hohenberg–Kohn theorem** immediately holds:

$$E_v[\rho(\boldsymbol{r})] \geq E_v[n(\boldsymbol{r})] = E_{gs}. \tag{141}$$

Here, note that $n(\boldsymbol{r})$ is the ground-state density corresponding to the external potential $v(\boldsymbol{r})$.

From Eq. (141), it follows that the energy functional $E_v[\rho(\boldsymbol{r})]$ can never be less than the ground-state energy E_{gs} of the Hamiltonian $\hat{H}$ constructed from the external potential $v(\boldsymbol{r})$, for any $\rho(\boldsymbol{r})$. Moreover, the minimum value of $E_v[\rho(\boldsymbol{r})]$ is the ground-state energy E_{gs} of $\hat{H}$, and the only density that gives this value is $\rho(\boldsymbol{r}) = n(\boldsymbol{r})$.

Thanks to the second Hohenberg–Kohn theorem, it becomes possible to adopt a variational principle that minimizes the energy functional in order to find the true ground-state density. Even in practical DFT calculations, finding the density that minimizes the energy functional constitutes the main computational cost of DFT calculations.

To examine the energy functional in Eq. (140) more closely, consider writing the Hamiltonian $\hat{H}$ as

$$\begin{aligned} E_v[\rho(\boldsymbol{r})] &= \langle\tilde{\Psi}_{gs}\,[\rho(\boldsymbol{r})]\,|\hat{V}|\tilde{\Psi}_{gs}\,[\rho(\boldsymbol{r})]\rangle + \langle\tilde{\Psi}_{gs}\,[\rho(\boldsymbol{r})]\,|\hat{T}+\hat{W}|\tilde{\Psi}_{gs}\,[\rho(\boldsymbol{r})]\rangle \\ &= \int d\boldsymbol{r}\, v(\boldsymbol{r})\,\rho(\boldsymbol{r}) + \langle\tilde{\Psi}_{gs}\,[\rho(\boldsymbol{r})]\,|\hat{T}+\hat{W}|\Psi_{gs}\,[\rho(\boldsymbol{r})]\rangle \\ &= \int d\boldsymbol{r}\, v(\boldsymbol{r})\,\rho(\boldsymbol{r}) + F_{HK}\,[\rho(\boldsymbol{r})]\,, \end{aligned} \tag{142}$$

where $\hat{V}$ is the one-body potential, $\hat{T}$ is the kinetic energy, and $\hat{W}$ is the two-body interaction potential.

Here, the energy functional $E_v[\rho(\boldsymbol{r})]$ is seen to consist of a term that depends on the one-body potential $v(\boldsymbol{r})$ and a term that does not:

$$F_{HK}\,[\rho(\boldsymbol{r})] = \langle\tilde{\Psi}_{gs}\,[\rho(\boldsymbol{r})]\,|\hat{T}+\hat{W}|\tilde{\Psi}_{gs}\,[\rho(\boldsymbol{r})]\rangle. \tag{143}$$

Since $F_{HK}\left[\rho(\boldsymbol{r})\right]$ does not depend on the one-body potential (i.e., it is system-independent), it is called the **universal functional**. In principle, if this universal functional were known in an explicit form, one could investigate the ground state of any system (any $v(\boldsymbol{r})$) by minimizing the energy functional in Eq. (142). However, in practice, it is difficult to determine the universal functional $F_{HK}\left[\rho(\boldsymbol{r})\right]$ explicitly, and practical calculations are performed using various approximations. Hence, the accuracy of DFT calculations significantly depends on the approximation of exchange-correlation functionals.

4.1.4 Kohn–Sham Method

In addition to the difficulty of explicitly determining the universal functional $F_{HK}[\rho(\boldsymbol{r})]$, it is also not easy to construct an accurate approximate functional. In particular, describing the kinetic energy term of the universal functional in terms of the density is not straightforward[3].

Kohn and Sham proposed a method to evaluate this kinetic energy term by introducing a non-interacting fictitious system (the Kohn–Sham system). This method, known as the **Kohn–Sham method**, has become the foundation for practical DFT calculations.

To discuss the Kohn–Sham method, let us first introduce a non-interacting fictitious particle system called the Kohn–Sham system. The original many-body problem of interest was described by the Hamiltonian of an interacting many-body system given by Eq. (136). In contrast, let us consider the Hamiltonian $\hat{H}_s$ of the non-interacting particle system as follows:

$$\hat{H}_s = \sum_{j=1}^{N} \left[\frac{\boldsymbol{p}_j^2}{2m_e} + v_s(\boldsymbol{r}_j) \right]. \tag{144}$$

Let us denote the ground-state density of the Kohn–Sham system by $\rho(\boldsymbol{r})$, the first Hohenberg–Kohn theorem guarantees a one-to-one correspondence between $v_s(\boldsymbol{r})$ and $\rho(\boldsymbol{r})$. Furthermore, the ground-state wavefunction $|\Phi_s[\rho(\boldsymbol{r})]\rangle$ of $\hat{H}_s$ is a functional of $\rho(\boldsymbol{r})$. Using the ground state wavefunction of the Kohn–Sham system $|\Phi_s[\rho(\boldsymbol{r})]\rangle$ introduced in this way, let us rewrite the universal functional $F_{HK}[\rho(\boldsymbol{r})]$ as follows:

$$\begin{aligned} F_{HK}[\rho(\boldsymbol{r})] &= \langle \tilde{\Psi}_{gs}\left[\rho(\boldsymbol{r})\right] | \hat{T} + \hat{W} | \tilde{\Psi}_{gs}\left[\rho(\boldsymbol{r})\right] \rangle \\ &= \langle \Phi_s\left[\rho(\boldsymbol{r})\right] | \hat{T} | \Phi_s\left[\rho(\boldsymbol{r})\right] \rangle + \frac{1}{2} \int d\boldsymbol{r} d\boldsymbol{r}' \rho(\boldsymbol{r}) \rho(\boldsymbol{r}') w(|\boldsymbol{r} - \boldsymbol{r}'|) + E_{xc}\left[\rho(\boldsymbol{r})\right]. \end{aligned} \tag{145}$$

Here, the first term on the right-hand side is the kinetic energy of the Kohn–Sham system, the second term is the Hartree energy, and the third term is a quantity called the exchange-correlation energy $E_{xc}[\rho(\boldsymbol{r})]$. This exchange-correlation energy is introduced as the term that accounts for all the energy not captured by the first and second terms. Hence, the exchange-correlation energy is defined by

$$E_{xc}\left[\rho(\boldsymbol{r})\right] = F_{HK}[\rho(\boldsymbol{r})] - \langle \Phi_s\left[\rho(\boldsymbol{r})\right] | \hat{T} | \Phi_s\left[\rho(\boldsymbol{r})\right] \rangle - \frac{1}{2} \int d\boldsymbol{r} d\boldsymbol{r}' \rho(\boldsymbol{r}) \rho(\boldsymbol{r}') w(|\boldsymbol{r} - \boldsymbol{r}'|). \tag{146}$$

Up to this point, we have introduced the Kohn–Sham system and rewritten the universal functional $F_{KS}[\rho(\boldsymbol{r})]$ in the form of Eq. (145). Note that no approximations have been used in the discussion so far. In other words, Eq. (145) still represents an exact universal functional. Just as we did not know the explicit expression for $F_{KS}\left[\rho(\boldsymbol{r})\right]$, we still do not know the explicit expression for $E_{xc}\left[\rho(\boldsymbol{r})\right]$, and for practical calculations, it is necessary to approximate this exchange-correlation energy functional.

By rewriting the universal functional $F_{KS}\left[\rho(\boldsymbol{r})\right]$ using the Kohn–Sham system, the kinetic energy term within the universal functional $F_{KS}\left[\rho(\boldsymbol{r})\right]$ can be approximately, yet accurately, evaluated using the wavefunction of the Kohn–Sham system. Furthermore, by explicitly writing out the Hartree energy term in addition to the kinetic energy, it becomes possible to isolate the

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[3] For example, see Chapter 6 of [1].

majority of contributions in $F_{KS}\left[\rho(\boldsymbol{r})\right]$, and the remaining relatively small correction term is introduced as the unknown exchange-correlation functional $E_{xc}\left[\rho(\boldsymbol{r})\right]$. Through this decomposition of the energy functional, it becomes feasible to develop approximations and corrections for the exchange-correlation functional, which has relatively small contributions, thereby establishing the foundation for DFT calculations to achieve practical computational accuracy.

Here, we derive the fundamental equation of DFT calculations using the Kohn–Sham method, known as the **Kohn–Sham equation**. Noting that the Kohn–Sham system is a non-interacting system, its ground state wavefunction $|\Phi_s[\rho(\boldsymbol{r})]\rangle$ can be written as a Slater determinant composed of orthonormal single-particle orbitals $\{\phi_k(\boldsymbol{r})\chi_k(s_z)\}$. These single-particle orbitals are referred to as Kohn–Sham orbitals. The energy functional in Eq. (140) can be rewritten using the Kohn–Sham method as follows:

$$\begin{aligned} E_v[\rho(\boldsymbol{r})] &= \int d\boldsymbol{r} v(\boldsymbol{r})\rho(\boldsymbol{r}) + F_{HK}\left[\rho(\boldsymbol{r})\right] \\ &= \int d\boldsymbol{r} v(\boldsymbol{r})\rho(\boldsymbol{r}) + \int d\boldsymbol{r} \phi_k^*(\boldsymbol{r})\frac{-\hbar^2}{2m}\nabla^2\phi_k(\boldsymbol{r}) + \frac{1}{2}\int d\boldsymbol{r} d\boldsymbol{r}' \rho(\boldsymbol{r})\rho(\boldsymbol{r}')w(|\boldsymbol{r}-\boldsymbol{r}'|) + E_{xc}\left[\rho(\boldsymbol{r})\right]. \end{aligned} \tag{147}$$

Here, by the definition of the Kohn–Sham system, the density $\rho(\boldsymbol{r})$ is given as:

$$\rho(\boldsymbol{r}) = \sum_{k=1}^{N} |\phi_k(\boldsymbol{r})|^2 . \tag{148}$$

Furthermore, let us derive the equation that the Kohn–Sham orbitals must satisfy using the variational principle. Just as we introduced the Hartree–Fock equation in Sec. 3.8.2, we consider the problem of minimizing the energy under the constraint that the Kohn–Sham orbitals are orthonormal. Using the method of Lagrange multipliers, it is found that the following quantity L should be minimized:

$$L = E_v[\rho(\boldsymbol{r})] - \sum_{mn}^{N} \lambda_{mn}\left(\int d\boldsymbol{r}\phi_m^*(\boldsymbol{r})\phi_n(\boldsymbol{r})\sum_{s_z}\chi_m^*(s_z)\chi_n(s_z) - \delta_{mn}\right). \tag{149}$$

Here, evaluating the functional derivative of L with respect to the Kohn–Sham orbitals yields the following:

$$\frac{\delta L}{\delta\phi_k^*(\boldsymbol{r})} = \left[-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r}) + \int d\boldsymbol{r}'\rho(\boldsymbol{r}')w(|\boldsymbol{r}-\boldsymbol{r}'|) + \frac{\delta E_{xc}\left[\rho(\boldsymbol{r})\right]}{\delta\rho(\boldsymbol{r})}\right]\phi_k(\boldsymbol{r}) - \sum_m \varepsilon_{km}\phi_m(\boldsymbol{r}). \tag{150}$$

Here, the complex number ε_{mn} is introduced as $\varepsilon_{mn} = \lambda_{mn}\sum_{s_z}\chi_m^*(s_z)\chi_n(s_z)$.

When the Kohn–Sham orbitals minimize L, this functional derivative becomes zero. Therefore, the Kohn–Sham orbitals satisfy the following equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r}) + \int d\boldsymbol{r}'\rho(\boldsymbol{r}')w(|\boldsymbol{r}-\boldsymbol{r}'|) + \frac{\delta E_{xc}\left[\rho(\boldsymbol{r})\right]}{\delta\rho(\boldsymbol{r})}\right]\phi_k(\boldsymbol{r}) = \sum_m \varepsilon_{km}\phi_m(\boldsymbol{r}). \tag{151}$$

Since the Slater determinant is invariant under unitary transformations of the orbitals, this arbitrariness allows the diagonalization of ε_{mn}[4]. As a result, the Kohn–Sham orbitals satisfy the following equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r}) + \int d\boldsymbol{r}'\rho(\boldsymbol{r}')w(|\boldsymbol{r}-\boldsymbol{r}'|) + v_{xc}\left[\rho(\boldsymbol{r})\right](\boldsymbol{r})\right]\phi_k(\boldsymbol{r}) = \varepsilon_k\phi_k(\boldsymbol{r}). \tag{152}$$

---

[4] For details, refer to the derivation of the Hartree–Fock equations in Section 3.8.2.

This equation is called the **Kohn–Sham equation** and is the fundamental equation of density functional theory. Also, $v_{xc}[\rho(\boldsymbol{r})](\boldsymbol{r})$ is called the exchange-correlation potential, and it is defined by

$$v_{xc}[\rho(\boldsymbol{r})](\boldsymbol{r}) = \frac{\delta E_{xc}\left[\rho(\boldsymbol{r})\right]}{\delta\rho(\boldsymbol{r})}. \tag{153}$$

Since the explicit form of the exact exchange-correlation functional $E_{xc}\left[\rho(\boldsymbol{r})\right]$ is not known, it is necessary to approximate $E_{xc}\left[\rho(\boldsymbol{r})\right]$ in order to carry out practical DFT calculations. At present, various approximate exchange-correlation functionals have been developed, offering a range of choices depending on the trade-off between approximation accuracy and computational cost. Here, we introduce the simplest approximation, known as the **local density approximation (LDA)**.

The exchange-correlation functional is often written as the sum of the exchange energy and the correlation energy:

$$E_{xc}\left[\rho(\boldsymbol{r})\right] = E_x\left[\rho(\boldsymbol{r})\right] + E_c\left[\rho(\boldsymbol{r})\right]. \tag{154}$$

The exchange energy $E_x\left[\rho(\boldsymbol{r})\right]$ corresponds to the exchange energy in Eq. (113), while the correlation energy $E_c\left[\rho(\boldsymbol{r})\right]$ corresponds to the remaining energy.

To consider the local density approximation, let us first examine the problem of a uniform electron gas. We consider an N-electron system confined within a region of volume V. Furthermore, we examine the limit in which both the volume V and the number of particles N approach infinity while keeping the particle number density $\rho = N/V$ fixed. To ensure charge neutrality of the system, a uniform positive charge density $e\rho$ is assumed to be spread throughout the volume V. As the volume V of the system increases, the volume corresponding to the surface becomes relatively small. In the limit where the volume becomes infinite, the contribution of the surface region to physical quantities becomes negligible. Under these conditions, the energy per unit volume $\varepsilon = E/V$ becomes a quantity that depends only on the density ρ.

Applying the Hartree–Fock approximation discussed in Sec. 3.8.2 to such a uniform electron gas system, the energy density per unit volume can be evaluated as follows [5]:

$$\varepsilon_{HF}(\rho) = \frac{3}{5}\frac{\hbar^2}{2m_e}\left(3\pi\right)^{\frac{3}{2}}\rho^{\frac{5}{3}} - \frac{e^2}{4\pi\varepsilon_0}\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho^{\frac{4}{3}}. \tag{155}$$

Here, the first term represents the contribution from the kinetic energy of the electrons, and the second term represents the contribution from the exchange energy. Moreover, the contribution of the direct term (Hartree term) cancels out due to the electrostatic potential arising from the background positive charge and thus becomes zero. In a uniform electron gas, the only parameter characterizing the system is the electron density ρ, and physical quantities such as the energy density become functions solely of ρ.

Here, let us introduce the local density approximation for the exchange energy functional $E_x[\rho(\boldsymbol{r})]$. Using the expression for the exchange energy in the second term of Eq. (155), we introduce the following approximate exchange energy functional:

$$E_x^{\mathrm{LDA}}[\rho(\boldsymbol{r})] = \int d\boldsymbol{r}\varepsilon_x^{\mathrm{LDA}}\left(\rho(\boldsymbol{r})\right), \tag{156}$$

$$\varepsilon_x^{\mathrm{LDA}}\left(\rho(\boldsymbol{r})\right) = -\frac{e^2}{4\pi\varepsilon_0}\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho^{\frac{4}{3}}(\boldsymbol{r}). \tag{157}$$

This means that the exchange energy density is evaluated at each point in space using the electron density $\rho(\boldsymbol{r})$ at that point, based on the expression for the exchange energy density of a free electron gas, and then summed over all space. This kind of approximation, in which the energy is evaluated

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[5] For example, detailed calculations are described in [2]

locally using the density at each point in space, is called the Local Density Approximation (LDA). Moreover, the exchange potential $v_x^{\mathrm{LDA}}(\boldsymbol{r})$ corresponding to the exchange energy functional in Eq. (156) is obtained as follows:

$$v_x^{\mathrm{LDA}}(\boldsymbol{r}) = \frac{\delta E_x^{\mathrm{LDA}}[\rho(\boldsymbol{r})]}{\delta \rho(\boldsymbol{r})} = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho^{\frac{1}{3}}(\boldsymbol{r}). \tag{158}$$

Let us also briefly discuss the local density approximation for the correlation-energy functional. In the above discussion, the energy density of a free electron gas was evaluated using the Hartree–Fock approximation. However, there is, of course, a difference between the exact energy of the electron gas and the energy given by the Hartree–Fock approximation. This difference in energy between the Hartree–Fock approximation and the exact calculation is called the **correlation energy** or **electron correlation**. The correlation energy functional is the energy term introduced to account for this electron correlation.

Although it is difficult to analytically determine the exact ground-state energy density of a free electron gas, it is possible to obtain it numerically using methods such as Monte Carlo simulations. When the exact ground-state energy density obtained in this way is denoted as $\varepsilon_{\mathrm{exact}}^{\mathrm{HEG}}(\rho)$, the correlation energy density of the free electron gas is given by

$$\varepsilon_c^{\mathrm{HEG}}(\rho) = \varepsilon_{\mathrm{exact}}^{\mathrm{HEG}}(\rho) - \varepsilon_{HF}(\rho) \tag{159}$$

If such a density dependence is provided, the local density approximation of the correlation energy functional is given by

$$E_c^{\mathrm{LDA}}[\rho(\boldsymbol{r})] = \int d\boldsymbol{r} \varepsilon_c^{\mathrm{LDA}}\left(\rho(\boldsymbol{r})\right), \tag{160}$$

$$\varepsilon_c^{\mathrm{LDA}}\left(\rho(\boldsymbol{r})\right) = \varepsilon_c^{\mathrm{HEG}}(\rho(\boldsymbol{r})) \tag{161}$$

Expressions for specific local density approximations of the correlation functional can be found, for example, in Ref. [3].

4.2 Numerical solution of the Kohn–Sham equation assuming spherical symmetry

Let us now move on to a numerical calculation to investigate the ground state of an atom using the density functional theory introduced in the previous section. When the exchange-correlation potential $v_{xc}(\boldsymbol{r})$ is given, the Kohn–Sham equation to be solved is expressed as follows.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r} + v_H(\boldsymbol{r}) + v_{xc}(\boldsymbol{r})\right]\phi_k(\boldsymbol{r}) = \varepsilon_k \phi_k(\boldsymbol{r}). \tag{162}$$

Here, the Hartree potential $v_H(\boldsymbol{r})$ is defined by the following expression.

$$v_H(\boldsymbol{r}) = \frac{e^2}{4\pi\varepsilon_0}\int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}. \tag{163}$$

When $v_H(\boldsymbol{r})$ and $v_{xc}(\boldsymbol{r})$ possess spherical symmetry, it is possible to assume a solution of the following form, as in the numerical calculations for the hydrogen and helium atoms.

$$\phi_k(\boldsymbol{r}) = \frac{\chi_{k,l}(r)}{r} Y_{lm}(\theta,\phi). \tag{164}$$

The radial wave function $\chi_{k,l}(r)$ introduced in this manner satisfies the following radial Kohn–Sham equation.

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} + v_H(r) + v_{xc}(r)\right]\chi_{k,l}(r) = \varepsilon_{k,l}\chi_{k,l}(r). \tag{165}$$

This kind of eigenvalue equation can be solved using the shooting method introduced in Section 2.2.3.

By the way, it is not at all clear whether $v_H(\boldsymbol{r})$ and $v_{xc}(\boldsymbol{r})$ appearing in Eq. (162) are spherically symmetric. In fact, when the Kohn–Sham equation [Eq. (162)] is solved self-consistently using the local density approximation, the spherical symmetry of the density $\rho(\boldsymbol{r})$, $v_H(\boldsymbol{r})$, and $v_{xc}(\boldsymbol{r})$ may be broken for open-shell atoms. On the other hand, for closed-shell atoms such as noble gases, even in calculations that do not explicitly assume spherical symmetry, solutions with spherical symmetry are automatically obtained as a result of the computation.

Before explaining why symmetry may be broken in open-shell systems, let us explain why spherically symmetric solutions can be obtained in closed-shell systems. Suppose that in a certain closed-shell atom, the orbital angular momentum quantum number of the outermost electrons is l. In this case, the orbitals are $(2l+1)$-fold degenerate, and all orbitals are equally occupied. Under such conditions, when the density is evaluated as follows, the properties of spherical harmonics yield a spherically symmetric density.

$$\rho_{kl}(\boldsymbol{r}) = \sum_{m=-l}^{l} \left| \frac{\chi_{kl}(r)}{r} \right|^2 |Y_{lm}(\theta,\phi)|^2 = \frac{2l+1}{4\pi} \left| \frac{\chi_{kl}(r)}{r} \right|^2 = \rho(r). \tag{166}$$

Here, the property of spherical harmonics[6]

$$\sum_{m=-l}^{l} |Y_{lm}(\theta,\phi)|^2 = \frac{2l+1}{4\pi} \tag{167}$$

was used.

In such cases, the fact that the $(2l+1)$ degenerate orbitals are occupied with equal occupancy plays an important role in producing a spherically symmetric density. On the other hand, an open-shell atom is a system in which only some of the $2l+1$ outermost orbitals are occupied. In such a system, since the spherical harmonics $Y_{lm}(\theta,\phi)$ with different magnetic quantum numbers m are occupied with different weights, the symmetry breaks when summed, and the spherical symmetry of the density is lost.

Such symmetry breaking arises from the mean-field approximation, but here we proceed with the calculation by explicitly imposing spherical symmetry to simplify the computation. Specifically, we assume that the degenerate $2l+1$ orbitals are each occupied by an equal number of electrons. For example, a carbon atom is an electron many-body system with six electrons, and by considering spin degeneracy, we can regard it as an atom in which the $1s$ orbital holds two electrons, the $2s$ orbital holds two electrons, and the $2p$ orbital holds two electrons. In this case, the $2p$ orbital is open-shell, but by allowing fractional occupation numbers, we assume that the three orbitals with $m = +1, 0, -1$ are each occupied by $2/3$ of an electron. In such a situation, the electron density can be calculated to yield the following expression:

$$\begin{aligned}
\rho(\boldsymbol{r}) &= 2\left|\frac{\chi_{1s}(r)}{r}\right|^2 |Y_{00}(\theta,\phi)|^2 + 2\left|\frac{\chi_{2s}(r)}{r}\right|^2 |Y_{00}(\theta,\phi)|^2 \\
&\quad + \frac{2}{3}\left|\frac{\chi_{2p}(r)}{r}\right|^2 |Y_{1,1}(\theta,\phi)|^2 + \frac{2}{3}\left|\frac{\chi_{2p}(r)}{r}\right|^2 |Y_{1,0}(\theta,\phi)|^2 + \frac{2}{3}\left|\frac{\chi_{2p}(r)}{r}\right|^2 |Y_{1,-11}(\theta,\phi)|^2 \\
&= \frac{2}{4\pi}\left|\frac{\chi_{1s}(r)}{r}\right|^2 + \frac{2}{4\pi}\left|\frac{\chi_{2s}(r)}{r}\right|^2 + \frac{2}{4\pi}\left|\frac{\chi_{2p}(r)}{r}\right|^2 = \rho(r).
\end{aligned} \tag{168}$$

By allowing such rational occupation numbers, it becomes possible to maintain spherical symmetry in the density. Moreover, the potentials $v_H(\boldsymbol{r})$ and $v_{xc}(\boldsymbol{r})$, which are constructed from the spherically symmetric density, are also spherically symmetric.

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[6] See, for example, Ref. [4].

Finally, if we denote the occupation number of each introduced orbital by f_k, the electron density can be written as follows:

$$\rho(r) = \frac{1}{4\pi}\sum_k f_k \left|\frac{\chi_{k,l}(r)}{r}\right|^2 . \tag{169}$$

Also, let us introduce the following convenient expression for the total energy of the system:

$$\begin{aligned} E_{tot} &= \sum_{k=1}^{N} f_k \int d\boldsymbol{r}\phi_k^*(\boldsymbol{r})\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2 Z}{4\pi\varepsilon_0}\frac{1}{r}\right]\phi_k(\boldsymbol{r}) + \frac{1}{2}\int d\boldsymbol{r}\rho(\boldsymbol{r})v_H(\boldsymbol{r}) + E_{xc}\left[\rho(\boldsymbol{r})\right] \\ &= \sum_{k}^{N} f_k\varepsilon_k - \int d\boldsymbol{r}\rho(\boldsymbol{r})\left[v_H(\boldsymbol{r}) + v_{xc}(\boldsymbol{r})\right] + \frac{1}{2}\int d\boldsymbol{r}\rho(\boldsymbol{r})v_H(\boldsymbol{r}) + E_{xc}\left[\rho(\boldsymbol{r})\right]. \end{aligned} \tag{170}$$

Here, it is assumed that each Kohn–Sham orbital is a solution of the Kohn–Sham equation.

Combining the knowledge explained in the previous sections, it is possible to write a computational code to investigate the ground state of atoms. However, due to the increased complexity of the problem compared to the helium atom, issues may arise where the self-consistent field (SCF) calculation does not converge. As a countermeasure in such cases, let us introduce the linear mixing method.

In the simple self-consistent field method, one constructs $v_H(\boldsymbol{r})$ and $v_{xc}(\boldsymbol{r})$ using a preliminarily estimated density $\rho^n(\boldsymbol{r})$, and calculates the Kohn–Sham orbitals by diagonalizing the Kohn–Sham Hamiltonian composed of these potentials. Then, a new density $\rho^{\text{new}}(\boldsymbol{r})$ is obtained from the resulting Kohn–Sham orbitals and used as the estimated density for the next iteration:

$$\rho^{n+1}(\boldsymbol{r}) = \rho^{\text{new}}(\boldsymbol{r}). \tag{171}$$

By repeating this sequence of steps, if one is lucky, the difference between the input density $\rho^n(\boldsymbol{r})$ and the output density $\rho^{\text{new}}(\boldsymbol{r})$ will become smaller with each iteration, eventually leading to agreement between input and output, thereby achieving a self-consistent field.

However, this procedure does not necessarily converge. In particular, when the difference between the input density $\rho^n(\boldsymbol{r})$ and the output density $\rho^{\text{new}}(\boldsymbol{r})$ is large during a single update, convergence often becomes difficult. To mitigate such problems, there is a method where the estimated density $\rho^{n+1}(\boldsymbol{r})$ used in the next iteration is made by mixing the previous density $\rho^n(\boldsymbol{r})$ and the new density $\rho^{\text{new}}(\boldsymbol{r})$ obtained from the new Kohn–Sham orbitals. For example, using a constant α, the new estimated density can be formed as follows:

$$\rho^{n+1}(\boldsymbol{r}) = \alpha\rho^{\text{new}}(\boldsymbol{r}) + (1-\alpha)\rho^n(\boldsymbol{r}). \tag{172}$$

This method is called the **simple mixing** or **linear mixing** method. The larger the constant α, the greater the mixing ratio of the new density, and the smaller the α, the greater the mixing ratio of the old density.

Based on the explanation so far, let's try writing your own code to perform density functional theory (DFT) calculations for atoms, imposing spherical symmetry. For reference, Source code 4 shows an example of a DFT calculation code for atoms. In this example, the local density approximation is used for the exchange functional, and the correlation functional is approximated as zero.

`https://github.com/shunsuke-sato/python_qe/blob/develop/note_atom_dft/src/atom.py`

Source code 4: Example code for ground-state atomic calculation using the local density approximation

```
import numpy as np
from matplotlib import pyplot as plt

```

```

def calc_atom_gs(orb_name, orb_occ, nscf, rmax, dr, zval):

    num_orb, l_ang_mom, occupation, num_node  = list_of_orbitals(orb_name, orb_occ)
    num_grid = int(rmax/dr)+1
    rj = np.linspace(0.0, rmax, num_grid)
    phi = np.zeros((num_grid, num_orb))
    rho_old = np.zeros(num_grid)
    update_rate = 0.5

    for iscf in range(nscf):

        rho = calc_density(num_orb, phi, occupation)
        rho = update_rate*rho + (1.0 - update_rate)*rho_old
        rho_old = rho

        vhxc, vh, vxc = calc_potential(rho, rj, dr, num_grid)
        phi, epsilon_s = calc_wavefunction(rj, dr, num_grid, vhxc, zval, num_orb, l_ang_mom, num_node)

        total_energy = calc_total_energy(rj, dr, num_grid, phi, epsilon_s, rho, num_orb, vhxc, vh, occupation)

        print("iscf,␣energy␣=",iscf, total_energy, "Hartree")

    return num_orb, rj, phi, epsilon_s, total_energy

def calc_wavefunction(rj, dr, num_grid, vhxc, zval, num_orb, l_ang_mom, num_node):

    phi = np.zeros((num_grid, num_orb))
    epsilon_s = np.zeros(num_orb)

    for iorb in range(num_orb):

        phi_t, ene_t = shooting_method(rj, dr, num_grid, vhxc, zval, l_ang_mom[iorb], num_node[iorb])
        phi[:,iorb] = phi_t[:]
        epsilon_s[iorb] = ene_t

    return phi, epsilon_s


def list_of_orbitals(orb_name, orb_occ):
    num_orb = len(orb_name)

    l_ang_mom = np.zeros(num_orb)
    occupation  = np.zeros(num_orb)
    num_node = np.zeros(num_orb, dtype=int)

    num_node_s = 0
    num_node_p = 0
    num_node_d = 0
    num_node_f = 0

    for iorb in range(num_orb):
        occupation[iorb] = orb_occ[iorb]
        if(’s’ in orb_name[iorb].lower()):
            l_ang_mom[iorb] = 0.0
            num_node[iorb] = num_node_s
            num_node_s = num_node_s + 1
        elif(’p’ in orb_name[iorb].lower()):
            l_ang_mom[iorb] = 1.0
            num_node[iorb] = num_node_p
            num_node_p = num_node_p + 1
        elif(’d’ in orb_name[iorb].lower()):
            l_ang_mom[iorb] = 2.0
            num_node[iorb] = num_node_d
            num_node_d = num_node_d + 1
        elif(’f’ in orb_name[iorb].lower()):
            l_ang_mom[iorb] = 3.0
            num_node[iorb] = num_node_f
            num_node_f = num_node_f + 1

    return num_orb, l_ang_mom, occupation, num_node


def calc_density(num_orb, phi, occupation):

    rho = np.zeros(phi.shape[0])
    for iorb in range(num_orb):
```

```
        rho += occupation[iorb]*phi[:,iorb]**2

    return rho

def calc_potential(rho, rj, dr, num_grid):

    vhxc = np.zeros(num_grid)
    vh = np.zeros(num_grid)

    for i in range(num_grid):

        v1 = 0.0
        for j in range(i):
            v1 = v1 + rj[j]**2*rho[j]*dr

        v1 = v1 + 0.5*rj[i]**2*rho[i]*dr
        if(i == 0):
            v1 = 0.0
        else:
            v1 = 4.0*np.pi*v1/rj[i]


        v2 = 0.5*rj[i]*rho[i]*dr
        for j in range(i+1, num_grid):
            v2 = v2 + rj[j]*rho[j]*dr

        v2 = 4.0*np.pi*v2

        vh[i] = v1 + v2


    vxc = -((3.0/np.pi)*rho)**(1.0/3.0)
    vhxc = vh + vxc

    return vhxc, vh, vxc



def shooting_method(rj, dr, num_grid, vhxc, zval, l_ang_mom_in, num_node_in):

    ene_max = 0.1 * zval**2
    ene_min = -0.6 * zval**2


    for iter in range(100):
        ene_t = 0.5 * (ene_max + ene_min)

        chi, num_node_t = get_wavefunction(rj, dr, num_grid, vhxc, zval, ene_t, l_ang_mom_in)

        if num_node_t >= num_node_in+1:
            ene_max = ene_t
        else:
            ene_min = ene_t

        if ene_max - ene_min < 1e-6:
            break

    ene_t = ene_max
    chi, num_node_t = get_wavefunction(rj, dr, num_grid, vhxc, zval, ene_t, l_ang_mom_in)

    # refine wavefunction
    num_node_t = 0
    for j in range(1, num_grid - 1):
        if chi[j + 1] == 0.0:
            num_node_t += 1
        elif chi[j + 1] * chi[j] < 0.0:
            num_node_t += 1

        if num_node_t == num_node_in + 1:
            chi[j+1:] = 0.0
            break

    norm = np.sum(chi**2)*dr
    chi = chi/np.sqrt(norm)

    phi_t = np.zeros(num_grid)
    phi_t[1:num_grid-1] = chi[1:num_grid-1]/rj[1:num_grid-1]
    phi_t[0] = 2*phi_t[1] - phi_t[2]
    phi_t = phi_t/(np.sqrt(4.0*np.pi))

```

```

    return phi_t, ene_t

def get_wavefunction(rj, dr, num_grid, vhxc, zval, energy, l_ang):

    chi = np.zeros(num_grid)
    num_node = 0


    chi[0] = 0.0
    chi[1] = dr / zval

    factor = 2 * dr**2
    for j in range(1, num_grid - 1):
        potential = - zval / rj[j] + vhxc[j] + 0.5*l_ang*(l_ang+1.0)/rj[j]**2
        chi[j + 1] = (
            2 * chi[j] - chi[j - 1]
            - factor * (energy - potential) * chi[j]
        )

        if chi[j+1] == 0.0:
            num_node += 1
        elif chi[j+1] * chi[j] < 0.0:
            num_node += 1

    return chi, num_node

def calc_total_energy(rj, dr, num_grid, phi, epsilon_s, rho, num_orb, vhxc, vh, occupation):
    total_energy = np.sum(occupation*epsilon_s)
    total_energy = total_energy - 4.0*np.pi*np.sum(rho*vhxc*rj**2)*dr
    total_energy = total_energy + 0.5*4.0*np.pi*np.sum(rho*vh*rj**2)*dr
    total_energy = total_energy - 4.0*np.pi*(3.0/4.0)*(3.0/np.pi)**(1.0/3.0)*np.sum(rho**(4.0/3.0)*rj**2)*dr

    return total_energy


zval = 10.0
nscf = 30
rmax = 20.0
dr = 0.005

orb_name = ['1s', '2s', '2p' ]
orb_occ  = [2.0, 2.0, 6.0 ]


num_orb, rj, phi, epsilon_s, total_energy = calc_atom_gs(orb_name, orb_occ, nscf, rmax, dr, zval)

# The conversion factor from Hartree to electronvolt (eV)
ev = 27.2114

print("Total␣energy␣=", total_energy, "Hartree", total_energy*ev, "eV")
print("Single␣particle␣energies")
for iorb in range(num_orb):
    print(orb_name[iorb], ":", epsilon_s[iorb], "Hartree", epsilon_s[iorb]*ev, "eV")
```

By running the above Python code, one can compute the ground state of a Ne atom, but the execution can take a significant amount of time. To perform the calculation more quickly, one can accelerate it using Numba or write high-speed code in the Julia language.

The following URLs provide a Python code accelerated using Numba and a Julia code version optimized for speed.

Python code using Numba
`https://github.com/shunsuke-sato/python_qe/blob/develop/note_atom_dft/src/atom_numba.py`

Julia code
`https://github.com/shunsuke-sato/python_qe/blob/develop/note_atom_dft/src_jl/atom.jl`

4.3 ΔSCF method for calculating the ionization potential of atoms

As an application example of the atomic ground-state calculation code, let us evaluate the ionization potential of atoms based on density functional theory. As discussed in the introduction, the ionization potential of an atom is defined as the energy difference between the ground states of the atom and its ion. Therefore, one can calculate the ground-state energies of the neutral atom and the singly charged ion using the code developed in the previous section and then take their difference. This method is called the ΔSCF method.

Let us calculate the ionization potential of atoms using the ΔSCF method and compare it with experimental values. If necessary, the ionization potential values from the literature [CRC Handbook of Chemistry and Physics (84th edition)] are extracted on the following page and can be used: `https://en.wikipedia.org/wiki/Ionization_energies_of_the_elements_(data_page)`

When actually calculating the ionization potential using the ΔSCF method, one will notice that, despite the simplicity of the approximation used (such as the local density approximation), it reproduces the experimental values with high accuracy. This result is achieved because the errors contained in the ground states of the neutral atom and the ion cancel each other out (Error cancelation) when calculating the energy difference using the ΔSCF method. In actual materials calculations, simple approximations like the local density approximation are often insufficient. In such cases, it becomes necessary to use more sophisticated approximate functionals.

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