Problem set 5: Thomas-Fermi model for many-electron atoms

For questions contact: tabea.buhler@epfl.ch

In this exercise sheet we will explore the Thomas-Fermi model, which was introduced independently by Llewellyn Thomas and Enrico Fermi in 1927 and describes many-electron atoms.

Exercise 1: From central field to the Thomas-Fermi equation for screening

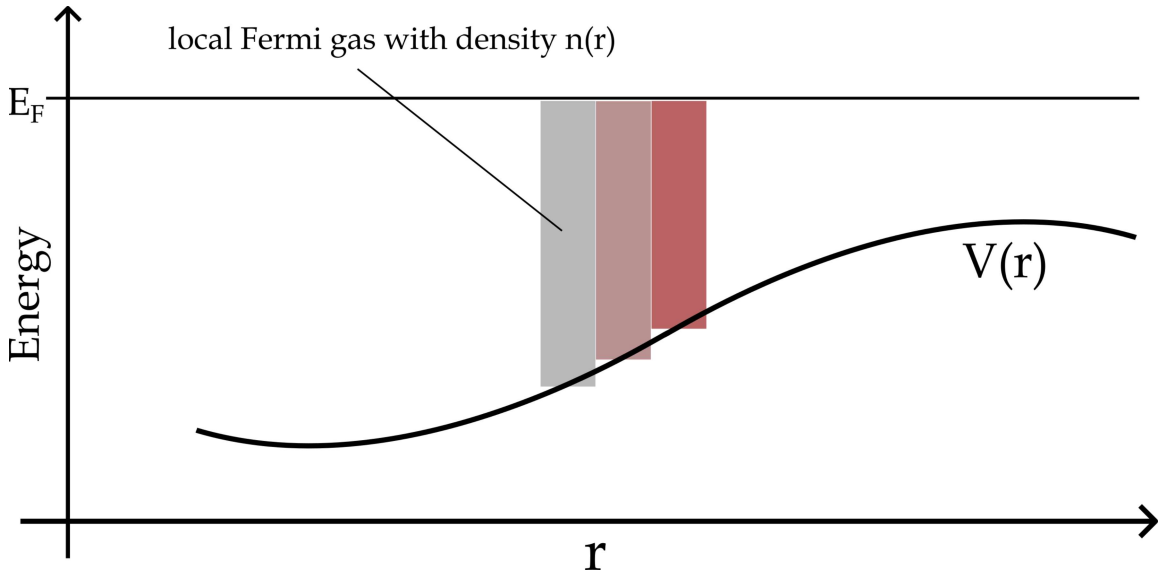
We consider an atom containing several electrons. Rather than analyzing the exact many-body Hamiltonian, we apply the concept of screening. In this approach, each electron is assumed to experience a centrally symmetric potential, which is not a pure Coulomb potential. Instead, the nuclear charge is effectively screened by the presence of other electrons within the atom. It follows the Ansatz for the potential $\phi(r)$ and the potential energy $V(r)$ experienced by an electron within the atom:

$$\phi(r) = \frac{1}{4\pi\epsilon_0}\frac{Ze}{r}F(r); \;\; V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}F(r),$$

where we call the dimensionless function $F(r)$ the screening function.

a) What should be the boundary condition $lim_{r\to 0}\, F(r)$ and why?

To derive properties of $V(r)$, the approach followed by Thomas and Fermi is to consider $V(r)$ to be *locally constant* and to describe the atomic electrons experiencing $V(r)$ locally as a degenerate Fermi gas with density $n(r)$ and Fermi wavevector $k_F(r)$:



b) The chemical potential μ is defined as the energy cost to add one particle to the system. Given the explanation and illustration above, write down μ considering the kinetic energy cost and the potential energy cost $V(r)$.
Hint: For an electron Fermi gas in 3 dimensions, recall the relation between density and Fermi wavevector: $k_F^3(r) = 3\pi^2 n(r)$.

We consider the atom to be in equilibrium (no net flow of electrons), which means that the total energy of an electron must be constant over the atom. This implies that the chemical potential μ is constant. Considering μ at $r \to \infty$, we further conclude $\mu = 0$.

c) Use the expression of the chemical potential μ to derive the electron density $n(r)$ as a function of the screening function $F(r)$.

It follows another, conceptually important step in the Thomas-Fermi treatment of atoms. It is imposed that the potential $\phi(r)$ obeys the electrostatic Poisson equation:

$$\frac{1}{r}\,\partial_r^2\,(r\phi(r)) = -\frac{\rho(r)}{\epsilon_0},$$

where we directly consider $\rho(r)$ to be spherically symmetric and write the Poisson equation for r only. $\rho(r)$ is the charge density of the electrons causing the electrostatic potential, related to the electron density as $\rho(r) = -e\,n(r)$.

d) Use the Poisson equation to show the following relation between the partial derivative of the screening function and the electron density:

$$\frac{Z}{r}\partial_r^2 F(r) = 4\pi n(r).$$

e) Use the results of c) and d) to derive a partial differential equation for the screening function $F(r)$. Show that, by changing variable $r = \alpha x$, $F \to \tilde{F}$, where x is a dimensionless

variable, this partial differential equation takes the form:

$$\partial_x^2 \tilde{F}(x) = x^{-1/2} \tilde{F}^{3/2}(x) \tag{1}$$

This is called the Thomas-Fermi equation for screening.
Hint:

- To shorten notation you can use the definition of the Bohr radius $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$.

Exercise 2: The universal scaling solution

In this exercise we explore more in detail the Thomas-Fermi equation for screening and solve it numerically. We further look at its implications on the scaling of physical quantities.

a) Give the scaling law as a function of Z of the Thomas-Fermi atom of the following quantities:

- the radius r
- the potential V
- the density n
- the kinetic energy

Besides the boundary condition $lim_{x\to 0}\tilde{F}(x) = 1$ (no screening near the nucleus), the function $\tilde{F}(x)$ has to be a normalizable density distribution. This implies $lim_{x\to\infty}\, x\, \tilde{F}(x) = 0$ and therefore, $\tilde{F}(x)$ has to decay sufficiently fast.

b) Show that the asymptotic behaviour of $\tilde{F}(x)$ goes like $\tilde{F}(x) \approx 144/x^3$ for large x.
Hint: Propose that the leading contribution as $x \to \infty$ is of the form $\tilde{F} \propto \beta x^{-b}$ and write the leading contribution to equation (1).

c) Solve the non-linear differential equation numerically.
Hints:

- To avoid the singularity when $\sqrt{x} = 0$, rewrite the potential as $\tilde{F}(x) = (1 + \frac{4}{3}x^{3/2})\, y(x)$ and solve numerically the differential equation for $y(x)$.
- Note that

$$\lim_{x\to 0}\big(1 - (1 + \frac{4}{3}x^{3/2})^{3/2}\, \sqrt{y(x)}\big)\frac{1}{\sqrt{x}} = 0,$$

which can be set to zero with an *if* statement to avoid numerical problems.

- You can use the provided initial value for $y'(0)$, which ensures $y \to 0$ for $x \to \infty$.

In [1]:
```python
import numpy as np
from scipy.integrate import solve_ivp
import matplotlib.pyplot as plt
import matplotlib.colors as mcolors
```

In [1]:
```python
def solve_differential_equation(func, x_span, y0, method='LSODA', atol=1e-8, rtol=1
    """
    Solver for nonlinear differential equations.

    Parameters:
    - func: Callable. Defines the system of equations dy/dx = f(x, y).
            It should take the form func(x, y), where y can be a scalar or a list o
    - x_span: Tuple. The range of x values (x_start, x_end).
    - y0: List or array-like. Initial conditions for the system.
    - method: String. Integration method ('RK45', 'RK23', 'LSODA', etc.).
    - t_eval: Array-like. Points at which to store the computed solution.
    - plot_result: Boolean. Whether to plot the result.

    Returns:
    - solution: ODE solution object from scipy.integrate.solve_ivp.
    """

    # Provide default evaluation points if not specified
    if t_eval is None:
        t_eval = np.linspace(x_span[0], x_span[1], 500)

    # Solve differential equation
    sol = solve_ivp(func, x_span, y0, method=method, t_eval=t_eval)

    if plot_result:
        plt.figure(figsize=(7, 5))
        plt.plot(sol.t, sol.y[0])
        plt.xlabel('x')
        plt.ylabel('y(x)')
        plt.show()
    return sol


def DGL_system(x, y):
    # Rewrite secon order differential equation as a system of first order differen
    # z = y'; z' = y''

    dydx = y[1]

    ########################################################
    # Todo: define the differential equation
    ########################################################

    dzdx =

    return [dydx, dzdx]
```

In [46]:
```python
# Define x range and initial conditions
x_range = (0, 10)
initial_conditions = [1, -1.5886]  #[y(0), y'(0)]
```

```
# Solve differential equation with initial conditions
solution = solve_differential_equation(DGL_system, x_range, initial_conditions, plo
```

d) Plot the obtained solution for $\tilde{F}(x)$ for $x \in [0, 10]$ and comment on the regime $x \to 0$.

The Thomas-Fermi function $\tilde{F}(x)$ represents a universal scaling solution. It is called universal because $\tilde{F}(x)$ is independent of Z, i.e. the shape of the function is the same for all atoms. It is a scaling solution because the variable x depends on Z, i.e. the radial profile of the electron density scales with atomic size.

We will use the obtained solution $\tilde{F}(x)$ to predict the filling of electron shells in the periodic table.

e) Consider the effective potential V_{eff} associated with the Thomas-Fermi function $\tilde{F}(x)$. Show that for each value of ℓ there is a minimal value of Z such that the effective potential has a bound state. Use the numerical solution $\tilde{F}(x)$ to calculate Z associated to the angular momentum values $\ell = 1, 2, 3$. *Hints*:

- Consider the effective potential in atomic units $V_{eff}(r) = -\frac{Z}{r}F(r) + \frac{\ell(\ell+1)}{2r^2}$. We obtain a bound state if V_{eff} has a minimum with negative energy. Using the same change of variable as before, show that the minimal Z to obtain a bound state is

$$Z(\ell) = \frac{4}{3\pi}\left(\frac{\ell(\ell+1)}{\tilde{F}(x)x}\right)^{3/2}$$

- Determine numerically the value of x for which $\tilde{F}(x)x$ is maximal.

f) Give one example of a drawback of the Thomas-Fermi model of atoms as we have introduced it in this exercise.

In [ ]: