Solution to Exercise 7 in *Orbital-Free DFT*

Radial OFDFT Equation

Euler-Lagrange equation for $u(r) = r\xi(r) = r\sqrt{\rho(r)}$, for atoms with spherically symmetric ground state electron density, was derived in live script *Orbital-Free DFT* and looks

$$\hat{\mathscr{H}}_r u(r) = \mu u(r), \qquad (1)$$

with

$$\hat{\mathscr{H}}_r = -\frac{\lambda}{2}\frac{\partial^2}{\partial r^2} + \underline{V_{\text{eff}}[\rho](r)} = -\frac{\lambda}{2}\frac{\partial^2}{\partial r^2} + \underline{V_{\text{TF}}[\rho](r) + V_{\text{ext}}(r) + V_{\text{H}}[\rho](r) + V_{\text{xc}}[\rho](r)}.$$

Solution of Eq. (1) is unique, due to requirement $u(r) \geq 0$ (in 1D only ground state does not have nodes), and it is necessarily the ground state of Hamiltonian $\hat{\mathscr{H}}_r$.

Using self-consistent field algorithm, sketched in Fig. 1, in this live script we will iteratively obtain ground state of Hamiltonian $\hat{\mathscr{H}}_r$, starting from some initially guessed ground state electron density $\rho_0(r)$.

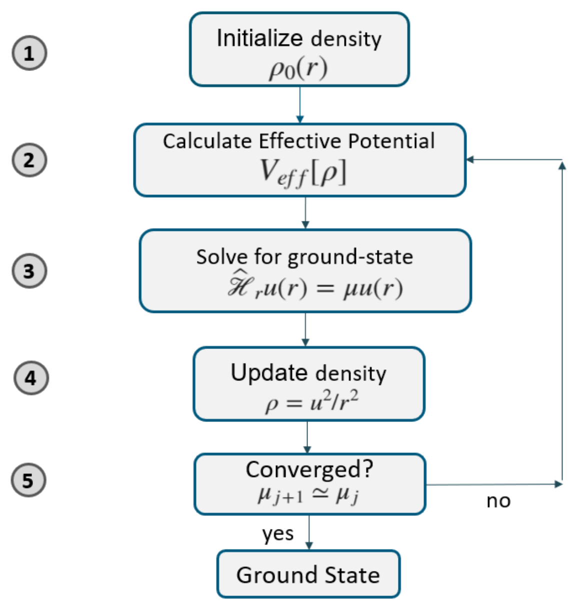


Figure 1: Sketch of numerical algorithm of self-consistent field method.

OFDFT Numerical Results

We start with selecting parameters for simulating ground state energy and electron density of atoms using the OFDFT solver based on self-consistent field method sketched in Fig. 1. We will compare OFDFT resutls with the TF results.

See live script on *Thomas-Fermi Approximation* where we saved structure variable `TFchi`, with `TFchi.x` and `TFchi.y` containing values of x and $\chi(x)$ - the universal parameter and the universal TF function respectively.

```
load TFchi.mat;
```

First we select the atom index Z, maximal radial length R_{max}, measured in Bohr radia, and number of grid points N_d in radial direction. Since in the TF model atom radius shrinks as $Z^{-1/3}$ wih increasing nuclear charge, and since densities produced by our OFDFT solver are not far from the TF results for large Z, we rescale R_{max} with the same factor.

```
Z = 4;
R_MAX = 60/Z^(1/3);
Nd=1200;
```

Next, we determine whether we allow the mixing of von Weizsäcker functional with non-zero parameter λ and use LDA-PZ (Local Density Approximation with Perdew-Zunger expression for correlation term) exchange-correlation (xc). When `xc=lda` is selected, $\lambda \simeq 0.212$ is a good choice for calculating ground state energies of atoms with $Z > 1$, for number of grid points in radial direction N_d up to 1200 sites and $R_{max} = 60/Z^{1/3}$.

```
lambda=0.212;
xc = 1;
```

Finally, we set up FDn - order for approximating derivatives by central finite differences, convergence tolerance `tol`, and density-mixing parameter `beta`.

```
FDn = 6;
tol = 1e-3;
beta=0.95;
```

Now we start our radial OFDFT simulation that is included and explained at the end of this script. We use the TF density profile for initial electron density.

```
fprintf("Analytical Thomas-Fermi energy for Z=%.d is %.4f Ha\n", Z,
-0.7687*Z^(7/3));
```

```
Analytical Thomas-Fermi energy for Z=4 is -19.5238 Ha
```

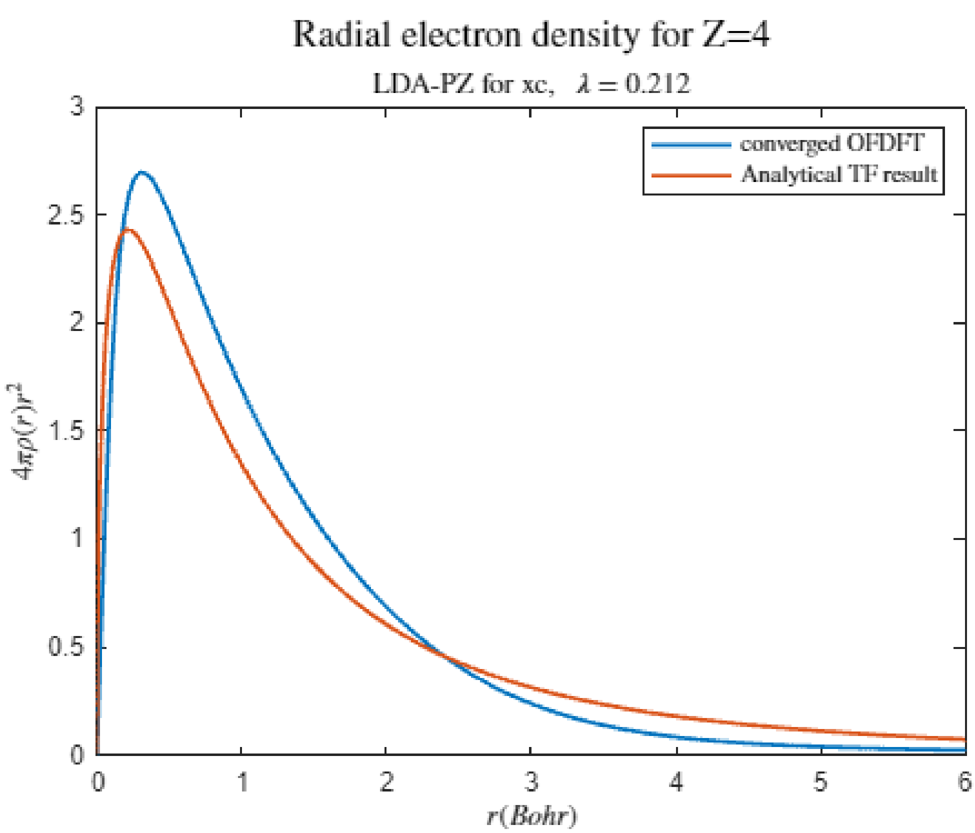
```
r_x = TFchi.x*Z^(-1/3)/1.1295; % see Eq. (32) in live script Thomas-Fermi
Approximation, where we saved variable TFchi
rho_r_x = 32/9/pi^3*(TFchi.y./TFchi.x).^(3/2)*Z^2; % see Eq. (35) in live script
Thomas-Fermi Approximation

S_OFDFT = init_OFDFT(Z,R_MAX,Nd,tol,FDn,lambda,xc,[r_x, rho_r_x],beta);
S_OFDFT = SCF(S_OFDFT); % run self-consistent field algorithm
```

```
Finished SCF method in 25 steps with μ = -0.2495
Energy decomposition
Ek   =  13.372909 Ha
Eh   =   6.987292 Ha
Exc  =  -2.407369 Ha
Ex  =  -2.178815 Ha
Ec  =  -0.228554 Ha
```

```
Eext = -32.554199 Ha
Etot = -14.601367 Ha, -397.323757 eV
```

After the electron density $\rho(r)$ is converged, we plot radial electron density $4\pi\rho(r)r^2$ as a function of distance from the nucleus (measured in units of Bohr radius), together with the TF result (that we loaded in variable `TFchi`).

```
plot([0;S_OFDFT.r],[0;4*pi*S_OFDFT.rho.*S_OFDFT.r.^2],r_x,4*pi*rho_r_x.*r_x.^2)
xlabel("$r (Bohr)$",Interpreter='latex')
ylabel("$4\pi \rho(r) r^2$",Interpreter='latex')
xlim([0 6])
legend("converged OFDFT","Analytical TF result",Interpreter='latex')
title(['Radial electron density for Z=',num2str(Z)],'Interpreter','latex',
fontsize=14)
if xc==1
    subtitle(['LDA-PZ for xc, \,\, $\lambda=$',num2str(lambda)],Interpreter='latex')
else
    subtitle(['No xc, \,\, $\lambda=$',num2str(lambda)],Interpreter='latex')
end
```



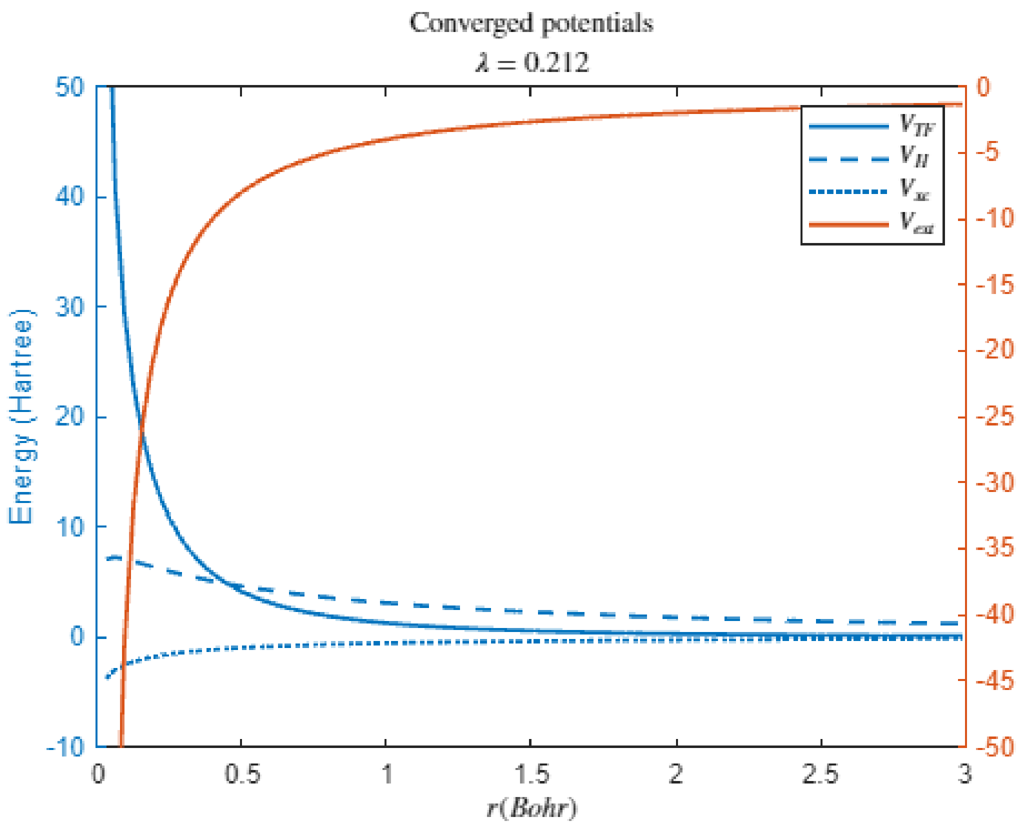
Next, we plot the radial dependence of

- External potential $V_{\text{ext}}(r)$

and of the converged values of (for converged ρ):

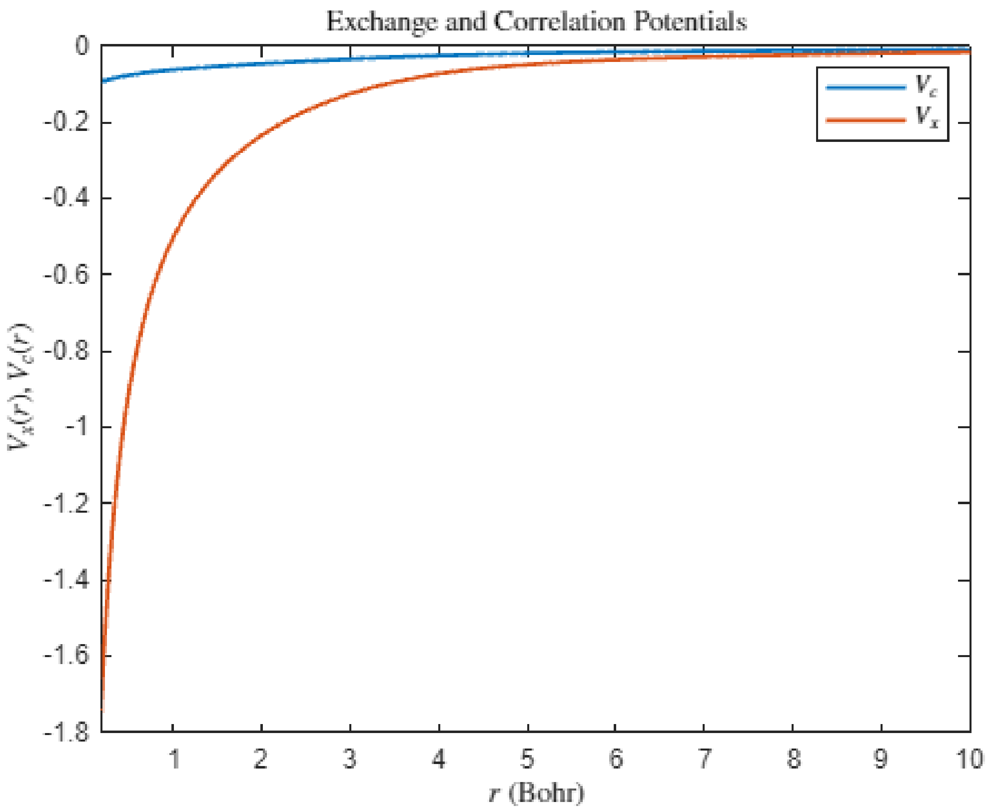
- The TF potential $V_{\mathrm{TF}}[\rho](r)$
- Hartree potential $V_{\mathrm{H}}[\rho](r)$
- Exchange-correlation potential $V_{\mathrm{xc}}[\rho](r)$ (if selected)

```
figure
yyaxis left
plot(S_OFDFT.r,S_OFDFT.Vtf,S_OFDFT.r,S_OFDFT.Vh)
if S_OFDFT.xc == 1
    hold on
    plot(S_OFDFT.r,S_OFDFT.Vx+S_OFDFT.Vc);
    hold off
end
ylim([-10 50])
ylabel("Energy (Hartree)")
yyaxis right
plot(S_OFDFT.r,S_OFDFT.Vext)
ylim([-50 0])
if S_OFDFT.xc == 1
    legend("$V_{TF}$","$V_H$","$V_{xc}$","$V_{ext}$",Interpreter='latex')
else
    legend("$V_{TF}$","$V_H$","$V_{ext}$",Interpreter='latex')
end
xlabel("$r (Bohr)$",Interpreter='latex')
xlim([0 3])
title("Converged potentials",Interpreter='latex')
if xc==1
    subtitle(['$\lambda=$',num2str(lambda)],Interpreter='latex')
else
    subtitle(['No xc, \,\, $\lambda=$',num2str(lambda)],Interpreter='latex')
end
box on
hold off
```



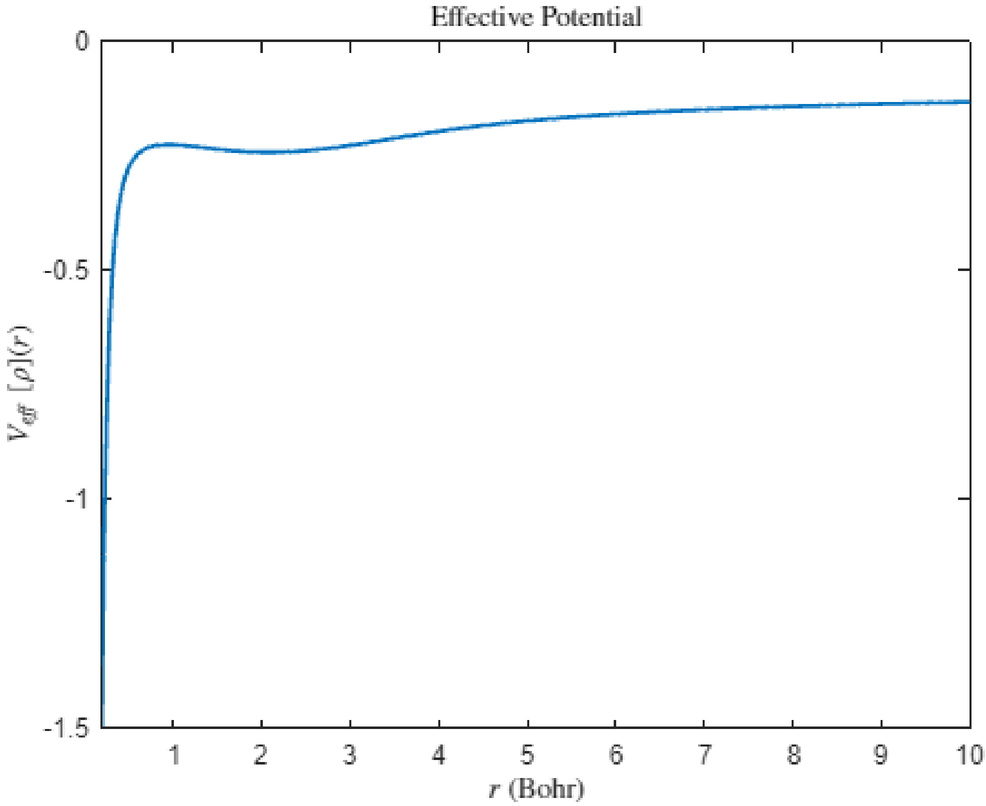
Next, for the case when xc is activated, we plot separately radial dependence of exchange and correlation potentials to see which contribution is dominant.

```
if xc==1
    figure
    plot( S_OFDFT.r ,S_OFDFT.Vc,S_OFDFT.r,S_OFDFT.Vx)
    legend("$V_{c}$","$V_{x}$",Interpreter='latex')
    xlim([0.2,10])
    ylabel("$V_{x}(r),V_{c}(r) $",Interpreter='latex')
    xlabel("$r$ (Bohr)",'Interpreter','latex')
    title( "Exchange and Correlation Potentials",Interpreter='latex')
end
```



And lastly we plot the converged effective potential $V_{\text{eff}}[\rho_{converged}](r) = V_{TF} + V_{\text{ext}} + V_{\text{H}} + \text{xc}(V_{\text{x}} + V_{\text{c}})$

```
figure
plot(S_OFDFT.r,S_OFDFT.Veff)
xlim([0.2,10])
ylabel("$V_{eff}\,\,[\rho](r)$",Interpreter='latex')
xlabel("$r$ (Bohr)",Interpreter='latex')
title( "Effective Potential",Interpreter='latex')
```



Self-Consistent Field method for radial OFDFT

We start by implementing action of Hamiltonian $\widehat{\mathscr{H}}_r$ (N_dxN_d matrix) on vector.

```
function Hr_u = Hamiltonian(S,u)
% Hamiltonian times vector routine

    Hr_u = - S.lambda/2*S.Lap*u + S.Veff.*u;
end
```

Next we implement effective potential.

```
function S = compute_effective_potential(S,rho)
% After S=compute_effective_potential(S,rho) -> structure S
% picks up additional fields, various potentials, including effective potential.

    S.Vtf = (5/3)*S.Cf*rho.^(2/3);
    S.Vh = compute_hartree_potential(S,rho);
    S.Veff = S.Vtf + S.Vext + S.Vh;

    if S.xc == 1
        rho(rho < 1e-10) = 1e-6;
        [S.Ex,S.Vx] = slater(rho);
```

```
        [S.Ec,S.Vc] = pz(rho);
        % total potential
        S.Veff = S.Veff + S.Vx + S.Vc;  % complete effective potential when xc is
activated
    end
end
```

Next we impement Hartree potential.

```
function Vh = compute_hartree_potential(S,rho)

    phi = S.Lap\(-4*pi*rho.*S.r); % note the left divide sign mldivide \
    Vh = phi./S.r;
end
```

Helper function to convert 3D integrals to 1D radial sum for spherically symmetric functions.

```
function intf = int3d(S,f)
% Computes integral of function in R3 in spherical coordinates assuming f is
spherically symmetric
    intf = 4*pi*S.h*sum(f.*S.r.^2);
end
```

The total energy expressed in terms of $u(r)$

$$
\begin{aligned}
E = \;& T_{\mathrm{TF}} + \lambda T_{\mathrm{vW}}(\rho) + E_{\mathrm{ext}} + E_{\mathrm{xc}} + E_{\mathrm{H}} \\
= \;& 4\pi C_F \int u^{10/3}(r)/r^{4/3} dr - 2\pi\lambda \int u(r)u''(r)dr \\
& -4\pi \int \frac{Z}{r} u^2(r)dr + 4\pi \int \epsilon_{\mathrm{xc}}(r)u^2(r)dr + 2\pi \int V_{\mathrm{H}}(r)u^2(r)dr
\end{aligned}
$$

```
function S = energy(S)
% After S=energy(S) -> structure S picks up additional fields,
% various energies, including total energy.

    S.Ek = S.Cf * int3d(S,S.rho.^(5/3)) - S.lambda/2*int3d(S,S.u.*(S.Lap*S.u)./
S.r.^2);
    S.Eh = 0.5*int3d(S,S.Vh.*S.rho);
    S.Eext = int3d(S,S.Vext.*S.rho);
    S.Etot = S.Ek + S.Eh + S.Eext;
    if S.xc == 1
        S.Exc = int3d(S,(S.Ex+S.Ec).*S.rho);
        S.Exchange=int3d(S,S.Ex.*S.rho);
        S.Ecorr=S.Exc-S.Exchange;
        S.Etot = S.Etot + S.Exc;
    end
end
```

The normalization condition $\int \rho(\mathbf{r})d\mathbf{r} = 4\pi \int \rho(r)r^2 dr = Z$ translates to

$$4\pi \int u^2(r)dr = Z,$$

that we implement numerically after each iteration.

```
function u = normalize(S,u)
% normalizes u = r * rho^(1/2)
% in order to have the 3D integral of rho equal to Z for a neutral atom

    scale = S.Z / (u'*u*4*pi*S.h);   % S.h=dr, integration measure in radial
direction
    u = u * sqrt(scale);
    u = abs(u);
end
```

Initialization function

```
function S = init_OFDFT(Z,R_MAX,Nd,tol,FDn,lambda,xc,rho0,beta)

    S = struct();
    S.Z = Z;
    S.Nd = Nd;
    S.h = R_MAX/(Nd);
    S.r = linspace(S.h,R_MAX,Nd)'; % radial space
    S.FDn = FDn;
    S.tol = tol;
    S.Cf = (3/10)*(3*pi^2)^(2/3);
    S.lambda = lambda;
    S.beta=beta;
    S.xc = xc;  % xc=1 means that we are using LDA-PZ exchange-correlation
functional

    % energy
    S.Etot = 0; % total energy initially set to 0

    % external (nuclear) coulomb potential
    S.Vext = - S.Z./ S.r;

    % Laplacian matrix in 1D
    S.Lap = Laplacian(S.FDn,S.Nd,S.h);
```

Now we describe each step of our numerical implementation of Self-Consistent Field methos of radial OFDFT, sketched in Fig. 1.

Initialize the electron density by using some reasonable guess (we will use Thomas-Fermi result $\rho_0(r) = \rho_{TFNA}(r)$ for initial density), and interpolate it using `griddedInterpolant` function. Interpolation is needed due to a possible mismatch between the mesh of the initial guess and N_d and R_{max} parameters. Here we interpolate $r^2\rho(r)$, which is smoother than $\rho(r)$, by a cubic spline interpolation method.

```
    % initial electron density
    x = rho0(:,1);
    rho_r = rho0(:,2);
    r2rho = griddedInterpolant(x, x.^2.*rho_r, 'spline');
    r2rho = r2rho(S.r);
    r2rho(S.r>x(end)) = 0; % interpolate to zero density outside of the initial
grid used in guess
    rho0 = r2rho ./S.r.^2;
    S.u = normalize(S,S.r.*sqrt(rho0));
    S.rho= (S.u./S.r).^2;
end
```

Then we implement the Self-Consistent Field algorithm sketched in Fig. 1.

```
function S = SCF(S)
    S = compute_effective_potential(S,S.rho);
    opts = struct(maxit=5000, tol= 1e-5, isreal=1);
    % beta=0.9;  % density mixing parameter
    mu_prev=0;
    mu_next=1;
    j=0;
    while abs(mu_prev-mu_next) > S.tol
        mu_prev=mu_next;
        Hfun = @(x) Hamiltonian(S,x);
        [S.u, mu] = eigs(Hfun,S.Nd,1,'smallestreal',opts);
        mu_next=mu;
        S.u = normalize(S,S.u);
        S.rho = (1-S.beta)*(S.u./S.r).^2+S.beta*S.rho;
        S = compute_effective_potential(S,S.rho);
        S = energy(S);
        j=j+1;
    end

    fprintf('Finished SCF method in %d steps with \x03bc = %.4f', j+1, mu);
    fprintf("\nEnergy decomposition \n");
    fprintf("Ek   = %10.6f Ha\n", S.Ek);
    fprintf("Eh   = %10.6f Ha\n", S.Eh);
    if S.xc == 1
        fprintf("Exc  = %10.6f Ha\n", S.Exc);
        fprintf("Ex  = %10.6f Ha\n", S.Exchange);
        fprintf("Ec  = %10.6f Ha\n", S.Ecorr);
    end
    fprintf("Eext = %10.6f Ha\n", S.Eext);
    fprintf("Etot = %10.6f Ha, %10.6f eV\n", S.Etot, S.Etot * 27.2114079527);
end
```

Below are pair of functions (`slater` and `pz`) for implementing LDA exchange and LDA-PZ correlation functional and potential.

```
function [ex,vx] = slater(rho)
```

```
% slater exchange

    % rho, electron density
    % ex, exchange energy density
    % vx, exchange potential

    C2 = 0.73855876638202; % 3/4*(3/pi)^(1/3)
    C3 = 0.9847450218427;  % (3/pi)^(1/3)
    ex = - C2 * rho.^(1./3.);
    vx = - C3 * rho.^(1./3.);
end

function [ec,vc] = pz(rho)
% pz correlation: Perdew-Zunger implementation of LDA correlation energy and
potential

    % rho, electron density
    % ec, correlation energy density
    % vc, correlation potential

    A = 0.0311;
    B = -0.048;
    C = 0.002;
    D = -0.0116;
    gamma1 = -0.1423;
    beta1 = 1.0529;
    beta2 = 0.3334;

    % compuatation
    ec = zeros(size(rho,1),1);
    vc = zeros(size(rho,1),1);
    rs = (0.75./(pi*rho)).^(1.0/3.0) ;
    islt1 = (rs < 1.0);
    lnrs = log(rs(islt1));
    sqrtrs = sqrt(rs(~islt1));
    ec(islt1) = A * lnrs + B + C * rs(islt1) .* lnrs + D * rs(islt1);
    ox = 1.0 + beta1*sqrtrs + beta2*rs(~islt1);
    ec(~islt1) = gamma1 ./ ox;
    vc(islt1) = lnrs.*(A + (2.0/3.0)*C*rs(islt1)) + (B-(1.0/3.0)*A) +
(1.0/3.0)*(2.0*D-C)* rs(islt1);
    vc(~islt1) = ec(~islt1) .* (1 + (7.0/6.0)*beta1*sqrtrs +
(4.0/3.0)*beta2*rs(~islt1)) ./ ox;
end
```

Finally, we provide functions for creating discrete Laplacian using central finite difference method.

```
%%%%%% finite difference functions %%%%%%

function Lap = Laplacian(FDn,Nd,h)
% the sparse 1D Laplacian matrix
```

```
    % FDn, half order of accuracy
    % Nd, number of grid points
    % h, mesh

    w2 = w2_c(FDn);
    e = ones(Nd,1)/h^2;
    Lap = spdiags(w2(1)*e,0,Nd,Nd);
    for i = 1:FDn
        Lap = Lap + spdiags(w2(i+1)*e,i,Nd,Nd);
        Lap = Lap + spdiags(w2(i+1)*e,-i,Nd,Nd);
    end
end

function w2 = w2_c(FDn)
% generate central finite difference coefficients for second order derivative

    % FDn, half order of accuracy
    % w2, central finite difference coefficients

    w2 = zeros(1,FDn+1) ;
    for k=1:FDn
        w2(k+1) = (2*(-1)^(k+1))*(factorial(FDn)^2)/...
            (k*k*factorial(FDn-k)*factorial(FDn+k));
        w2(1) = w2(1)-2*(1/(k*k));
    end
end
```