Lab Session:
Hartree-Fock Simulations

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Contents

Contents

Hartree-Fock method

- **Hartree-Fock (HF) equation**

  Adopting the separation of variables, the $\Psi(r, \theta, \phi)$ can be decomposed as

  $R_{nl}(r)Y_{lm}(\theta, \phi)$. Then, one can define the radial differential equation as:

  Ion-electron interaction   ***Electron-electron interaction***

  $$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{r} + \Phi(r) - \epsilon_{nl} \right) R_{nl}(r) = -F_{nl}(r)$$

  Kinetic energy operator   *Centrifugal term*   ***Coulomb interaction (J)***   ***Exchange interaction* (K)**

- ❑ **Objective:** Obtain the $R_{nl}(r)$ and their eigenvalues ϵ_{nl} by solving the HF equation
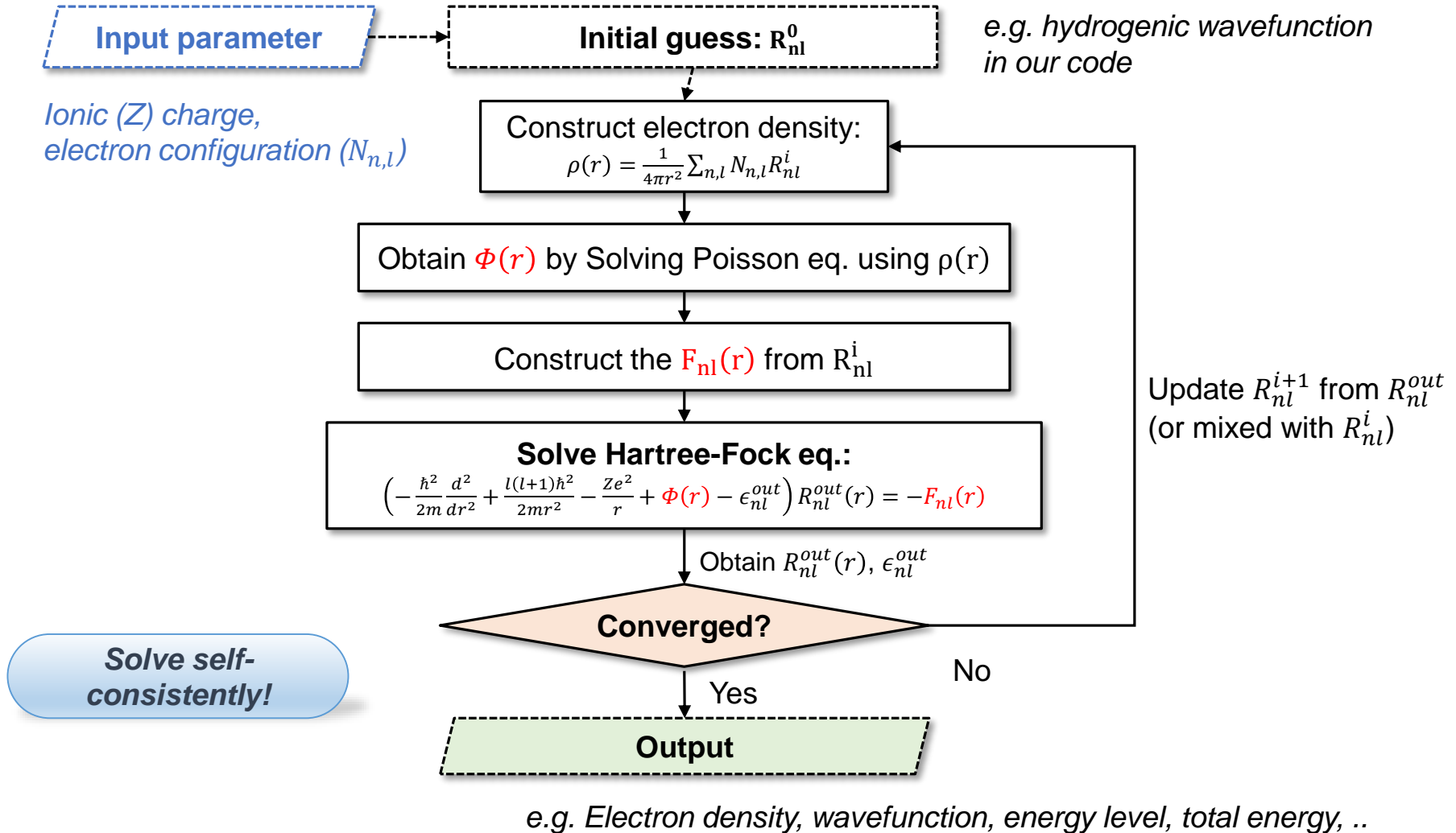
- ✓ **Key idea:**

  Since the $\Phi(r)$ & $F_{nl}(r)$ terms are depend on the $R_{nl}(r)$,

  we should solve the HF equation "iteratively" ➔ *self-consistent field (SCF) method*

Self-consistent field approach

- **SCF algorithm for HF equations**

Input parameter ----▶ **Initial guess: R_{nl}^0**

e.g. hydrogenic wavefunction in our code

Ionic (Z) charge, electron configuration ($N_{n,l}$)

Construct electron density:
$$\rho(r) = \frac{1}{4\pi r^2}\sum_{n,l} N_{n,l} R_{nl}^i$$

Obtain $\Phi(r)$ by Solving Poisson eq. using $\rho(r)$

Construct the $F_{nl}(r)$ from R_{nl}^i

Solve Hartree-Fock eq.:
$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{r} + \Phi(r) - \epsilon_{nl}^{out}\right) R_{nl}^{out}(r) = -F_{nl}(r)$$

Obtain $R_{nl}^{out}(r), \epsilon_{nl}^{out}$

Update R_{nl}^{i+1} from R_{nl}^{out} (or mixed with R_{nl}^i)

Converged?

Solve self-consistently!

No

Yes

Output

e.g. Electron density, wavefunction, energy level, total energy, ..

Contents

Program overview

Calculation platforms:

(1) Google Colab (recommend):

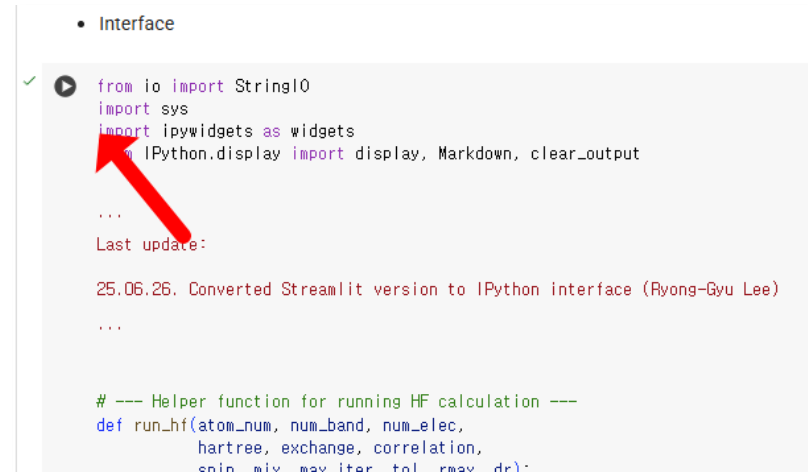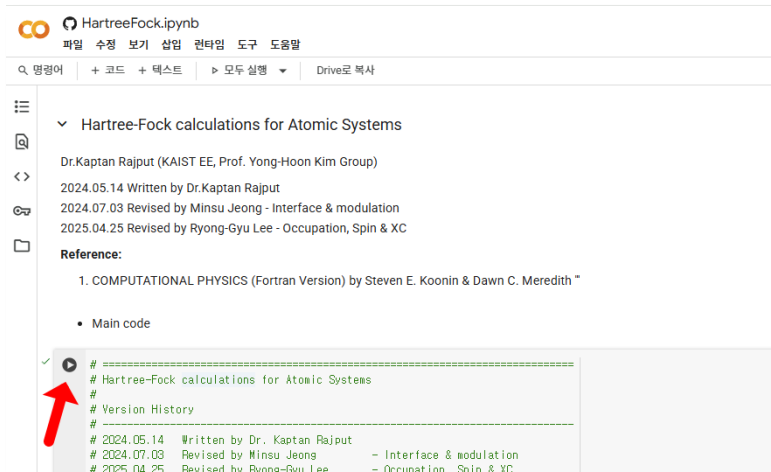*https://colab.research.google.com/github/yhkimlab/ESCSchool/blob/main/exercise1/HartreeFock.ipynb*

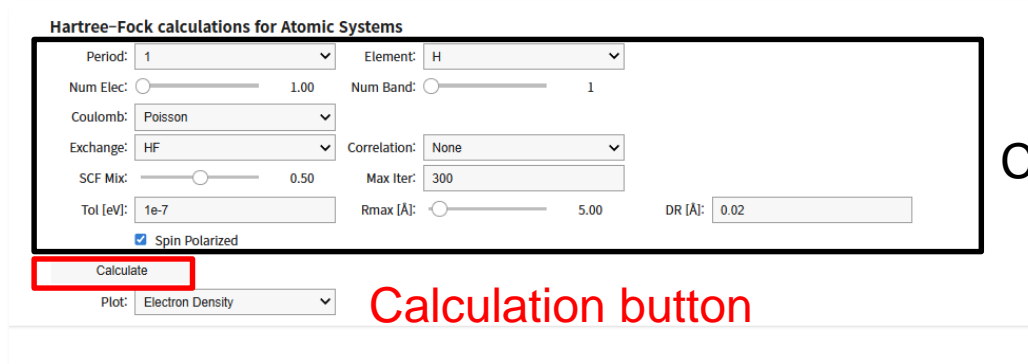*(2) Edison website:*

https://nano2.edison.re.kr/

→ *If you want to perform the calculation through the Edison website, you need to create an account first.*

Program overview: (1) Colab

1. Enter the Google Colab website [Link]

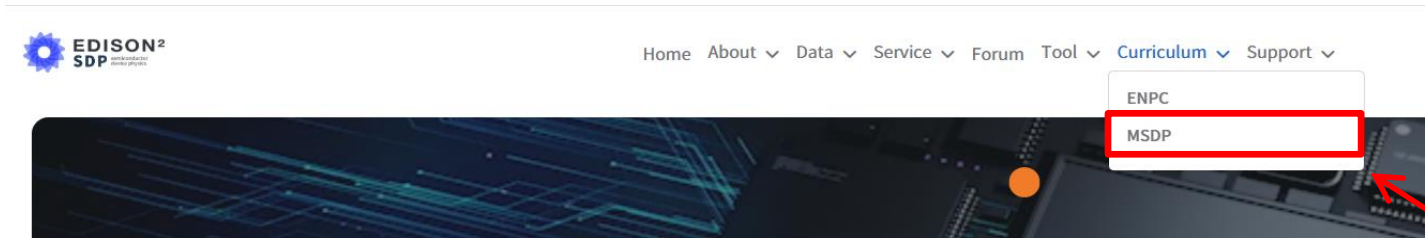2. Run both the main code cell, and interface cell

3. You will see the interactive Ipython widget to perform the calculations

Calculation options

Calculation button

Program overview: (2) Edison

1. Login to Edison website [Link]

2. Enter to *[Curriculum] / [MSDP]* menu

3. Choose *"Hartree-Fock Solutions of Small Atomic System (Central-Field Approximation)"* course

Program overview: (2) Edison

Calculation results & descriptions

Calculation button

Calculation options

Calculate

Period

1 ▾

Element

H ▾

Num Elec

1.00

1.00   3.00

Exchange

Hartree-Fock ▾

Correlation

None ▾

☐ Spin Polarized

SCF Mix

0.50

0.00   1.00

SCF Iter

300   −   +

Tol [eV]

1.0e-7   −   +

Hartree-Fock calculations for Atomic Systems

Dr.Kaptan Rajput (KAIST EE, Prof. Yong-Hoon Kim Group)

2024.05.14 Written by Dr.Kaptan Rajput
2025.04.25 Revised by Ryong-Gyu Lee

Reference:

1. COMPUTATIONAL PHYSICS (Fortran Version) by Steven E. Koonin & Dawn C. Meredith

> Click "Calculate" to run the SCF simulation and view results.

Input Parameters Description

- **Period:**
  The selected row of the periodic table to filter elements. Determines the default number of electrons and target atom.

- **Element:**
  The atomic symbol of the target element for which the Hartree-Fock calculation will be performed.

- **Num Elec** *(float; slider)*:
  Total number of electrons in the system. Can be adjusted to simulate charged species (e.g., cations/anions).

- **Exchange** *(dropdown)*:
  Choice of exchange potential:

  - `Hartree-Fock` : Exact exchange from Hartree-Fock theory.
  - `Dirac-exchange (LDA)` : Local approximation based on the Dirac exchange expression.
  - `None` : Disables the exchange term.

- **Exchange Scaling** (α_x) *(float; slider)*:
  Scaling factor for the exchange potential. *(Only visible when exchange ≠ Hartree-Fock)*

- **Correlation** *(dropdown)*:
  Choice of correlation functional:

Input settings

Period

1 ▾

Element

H ▾

Num Elec

1.00

●————————————————

1.00   3.00

- **Period:** The selected row of the periodic table to filter elements.
- **Element:** The atomic symbol of the target element (Z)
- **Num Elec:** Total number of electrons in the system

  Note. Can be adjusted to simulate charged species (e.g., cations/anions)

Exchange

Hartree-Fock ▾

Correlation

None ▾

- **Exchange:** Choice of exchange energy functional

  e.g. Hartree-Fock, homogeneous electron gas

- **Correlation:** Choice of correlation energy functional

  Note. Hartree-Fock method does not include correlation effect

☐ Spin Polarized

- **Spin Polarized:** Enables spin-dependent calculation

  e.g. For C atom, $1s^2$ $2s^2$ $2p^2$ (non pol)

  → $1s^1$(up) $1s^1$(down) $2s^1$ (up) $2s^1$ (down) $2p^2$ (up)

Input settings

SCF Mix

0.50

0.00   1.00

SCF Iter

300   –   +

Tol [eV]

1.0e-7   –   +

- **SCF Mix:** Mixing ratio for updating R_{nl}^i in SCF calculations

  e.g. SCF.Mix = 0.1 → $R_{nl}^{i+1} = 0.1 R_{nl}^{out} + 0.9 R_{nl}^i$

- **SCF Iter:** Total number of SCF iterations

  Note. SCF.Iter = 0 → Non-SCF calculation (initial state)

- **Tol:** Convergence criteria for the total energy

Rmax [Å]

5.00

3.00   50.00

DR [Å]

0.01   –   +

- **Rmax:** Maximum radial distance in Angstrom unit for solving the radial equations

- **DR:** Radial grid spacing (resolution) in Angstrom unit.

Calculation output

- ***Example: He atom***

Click this button to perform calculation!

Calculate

Period

1

Element

He

Num Elec

2.00

1.00   4.00

Exchange

Hartree-Fock

Correlation

None

☐ Spin Polarized

SCF Mix

0.50

0.00   1.00

SCF Iter

300   − +

Tol [eV]

1.0e-7   − +

Rmax [Å]

5.00

3.00   50.00

DR [Å]

0.01   − +

Calculation input description

```
Nuclear Charge (Z): 6
Number of Electrons: 6.0
Occupation of the States:
  1s up: 2.0
  2s up: 2.0
  2p up: 2.0
Radial Step (Å): 0.01
Maximum Radius (Å): 5.0
Effective Nuclear Charge (Z*): 5.603664967814122
All energies are in electron volts (eV).
```

SCF iteration log

```
Iteration: 0
Iteration: 1      Total Energy: -999.91778960 eV      Ediff: -103.58135537 eV
Iteration: 2      Total Energy: -1002.97348617 eV     Ediff:    3.05569657 eV
Iteration: 3      Total Energy: -994.95843250 eV      Ediff:   -8.01505367 eV
Iteration: 4      Total Energy: -1033.61329794 eV     Ediff:   38.65486544 eV
Iteration: 5      Total Energy: -1024.70697159 eV     Ediff:   -8.90632635 eV
Iteration: 6      Total Energy: -1014.81432290 eV     Ediff:   -9.89264869 eV
Iteration: 7      Total Energy: -1011.24838606 eV     Ediff:   -3.56593684 eV
Iteration: 8      Total Energy: -1011.31955245 eV     Ediff:    0.07116639 eV
Iteration: 9      Total Energy: -1012.15613917 eV     Ediff:    0.83658672 eV
Iteration: 10     Total Energy: -1012.56442587 eV     Ediff:    0.40828670 eV
```

Total energy decreases

Calculation output

- ***Example: He atom***

```
**************************************************
Convergence reached at iteration: 25
States   Nocc          Ktot           Ven           Vee          Vex          Vtot          Etot
1s  up   2.00      38.79614244   -91.62082869   55.74276529  -27.87330964  -63.75137304  -24.95523060

TOTALS
NE : 2.0
KTOT : 77.59228487234482 eV
VENTOT : -183.2416573799501 eV
VEETOT : 55.742765291344526 eV
VXCTOT : -27.873309638819347 eV
VENTOT + VEETOT + VEXTOT : -155.37220172742494 eV
Total Energy : -77.77991685508012 eV
Final Converged Total Energy is : -77.77991685508012 eV
```

Eigenvalues

Total energy properties

KTOT: Kinetic energy [eV]
VENTOT: Ion-electron interaction energy [eV]
VEETOT: Electron-electron interaction energy (Coulomb) [eV]
VEXTOT: Electron-electron interaction energy (exchange) [eV]
VENTOT+VEETOT+VEXTOT: Total effective potential energy [eV]
Total energy [eV]

Calculation output

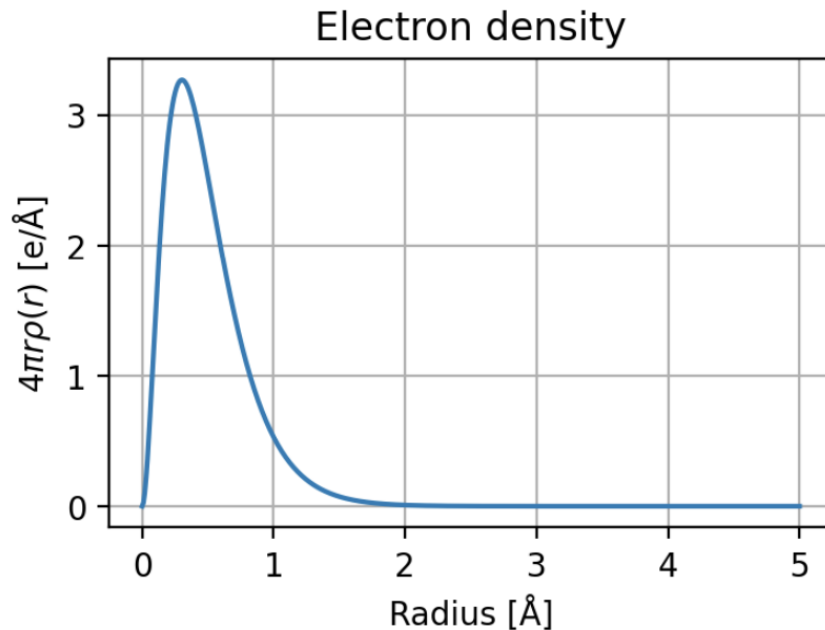- **_Example: He atom_**

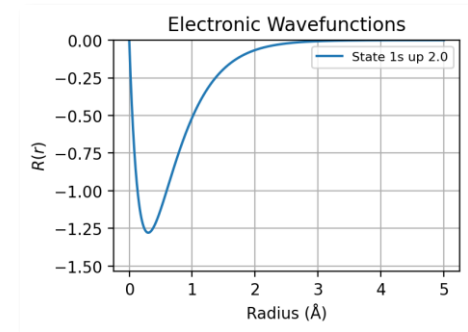 - Electron density $\rho(r)$

    Results Plot
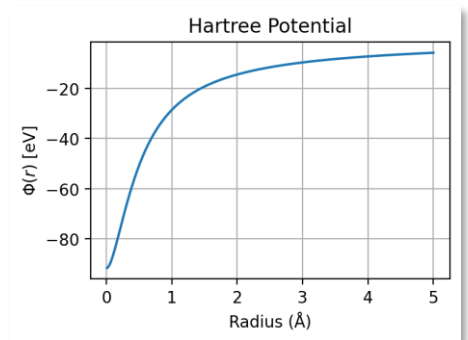
    Select properties to visualize

    Plot Type

    Electron Density

  - Wavefunction $R_{nl}(r)$

  - Hartree potential $\Phi(r)$

Contents

(1) Single-electron atom - hydrogen

- **Analytic solutions for hydrogen atom**

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{r} - \epsilon_{nl}\right)R_{nl}(r) = 0$$

→ No electron-electron (e-e) interaction term → *Can be analytically solved!*

- **Radial wavefunction R_{nl}:**

$$R_{1s}(r) = 2\left(\frac{1}{a}\right)^{\frac{1}{2}} \cdot \frac{r}{a}e^{-\frac{r}{a}}$$

$$R_{2s}(r) = 2\left(\frac{1}{2a}\right)^{\frac{1}{2}} \cdot \left(1 - \frac{r}{2a}\right) \cdot \frac{r}{2a}e^{-\frac{r}{2a}}$$

$$R_{2p}(r) = 2\left(\frac{1}{3a}\right)^{\frac{1}{2}}\left(\frac{r}{2a}\right)^2 e^{-\frac{r}{2a}}$$

$$\vdots$$

In a lot of text books, the radial function $u(\mathrm{r})$, which corresponds to $R(\mathrm{r})$ in our case, is defined as $u(\mathrm{r}) = rR(\mathrm{r})$

(1) Single-electron atom - hydrogen

- **Exercise 1: H atom**

☑ Spin Polarized

Coulomb

None ⌄

Num Band

12

1   42

SCF Iter

0   —   +

Rmax [Å]

20.00

3.00   50.00

(1) "Spin Polarized": Consider spin polarization (e.g. 1s → 1s-up 1s-down)

(2) Coulomb "None": No electron-electron interaction → Exclude Coulomb & exchange terms

(3) "Num Band = 12": Number of band to plot → 12 electrons states (*$1s^1$* *$1s^1$* *$2s^2$* *$2p^6$* *$3s^2$*)

Occupied   *Unoccupied*

(4) "SCF Iter = 0": Non self-consistent field calculation

(5) "Rmax = 20.0 Å": Radial grid size. To cover spatially delocalized unoccupied orbital

(1) Single-electron atom - hydrogen

- **Exercise 1: H atom**

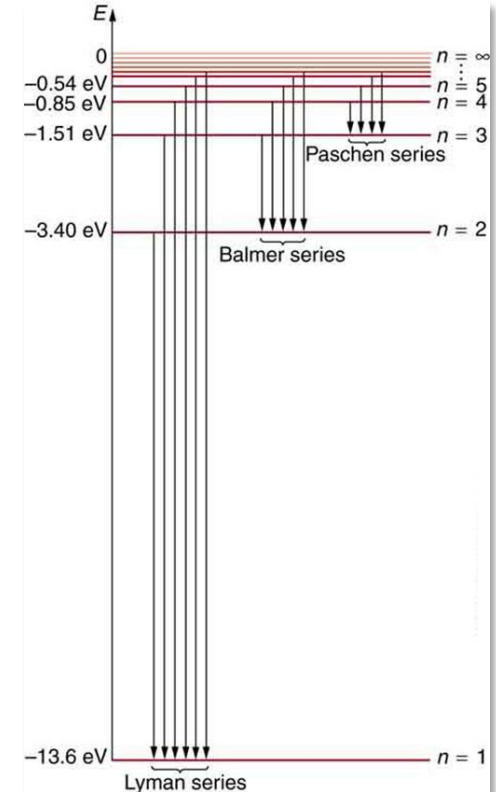- ➢ **Results:** Eigenvalues (single-particle energies)

Hydrogen energy diagram

```
***************
Iteration: 0
States  Nocc        Vtot          Etot
```

n=1
```
1s  up   1.00   -27.18021091   -13.59010584
1s  dw   0.00   -27.18021091   -13.59010584
```
E_1 = -13.59 eV

n=2
```
2s  up   0.00    -6.79666561    -3.39843388
2s  dw   0.00    -6.79666561    -3.39843388
2p  up   0.00    -6.79827931    -3.39883711
2p  up   0.00    -6.79827931    -3.39883711
2p  up   0.00    -6.79827931    -3.39883711
2p  dw   0.00    -6.79827931    -3.39883711
2p  dw   0.00    -6.79827931    -3.39883711
2p  dw   0.00    -6.79827931    -3.39883711
```
E_2 = -3.40 eV

n=3
```
3s  up   0.00    -3.02105533    -1.51054470
3s  dw   0.00    -3.02105533    -1.51054470
```
E_3 = -1.51 eV

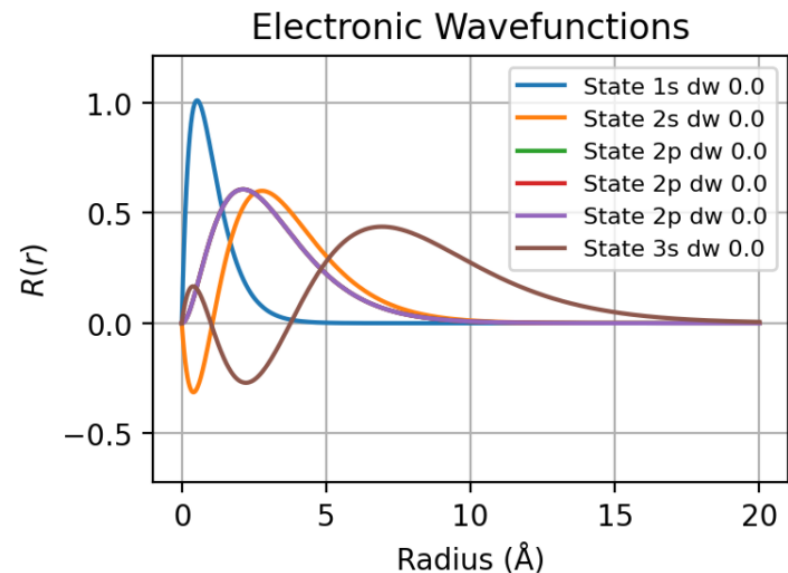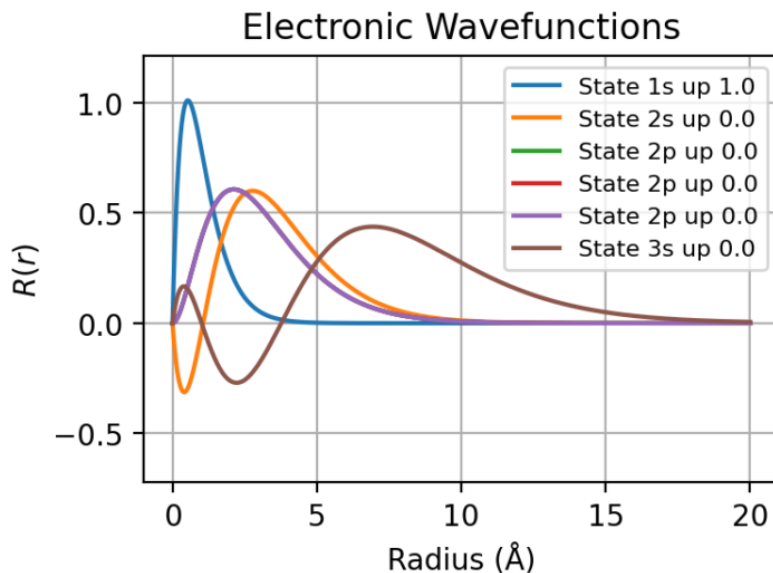*College Physics by OpenStax*

- • **Hydrogen energy level:** $E_n = -\dfrac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2}\dfrac{1}{n^2} = 13.6 \text{ eV } \dfrac{1}{n^2}$

(1) Single-electron atom - hydrogen

- **Exercise 1: H atom**

➤ **Results:** Atomic wavefunctions

- **Radial nodes**

$$Number\ of\ nodes = n - l - 1$$

- **Orthogonality**

$$0 = \int R_{n'l}^*(r) R_{nl}(r) dr$$

(1) Single-electron atom - hydrogen

- **Exercise 1: H atom**

Repeat the calculation with Coulomb "Poisson" = "Poisson" & Exchange = "Hartree-Fock". Then, examine the total energy properties, and compare the VEETOT (Hartree energy) and VEXTOT (exchange energy)


```
TOTALS
NE : 1.0
KTOT : 13.560381028126724 eV
VENTOT : -27.150347845570842 eV
VEETOT : 8.491855443685635 eV
VXCTOT : -8.492660406217787 eV
VENTOT + VEETOT + VEXTOT : -27.151152808102992 eV
Total Energy : -13.590771779976269 eV
```

✓ Cf. Hartree-Fock method is single-electron self-interaction free

(2) Many-electron atoms

- **Ion–electron interactions (w/o interacting electrons)**

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{l(l+1)\hbar^2}{2mr^2}-\frac{Ze^2}{r}-\epsilon_{nl}\right)R_{nl}(r)=0$$

- Radial wavefunction R_{nl}:

Hydrogen (e=1, Z=1) atom

$$R_{1s}(r)=2\left(\frac{1}{a}\right)^{\frac{1}{2}}\cdot\frac{r}{a}e^{-\frac{Z^*r}{a}}$$

$$R_{2s}(r)=2\left(\frac{1}{2a}\right)^{\frac{1}{2}}\cdot\left(1-\frac{r}{2a}\right)\cdot\frac{r}{2a}e^{-\frac{r}{2a}}$$

$$R_{2p}(r)=2\left(\frac{1}{3a}\right)^{\frac{1}{2}}\left(\frac{r}{2a}\right)^2e^{-\frac{r}{2a}}$$

Hydrogenic (e=1, Z≥1) atoms

$$R_{1s}(r)=2\left(\frac{Z^*}{a}\right)^{\frac{1}{2}}\cdot\frac{Z^*r}{a}e^{-\frac{Z^*r}{a}}$$

$$R_{2s}(r)=2\left(\frac{Z^*}{2a}\right)^{\frac{1}{2}}\cdot\left(1-\frac{Z^*r}{2a}\right)\cdot\frac{Z^*r}{2a}e^{-\frac{Z^*r}{2a}}$$

$$R_{2p}(r)=2\left(\frac{Z^*}{3a}\right)^{\frac{1}{2}}\left(\frac{Z^*r}{2a}\right)^2e^{-\frac{Z^*r}{2a}}$$
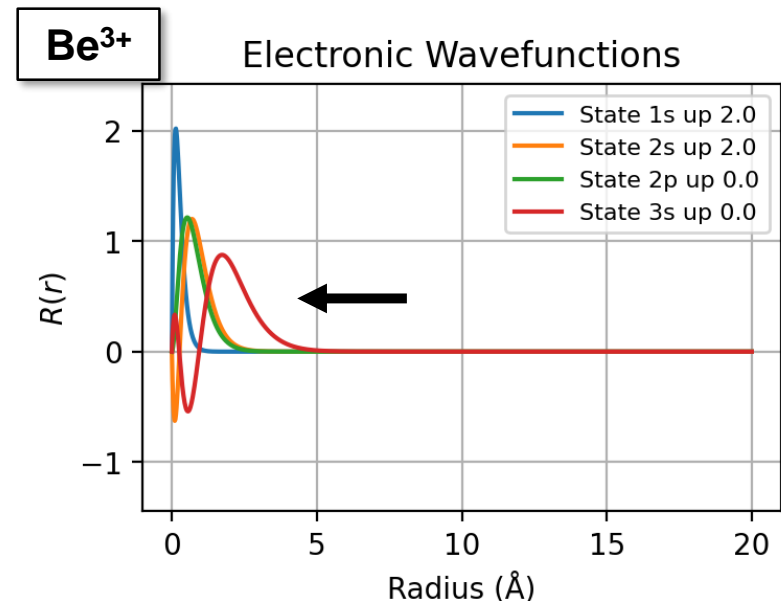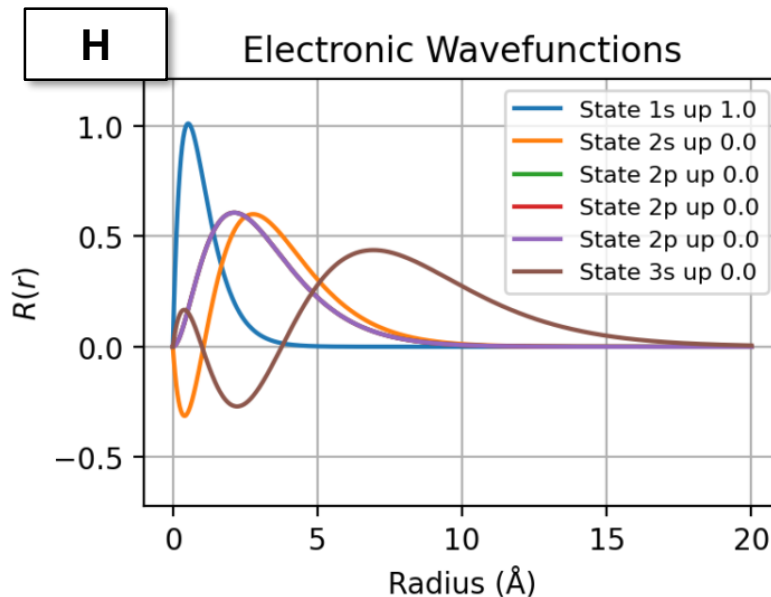
(2) Many-electron atoms

- **Exercise 2-1: Be^{3+} atom (non-interacting electrons)**

  → repeat "Exercise 1" for Be atom (now you can turn off the _"Spin Polarized"_)

- **Results:** Atomic wavefunction

✓ Radial wavefunctions of **Be atom** are contracted due to the stronger ion–electron attraction, compared to the case of the hydrogen atom

(2) Many-electron atoms

- **Exercise 2-1: Be^{3+} atom (non-interacting electrons)**

  → repeat "Exercise 1" for Be atom

- ➤ **Results:** Eigenvalues (single-particle energies)

```
        States    Nocc            Etot
n=1   1s   up    1.00    -216.28665319
      1s   dw    1.00    -216.28665319
n=2   2s   up    1.00     -54.30308073
      2s   dw    1.00     -54.30308073
      2p   up    0.00     -54.40561254
      2p   up    0.00     -54.40561254
      2p   up    0.00     -54.40561254
      2p   dw    0.00     -54.40561254
      2p   dw    0.00     -54.40561254
      2p   dw    0.00     -54.40561254
n=3   3s   up    0.00     -24.15370643
      3s   dw    0.00     -24.15370643
```

E_1 = -216.29 eV

E_2 = -54.30 eV

E_3 = -24.15 eV

- **Energy level (Be: Z = 4):**

$$E_n = -\frac{m_e e^4}{2(4\pi\varepsilon_0)^2 \hbar^2} \frac{Z^2}{n^2}$$
$$= 217.6 \text{ eV} \frac{1}{n^2}$$

- ✓ Energy levels of **Be^{+3} atom** become more deeper

(2) Many-electron atoms

- **Electron–electron interactions**

Coulomb interaction (J)   *Exchange interaction (K)*

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{r} + \overbrace{\Phi(r)} - \epsilon_{nl} \right) R_{nl}(r) = -\overbrace{F_{nl}(r)}$$

Includes Coulomb repulsion and exchange effects

- **Exercise 2-2: Be atom** (setting "*Rmax = 10 Å*")

Coulomb

| Poisson | ⌄ |

| Poisson |
| None |

Exchange

| Hartree-Fock | ⌄ |

| Hartree-Fock |
| Dirac-exchange (LDA) |

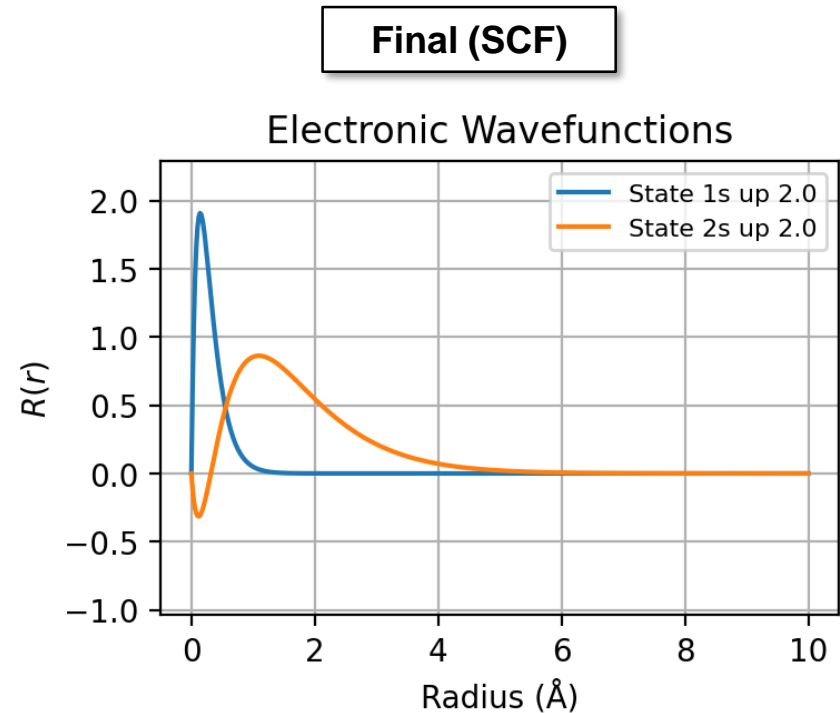**(1) Coulomb = "Poisson":** Include Coulomb (Hartree) potential by solving Poisson's equation
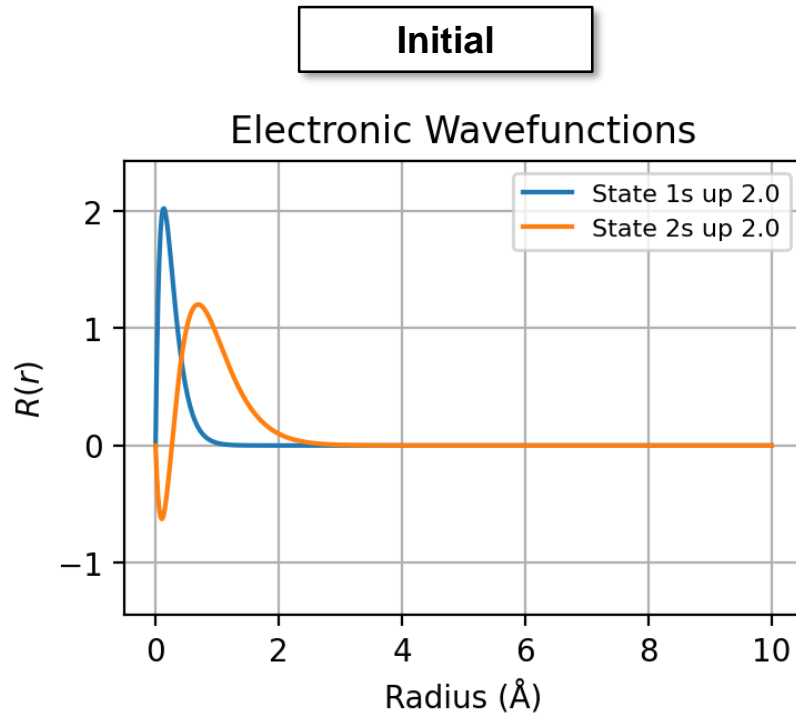
(2) Exchange = "Hartree-Fock": Include exchange term of $F_{nl}(r)$ from the Hartree-Fock method

(2) Many-electron atoms

- **Exercise 2-2: Be atom**

✓ Electronic wavefunctions from SCF calculations are **deformed by the electron-electron repulsion**, compared to the analytic solution of hydrogenic wavefunctions

(3) Exchange-correlation

- **Local approximation to exchange-correlation (XC) energy**

Exact exchange energy (E_X)
(Hartree-Fock method)

Local density approximation (LDA)
(density functional theory)

$$E_X^{HF} = \frac{1}{2}\sum_{i,j} \int d\boldsymbol{r} \int d\boldsymbol{r}' \frac{\phi_i^*(\boldsymbol{r})\phi_j^*(\boldsymbol{r}')\phi_j(\boldsymbol{r})\phi_i(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

➡

$$E_X[\rho(\boldsymbol{r})] = \int d\boldsymbol{r}\ \rho(\boldsymbol{r})\epsilon_X^{\mathrm{HEG}}(\rho(\boldsymbol{r}))$$

$$\epsilon_X^{\mathrm{HEG}}[\rho] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho^{\frac{1}{3}}$$

☺ **Pros:** Cost efficient + can include correlation energy (E_C) similar to E_X

☹ **Cons:** Does not provide the exact E_X

Exchange
Hartree-Fock|
Hartree-Fock
Dirac-exchange (LDA)
None

Correlation
Perdew-Zunger (LDA)
Perdew-Zunger (LDA)
None
0.00   2.00
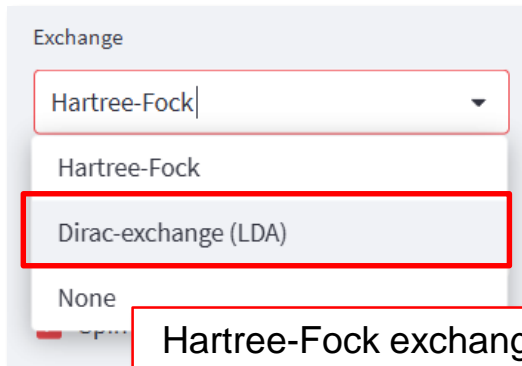
Hartree-Fock exchange
→ LDA local exchange

→ LDA correlation

(3) Exchange-correlation

- **Exercise 3-1: Two-electron system (H⁻ case)**

  To simulate a single nucleus with two-electron system (H⁻), you should modify the

  Num Elec as 0 (or you can just simulate the neutral He atom case)

Exchange

Hartree-Fock

Calculate

Period

1

Element

H

Num Elec

Modify the number of electron

2.00

1.00   3.00

Calculation result

```
TOTALS
NE : 2.0
KTOT : 13.622145555137095 eV
VENTOT : -37.916209347474165 eV
VEETOT : 22.19745117364867 eV
VXCTOT : -11.098865592163 eV
VENTOT + VEETOT + VEXTOT : -26.817623765988493 eV
Total Energy : -13.195478210851398 eV
```

- **Discussion:** What is the role of

  Coulomb interaction (VEE) energy and

  exchange interaction (VXC) energy

  in two-electron system?

(3) Exchange-correlation

- **Exercise 3-1: (Again) Single-electron system (H case)**

  Let's simulate the Hydrogen atom again with the LDA approximation

  ☑ Spin Polarized

  Period

  [1 ▼]

  Element

  [H ▼]

  Num Elec

  1.00

  ● ─────────────────────

  1.00   3.00

  Coulomb

  [Poisson ▼]

  Exchange

  [Dirac-exchange (LDA) ▼]

  ⇨

  Calculation result

  ```
  TOTALS
  NE : 1.0
  KTOT : 12.390759695635145 eV
  VENTOT : -25.937189833082538 eV
  VEETOT : 8.004617751605624 eV
  VXCTOT : -6.886537202933416 eV
  VENTOT + VEETOT + VEXTOT : -24.81910928441033 eV
  Total Energy : -12.428349588775186 eV
  ```

  - **Discussion:** Compare to the Hartree-Fock results

  Cf. Self-interaction correction (SIC) method in DFT[1]

(3) Exchange-correlation

- **Exercise 3-2: Two-electron system (H⁻ case)**

  To simulate a single nucleus with two-electron system (H⁻), you should modify the

  Num Elec as 2 (or you can just simulate the neutral He atom case)

Exchange

Dirac-exchange (LDA)

Calculate

Period

1

Element

H

Modify the number of electron

Num Elec

2.00

1.00   3.00

Calculation result

```
TOTALS
NE : 2.0
KTOT : 172.77282670228087 eV
VENTOT : -121.18697945834968 eV
VEETOT : 81.35375869155565 eV
VXCTOT : -35.083234582459994 eV
VENTOT + VEETOT + VEXTOT : -74.91645534925402 eV
Total Energy : 97.85637135302684 eV
```

- **Discussion:** Check the sign of highest

  occupied orbital's eigenvalue

  (whether bound or unbound state)

(3) Exchange-correlation

- **Exercise 3-2: Two-electron system (H⁻ case)**

  To simulate a single nucleus with two-electron system (H⁻), you should modify the

  Num Elec as 2 (or you can just simulate the neutral He atom case)
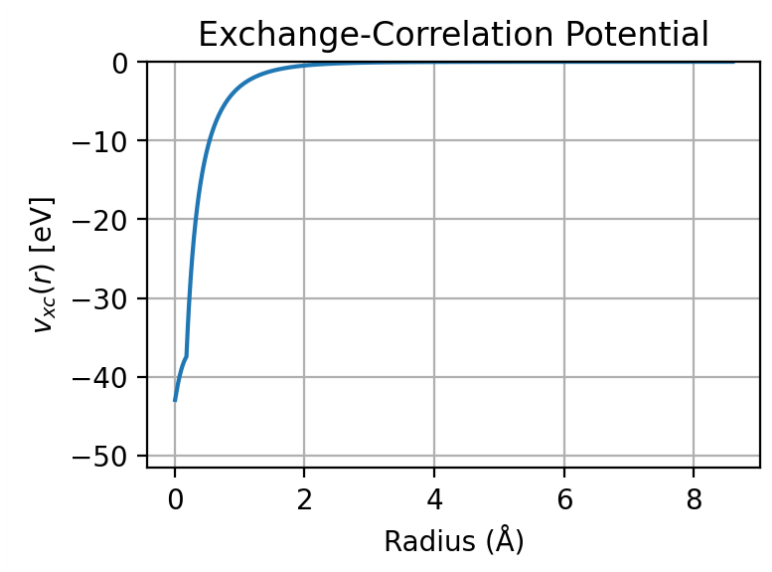
Exchange

| Dirac-exchange (LDA) | ∨ |

Calculate

Period

| 1 | ▼ |

Element

| H | ▼ |

Num Elec — Modify the number of electron

2.00

1.00   3.00

Exchange-Correlation Potential

- Exponentially decay behavior

  (exact condition ~ asymptotic -1/r)
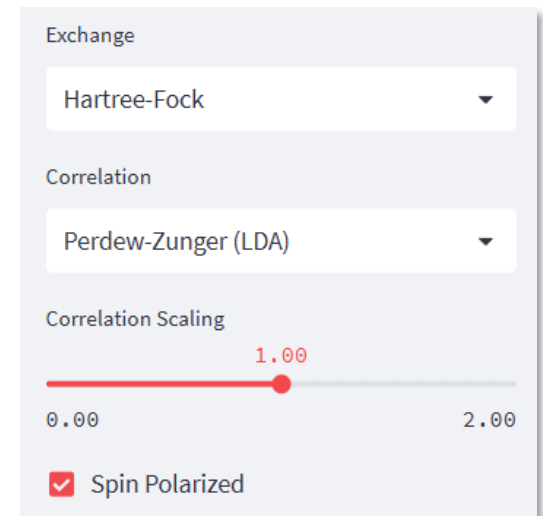
Advanced Topics

- **Hybrid scheme**

$$E_X^{HF} \quad \rightarrow \quad E_{XC} = E_X^{HF} + E_C^{LDA}$$

Conventional Hartree-Fock method cannot capture *correlation energy*

→ incorporating the LDA correlation energy into the Hartree-Fock equation

- **Exercise: He atom**

(1) Check *Spin Polarized* option

(2) Select "Hartree-Fock" for *Exchange* → Calculate

(3) Select "Hartree-Fock" for *Exchange*

and "Perdew-Zunger (LDA)" for *Correlation* → Calculate

(4) Compare the total energies from (2) & (3)

to **experimental "electronic binding energy"***

* "X-Ray DATA BOOKLET", *Lawrence Berkeley National Laboratory*

Advanced Topics

- **Ionization potential**

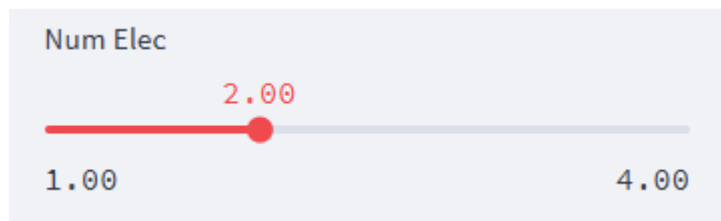$$IP = E(N - 1) - E(N) = -\epsilon_k$$

Negative of the highest occupied orbital energy $(-\epsilon_k)$ ~ ionization potential (IP)

(cf. assuming frozen orbital) → physical meaning of single-particle energy level
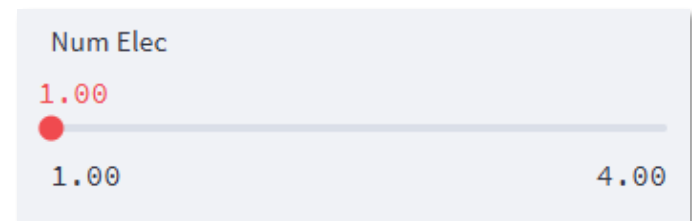

- **Exercise 4: He atom**

(1) Check *Spin Polarized* option

☑ Spin Polarized

(2) Modify the number of electron

N system

Num Elec
2.00

1.00   4.00

$N - 1$ system

Num Elec
1.00

1.00   4.00

Advanced Topics

- **Exercise 4: He atom (Hartree-Fock)**

N system

```
Convergence reached at iteration: 25
States   Nocc            Ktot              Ven              Vee              Vex              Vtot              Etot
1s  up   1.00      38.79614244     -91.62082869      55.74276529     -27.87330964     -63.75137304      -24.95523060
1s  dw   1.00      38.79614244     -91.62082869      55.74276529     -27.87330964     -63.75137304      -24.95523060
```

① $\epsilon_k^N = -23.31$ eV

```
Total Energy : -77.77991685508012 eV
Final Converged Total Energy is : -77.77991685508012 eV
```

② $E(N) = -77.78$ eV

$N - 1$ system

```
Total Energy : -54.36168863829733 eV
Final Converged Total Energy is : -54.36168863829733 eV
```

③ $E(N - 1) = -54.36$ eV

$$IP = E(N-1)^{③} - E(N)^{②} = 23.42 \text{ eV}$$
$$\approx -\epsilon_k^{N}{}^{①} = 23.31 \text{ eV}$$

Cf. Our calculation considers only the **orbital relaxation cases**

Advanced Topics

- **Exercise 4: He atom (LDA)**

N system

```
Convergence reached at iteration: 44
Final Converged Total Energy is : -74.06644510641495 eV
States   Nocc          Ktot            Ven              Vee              Vex            Vtot           Etot
1s  up    1.00      37.00307605   -89.26838786     53.66691270     -15.46848945    -51.06996461   -14.06688857
1s  dw    1.00      37.00307605   -89.26838786     53.66691270     -15.46848945    -51.06996461   -14.06688857
```

① $\epsilon_k^N = -14.06$ eV

Total Energy : -74.06644510641495 eV

② $E(N) = -74.06$ eV

$N - 1$ system

Total Energy : -52.00950148375505 eV

③ $E(N - 1) = -52.01$ eV

$$IP = E(N-1)^{③} - E(N)^{②} = 22.05 \text{ eV}$$
$$\approx -\epsilon_k^{N\,①} = 14.06 \text{ eV}$$

Accuracy:
total energy vs single-particle energy?