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Immersed Atom into Jellium Sphere

treated by CHAMP

Ryo Maezono

rmaezono@mac.com

School of Information Science,

Japan Advanced Institute of Science and Technology, Ishikawa, Japan.

JAIST
JAPAN ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY 1990

Collaborators

- Masayoshi Shimomoto
- Yasutami Takada
- Cyrus. J. Umrigar

Goal

Inhomogeneity effects on XC potentials

Inverse Kohn-Sham scheme

Charge Density

DMC evaluation

As a simplest system...

Immersed Atom into Jellium Sphere

Background (1)

Inverse Kohn-Sham Scheme

(Kohn-Sham)

Inverse KS scheme

$v_{XC}(r)$ — (Kohn-Sham) → $! (\vec{r})$

XC potential ← (Inverse Kohn-Sham) — Charge Density

In Principle,

$v_{XC}(\vec{r})$ can be constructed so that it can reproduce $\rho(\vec{r})$

$\rho(\vec{r})$ can be obtained by reliable treatment about electronic correlation

CI/DMC/ExactDiag.

Special Case ; 2-elec. systems

2-elec. Singlet systems（He atom)

Only the lowest orbital occupied...

$$v_{XC}([\rho];\vec{r}) = \varepsilon_{KS} + \frac{1}{2}\frac{\nabla^2\psi_{lowest}}{\psi_{lowest}} - v_{ext}(\vec{r}) - \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'$$

$$\psi_{lowest}(\vec{r}) = \sqrt{\frac{\rho(\vec{r})}{2}}$$; (Closed-shell in a lowest orbital)

$$\varepsilon_{KS} = E_G + \frac{Z^2}{2}$$; (KS-level equals to ionization energy)

$v_{XC}(\vec{r})$ is obtained analytically, directory from $\rho(\vec{r})$ & E_G

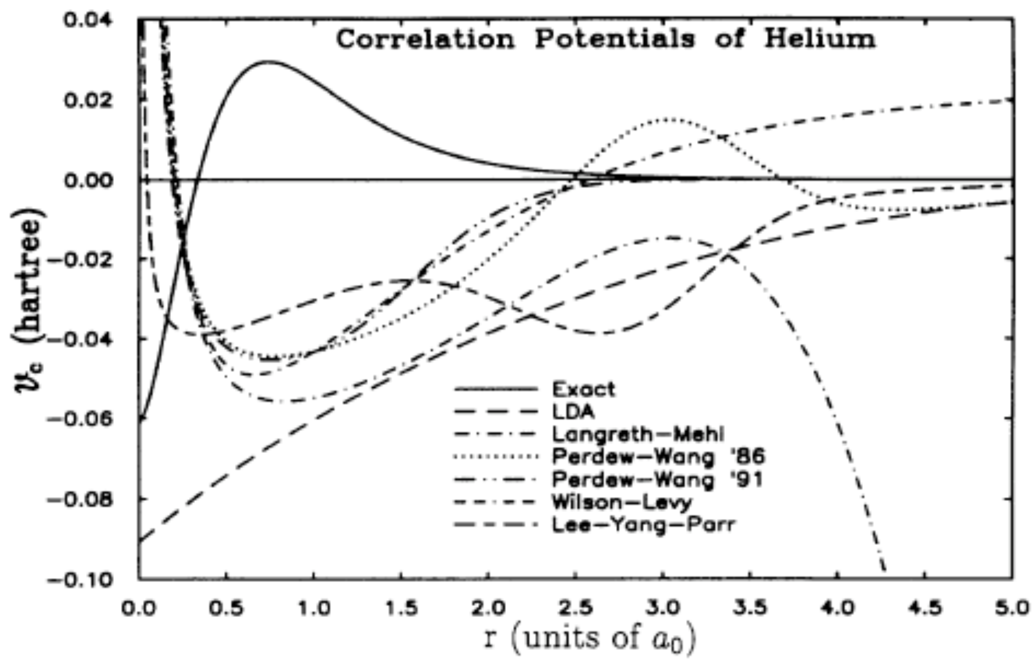
evaluated by Hylleraas-type Variational calc.

Umrigar and Gonze, PRA50, 3827 (1994)

Comparison with LDA/GGA

Relying on such special relations (analytically feasible inverse KS)

- A.C. Pedroza, PRA33, 804 (1986).
- Umrigar and Gonze, PRA50, 3827 (1994)



More General way

E. S. Kadantsev and M. J. Stott, Phys. Rev. A 69, 012502 (2004)

Exploiting "Haydock-Foulkes" functional for Inverse Kohn-Sham

General/numerical feasibility

$V_0(\vec{r})$; true potential to reproduce given $\rho_0(\vec{r})$

↑

$V_{Trial}(\vec{r})$; trial potential

Upper bound property

$$I\left[V_{Trial}(\vec{r});\rho_0(\vec{r})\right] := -\sum_{iocc.}\varepsilon_i\left[V_{Trial}(\vec{r})\right] + \int d^3r \cdot V_{Trial}(\vec{r})\rho_0(\vec{r}) \geq I\left[V_0(\vec{r});\rho_0(\vec{r})\right]$$

Haydock-Foulkes Functional

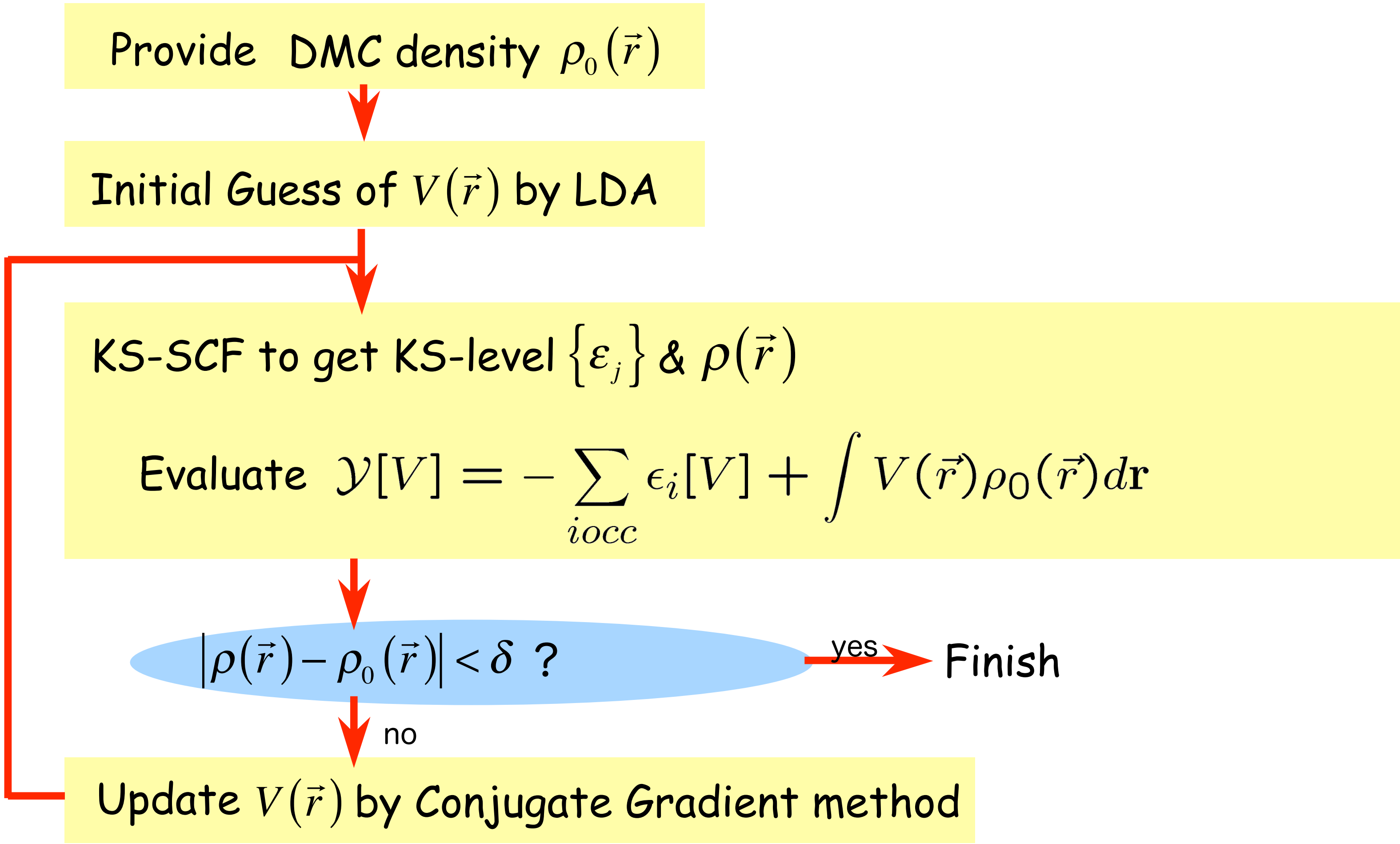
W.M.C. Foulkes and R. Haydock, PRB39, 12520 (1989).

How to get XC potential to reproduce a given $\rho_0(\vec{r})$ numerically?

Optimize $V_{Trial}(\vec{r})$ so that it may minimize $I\left[V_{Trial}(\vec{r});\rho_0(\vec{r})\right]$

$\rho_0(\vec{r})$ evaluated by CI methods for Ne atom and methane molecule

Procedure


Provide DMC density $\rho_0(\vec{r})$
Initial Guess of $V(\vec{r})$ by LDA
KS-SCF to get KS-level $\{\varepsilon_j\}$ & $\rho(\vec{r})$
Evaluate $\mathcal{Y}[V] = -\sum_{iocc} \epsilon_i[V] + \int V(\vec{r})\rho_0(\vec{r})d\mathbf{r}$
$|\rho(\vec{r}) - \rho_0(\vec{r})| < \delta$?
yes
Finish
no
Update $V(\vec{r})$ by Conjugate Gradient method

Background (2)

Immersed systems

Why interesting?

- Solid state theory

Firstly modelled as Homogeneous Electron Gas

➔ Inhomogeneity effects due to ionic cores

How it dominates for the origin of FCC/BCC structures?

Energy gain by immersing atom into Jellium (Embedding Energy)

Practical application of Embedding Energy --> Effective Medium Theory

M.J. Puska et.al., PRB24, 3037 (1981).

- Electronic Structure theory

Inhomogeneity effects on XC potential

Inverse Kohn-Sham

for immersed system

D.C. Thompson and Ali Alavi, PRB 66, 235118 (2002)

2-electrons in a sphere with and w/o background.

Exact diagonalization to get accurate densities

Then obtain XC potentials by Inverse Kohn-Sham.

Comparison with LYP, P91, PBE, PZ

Difference investigated

Setting up the Project

Project

- DMC calculation of a Immersed Atom into HEG

  to get Charge densities

- Inverse Kohn-Sham scheme using

  Haydock-Foulkes functional minimization

  to get XC potential $V_{XC}(r;Z,r_s)$

Immersed Atom into HEG

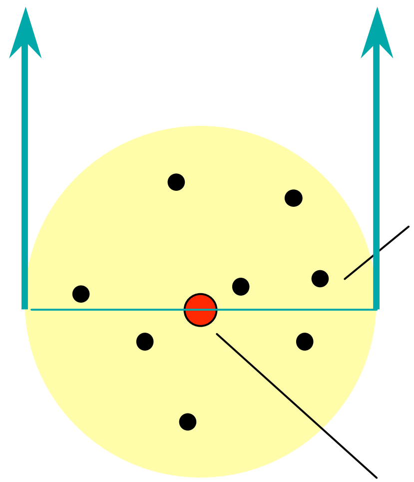
Localized basis | Delocalized basis

→ Immersed Atom into Jellium Sphere.

Systems

Specified by (r_s, Z)

Infinite Potential Wall



electrons $(-N)$

nucleus $(+Z)$

Jellium Sphere Background $(+N - Z)$

Infinite Potential Wall is introduced

for convergence reason

Procedure

Generate Trial Node by LDA

↓ Trial/Guiding WaveFunction

QMC by CHAMP

↓ DMC charge density

Inverse Kohn-Sham scheme

↓

Exchange Correlation Potential

Jellium Sphere

without impurity (Z=0)

Several reference QMC works available upto N=106

- P. Ballone, C. J. Umrigar, and P. Delaly, Phys. Rev. B 45, 6293 (1992) ; VMC
- F. Sottile and P. Ballone, Phys. Rev. B **64**, 045105 (2001) ; DMC

Technical stuff

to be prepared

- **LDA generation of trial WF**

  Implementation of DFT for shperically symmetric systems

  (LDA part of PBE/Numerov method)

- **QMC calculation :**

  - High angular momentum (upto any L by recursive generation)

  - Matrix operation with large size

    (General treatment for Multi-det. Sometimes fails)

- **Inverse Kohn-Sham scheme**

  Implemented by Conjugate Gradient method.

... Other extensions are quite straight forward.

Occupation

upto Higher angular momentum

(e.g., Z=2, rs=5,25, N=60)

1s(2)				
2s(2)	1p(6)			
3s(2)	2p(6)	1d(10)		
**	**	**	1f(14)	
**	**	**	**	1g(18)

We follow the unfamiliar convention such as ‘1p’ or ‘1d’ as in

- F. Sottile and P. Ballone, Phys. Rev. B **64**, 045105 (2001)

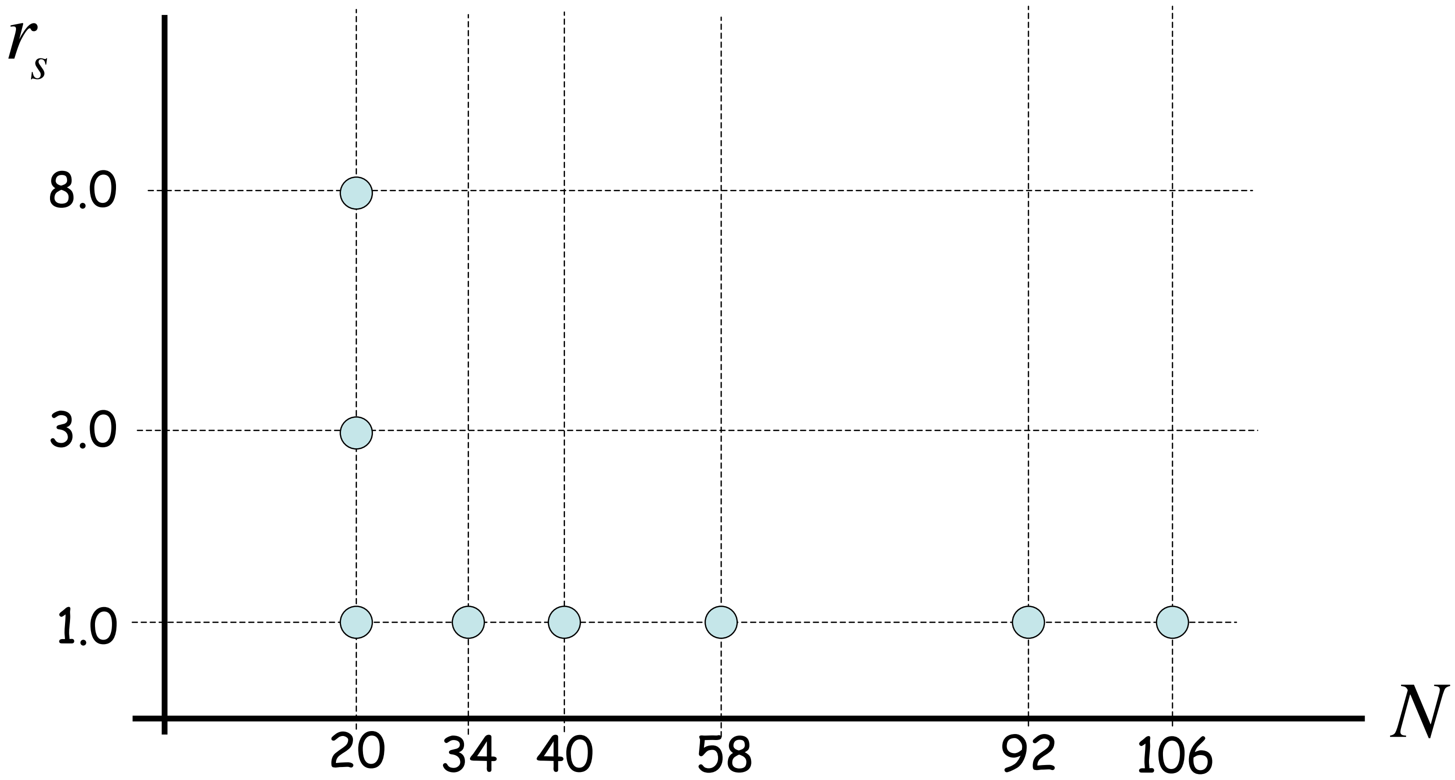
Results

(DMC charge density calc.)

System treated

(Simple Jellium sphere without impurity)

$$Z = 0$$



Comparison with prev. work

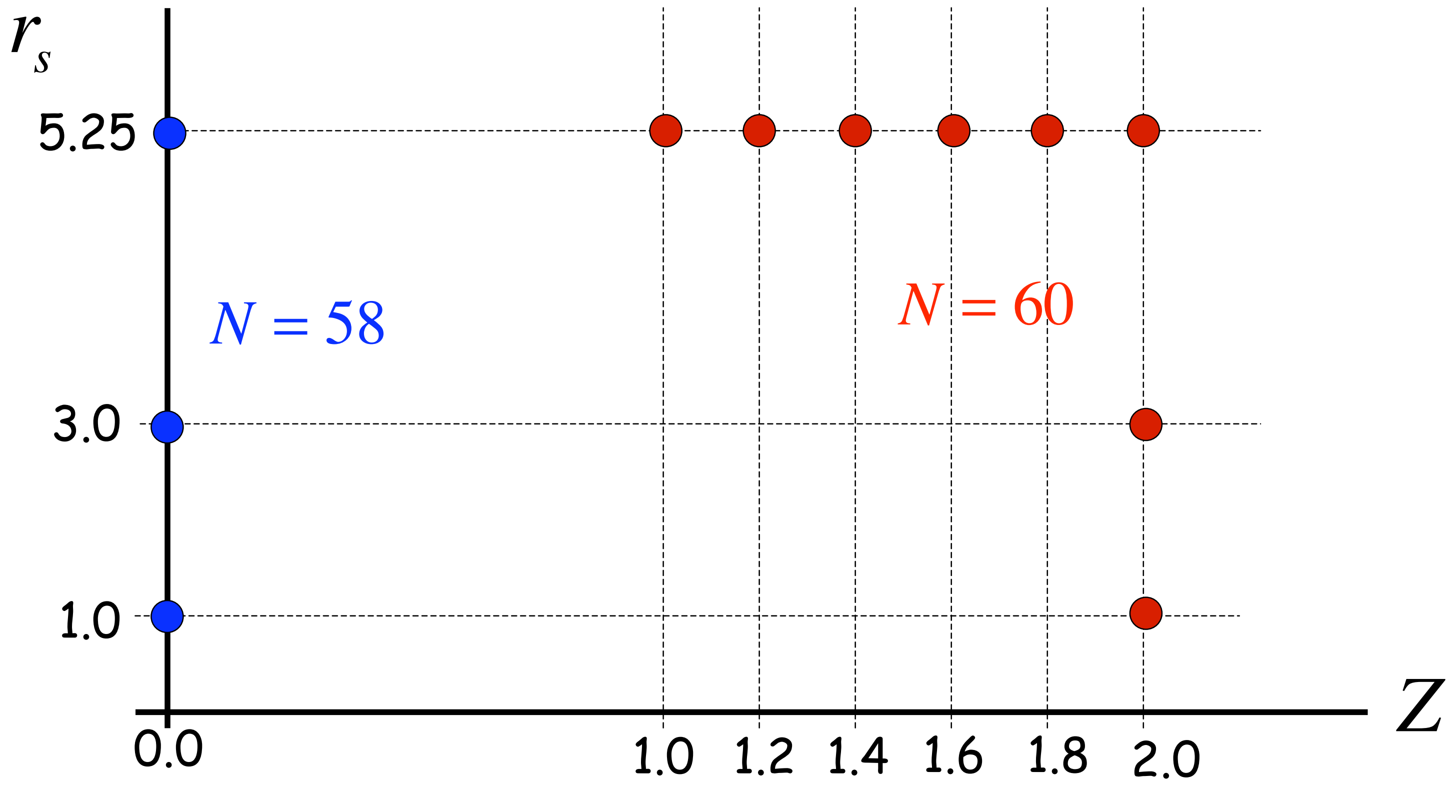
(Z=0, N=106, rs=1.0/ without Infinite pot. wall)

Energy (eV/electron.)	Std.err.	
12.7965	-	LDA,S&B
12.7987	-	LDA,present
12.8678	*	VMC,S&B
12.8539	0.0047	VMC,present
12.8184	0.0043	DMC,S&B
12.8158	0.0001	DMC,present

- F. Sottile and P. Ballone, Phys. Rev. B **64**, 045105 (2001)

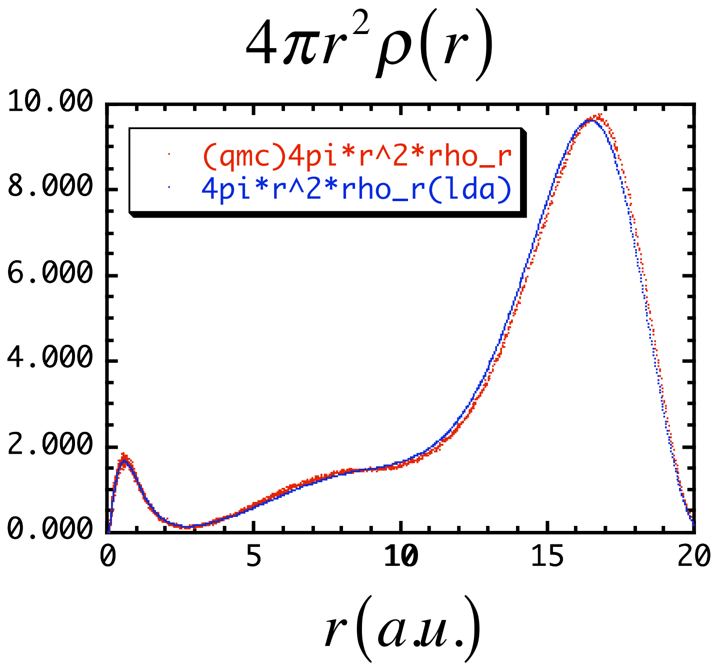
System treated

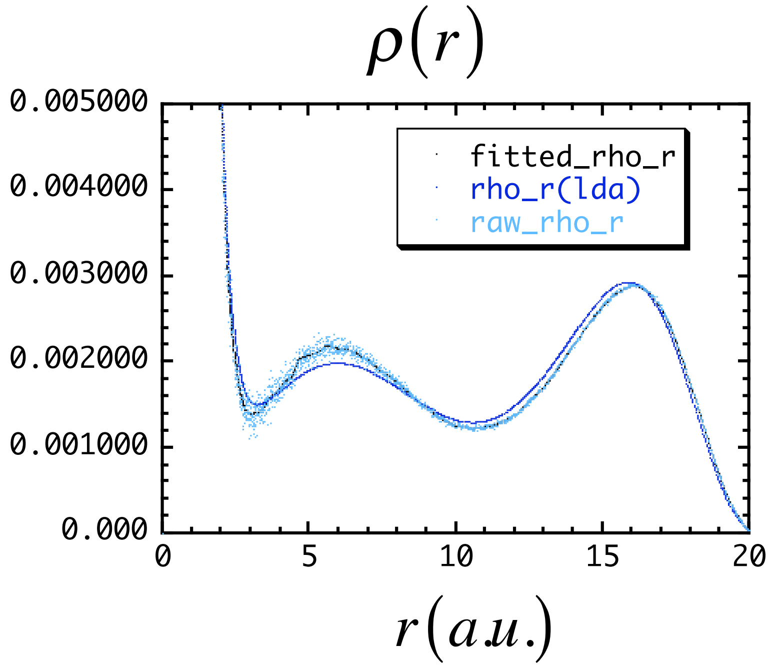
(with Infinite pot. wall)



Densities

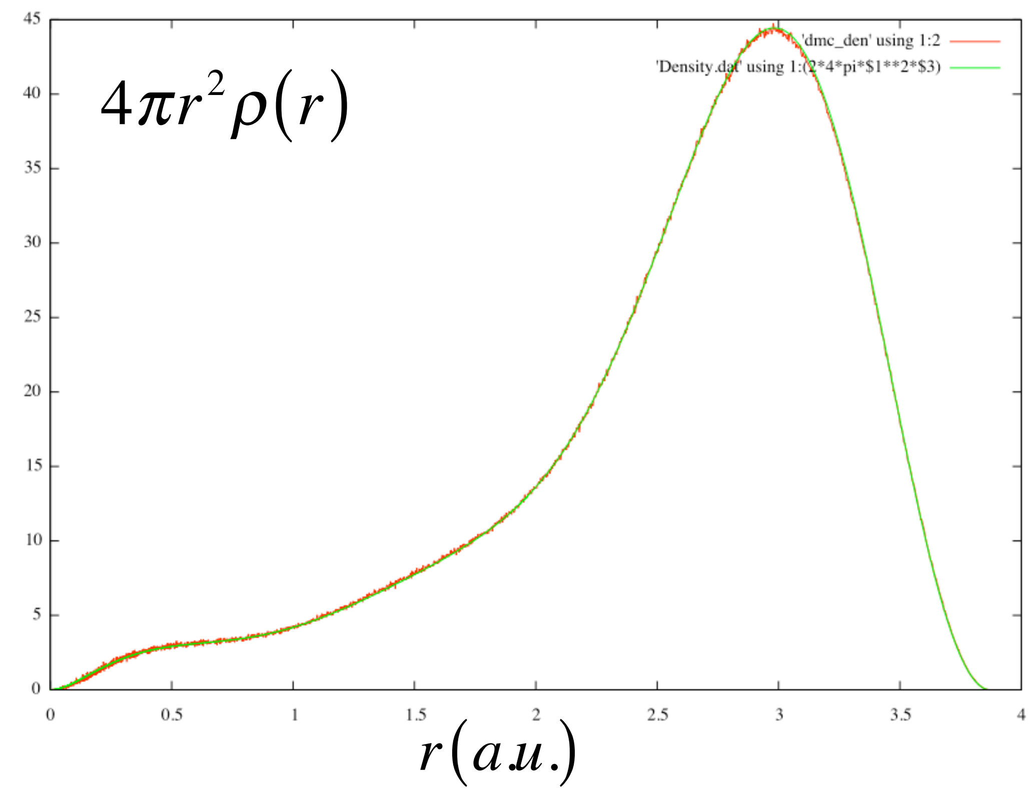
(Z=2, rs=5.25, N=60)





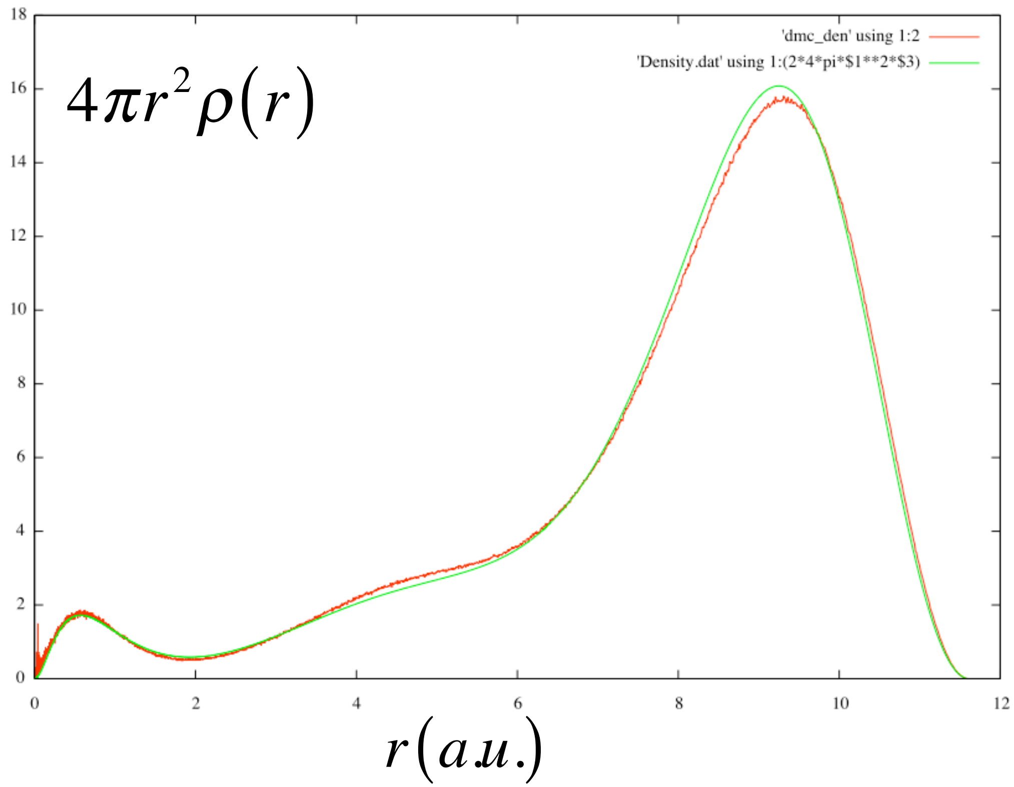
Densities

Z=2, rs=1.0, N=60



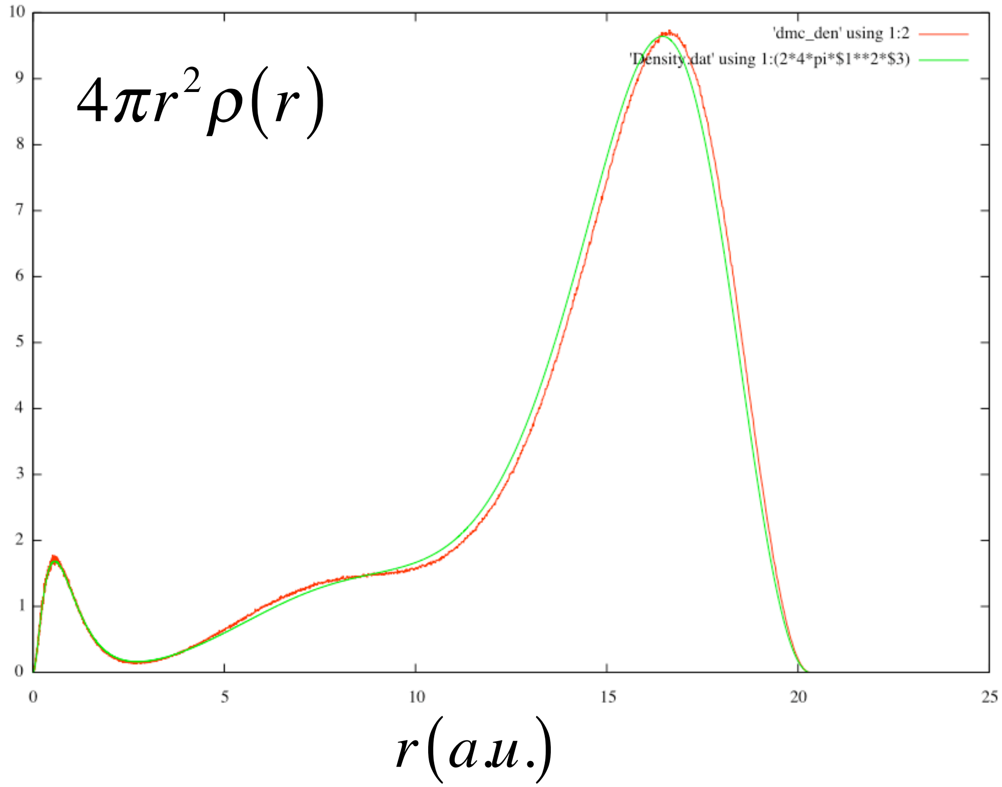
Densities

Z=2, rs=3.0, N=60



Densities

Z=2, rs=5.25, N=60

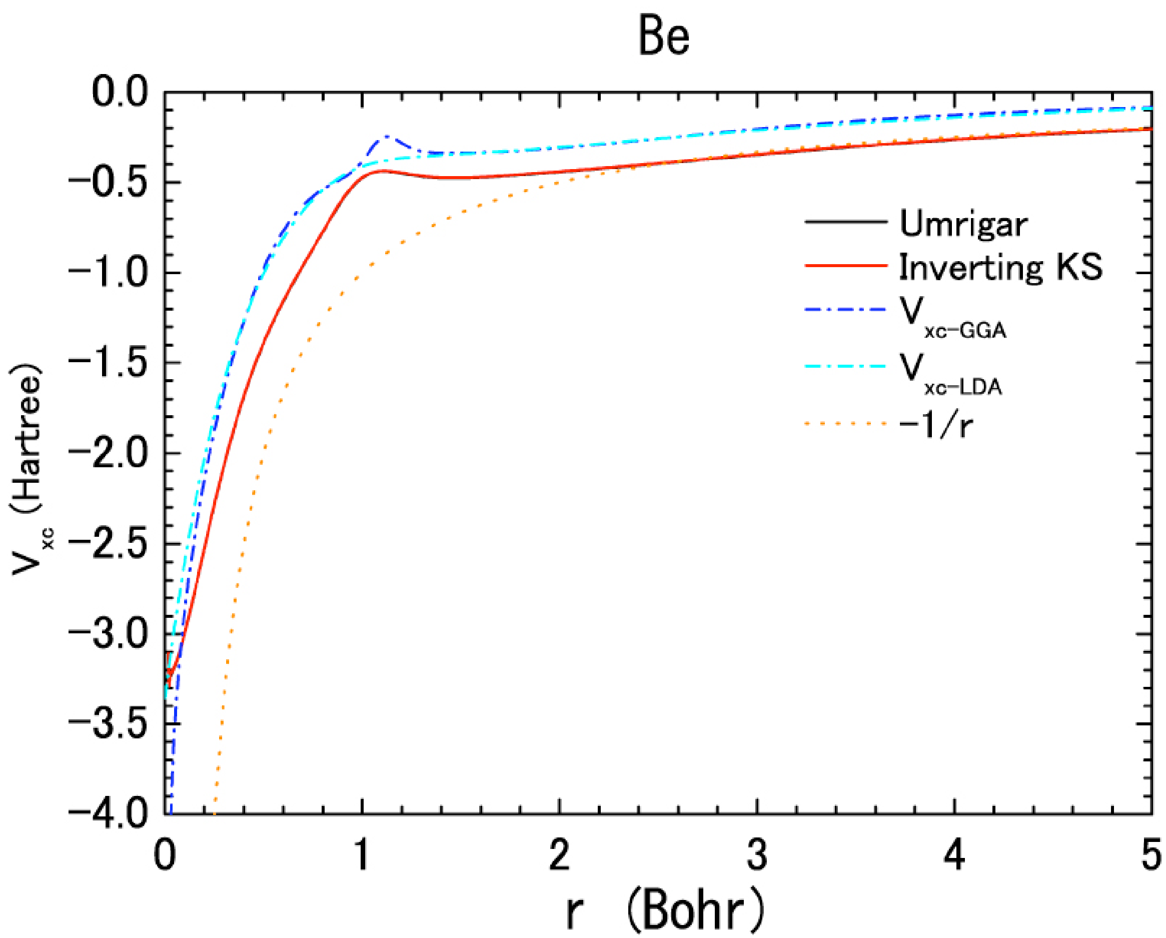


Results

(Inverse Kohn-Sham scheme)

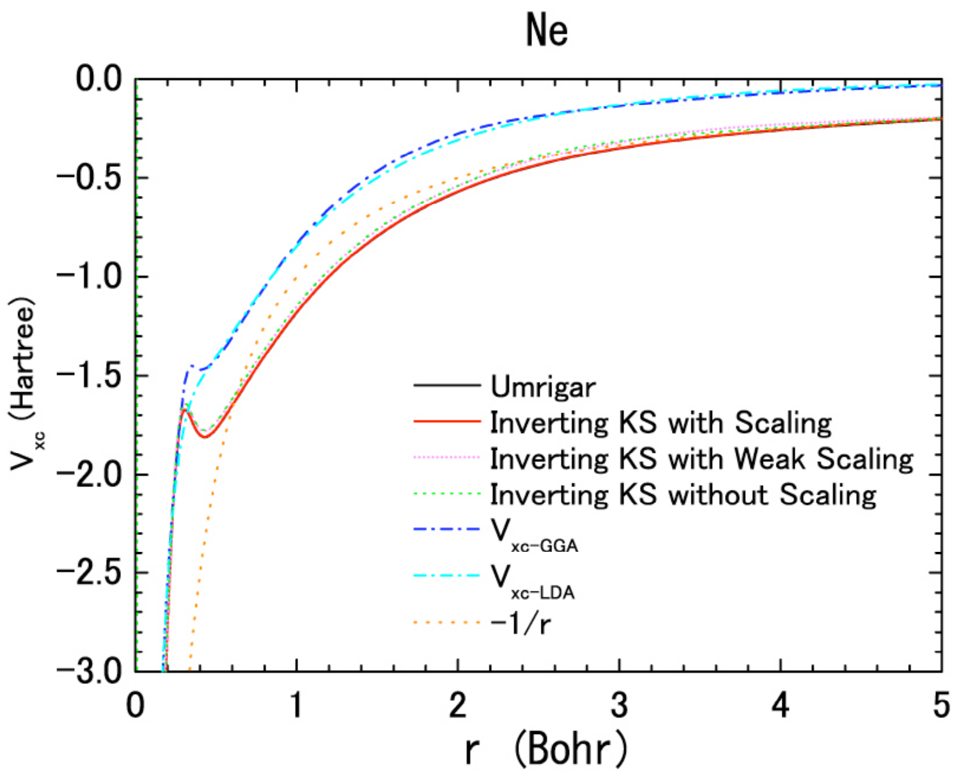
Atomic Case (Be)

(Benchmark)



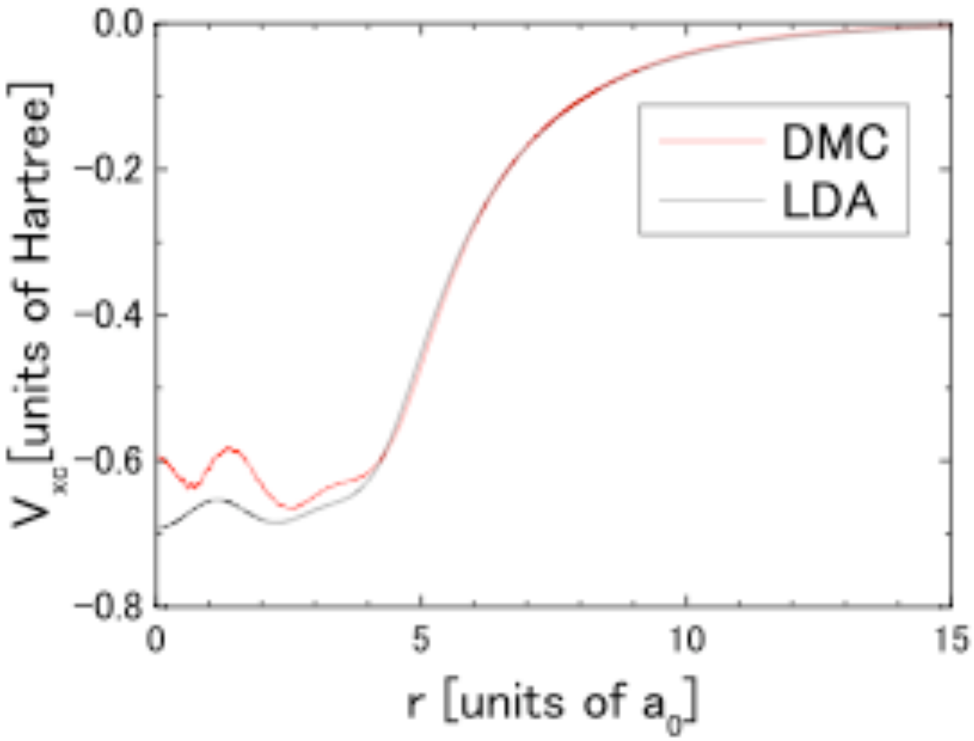
Atomic Case (Ne)

(Benchmark)



Jellium Sphere (z=0)

Z=0, rs=1, N=106



Jellium Sphere (z=2)

rs=5.25, N=60