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Embedded Atom into Jellium Sphere

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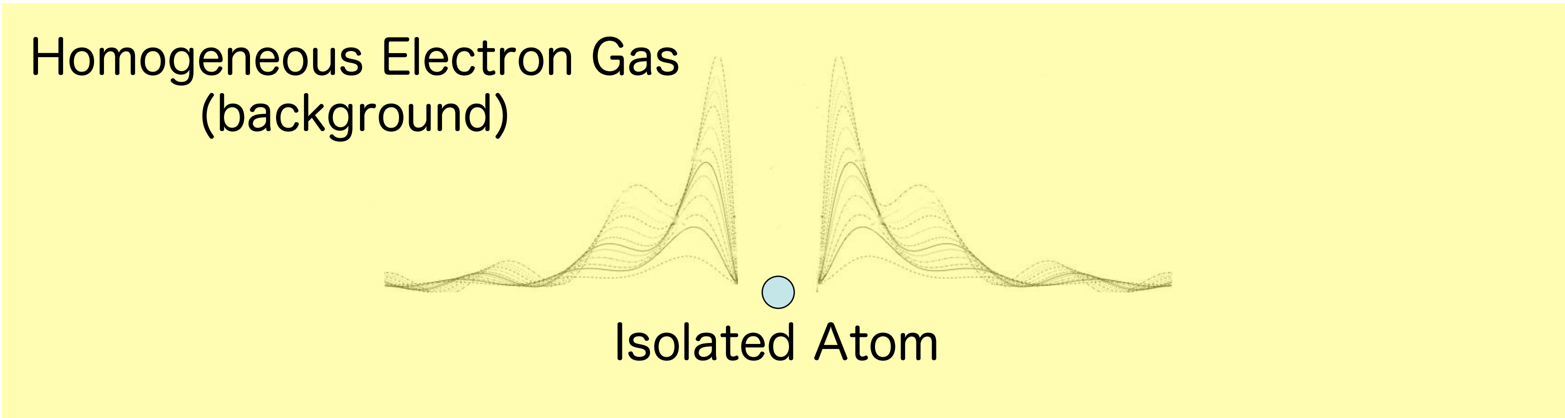
Collaborators

Since 2005

- Prof. Yasutami Takada (Tokyo University)
- Cyrus. J. Umrigar (Cornell University)
    - Dr. M. Shimomoto (ex. Takada group)
    - Dr. K. Yoshizawa (ex. Takada group)

Embedded Atom Model



(※ *Curves taken from M. Shimomoto's thesis*)

- Fundamental modeling of electrons in solids

  Screening, Solvent effect, Kondo coupling, etc.

- Inhomogeneous effects on DFT-XC

  HEG-based XC → Embedded Ions in HEG

- Effective Medium Theory for random systems

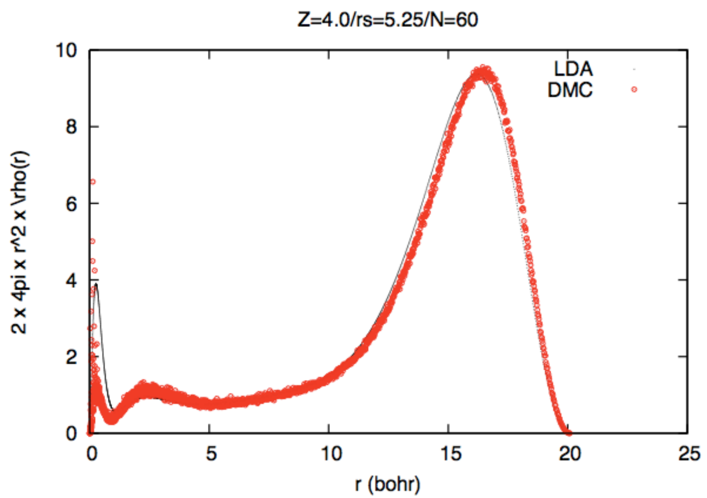
  M.J. Puska et.al., PRB24, 3037 (1981).

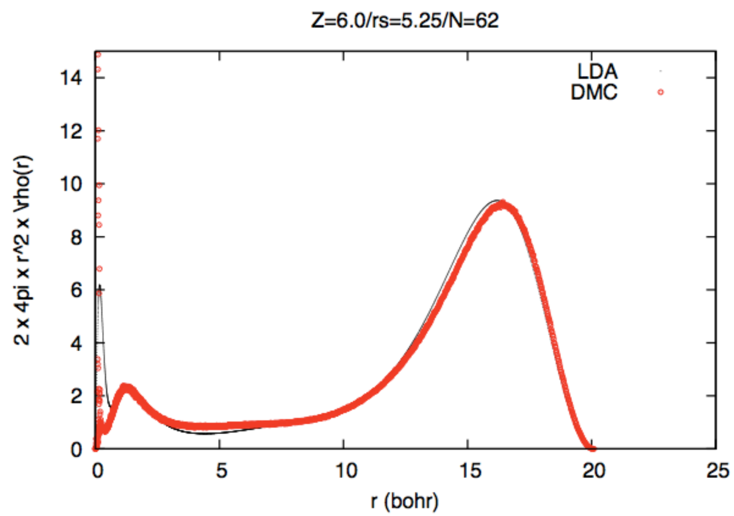
Present Study

Concentrating on Z=1

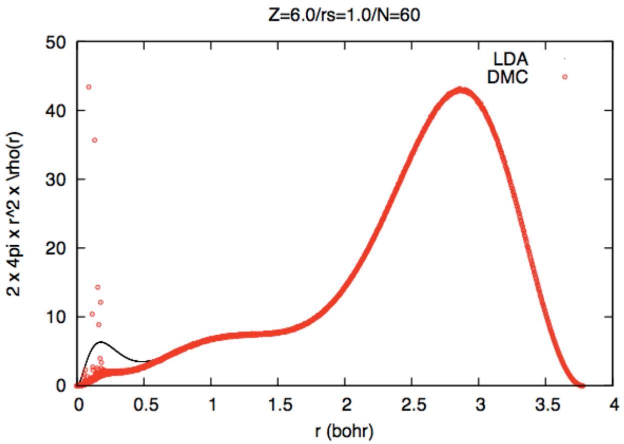
Z≦2 ; running well, some results are shown in this talk

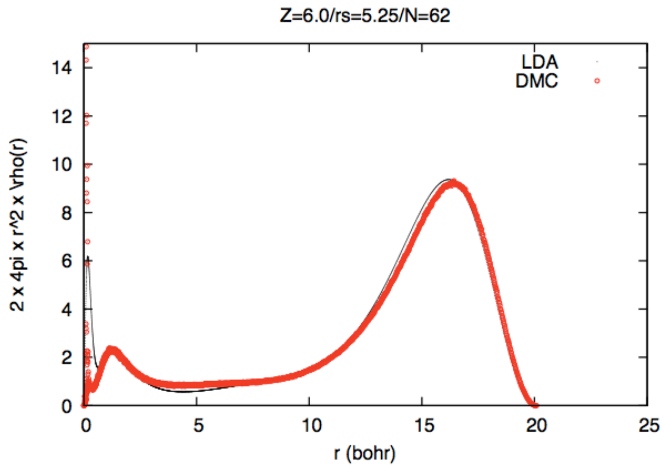
Z≧3 ; troubles in QMC samplings





Comments of other Z





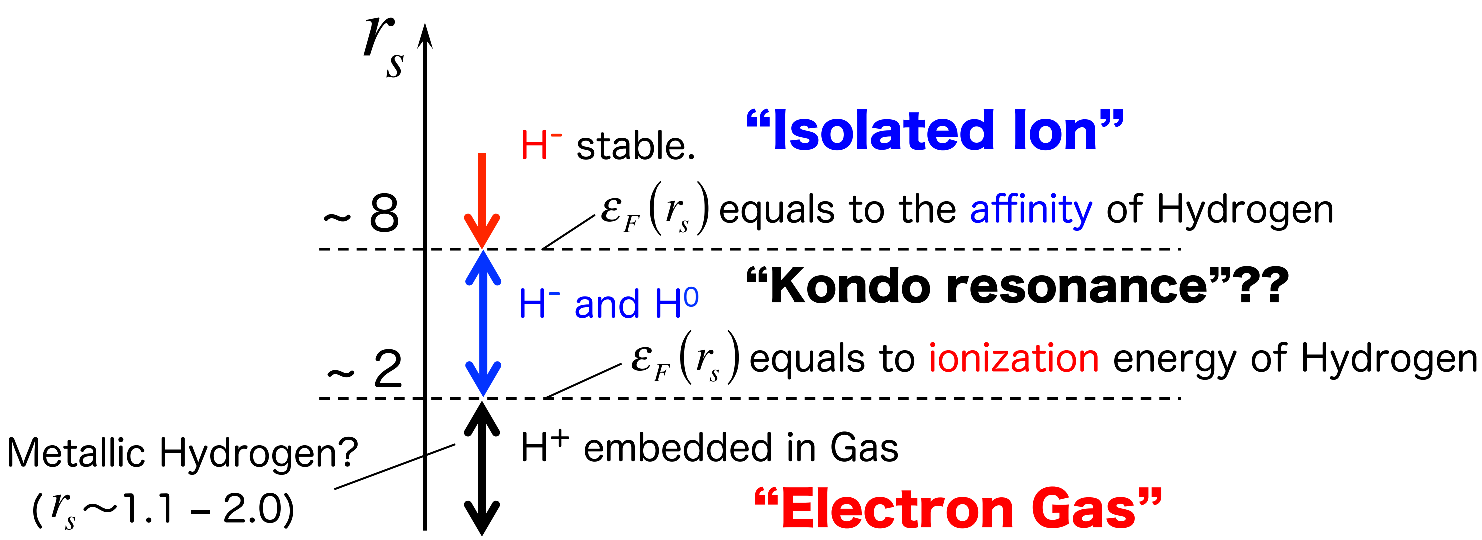
Spin polarization stable? for Z≧5. and at Z=7, the behavior is weird.

- V.U. Nazarov, C.S. Kim, and Y. Takada, Phys. Rev. B 72, 233205 (2005).

Kondo Ferro? ; 'LessThanHalf' gives J→∞ by the renormalization.

Z=7 corresponds to 1s(2)/2s(2)/2p(3), namely the half-filling.

Physics for Z=1



- Kondo resonance exist? $\varepsilon_F\left(r_s^{c;U}\right) \sim A(Hydrogen)$ = -0.0278 ha.
- Which region of rs? $\varepsilon_F\left(r_s^{c;L}\right) \sim I(Hydrogen)$ = +0.499 ha.
- Transition is sharp or cross-over?

DFT used for Metallic Hyd. is justified?

Isolated H^-

Difficult to describe itself...

HF cannot...

H. Hotop, W.C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975)
H.B. Shore, J.H. Rose, E. Zaremba, Phys. Rev. B 15, 2858 (1977)

LDA treatment as a 'proton@jellium'

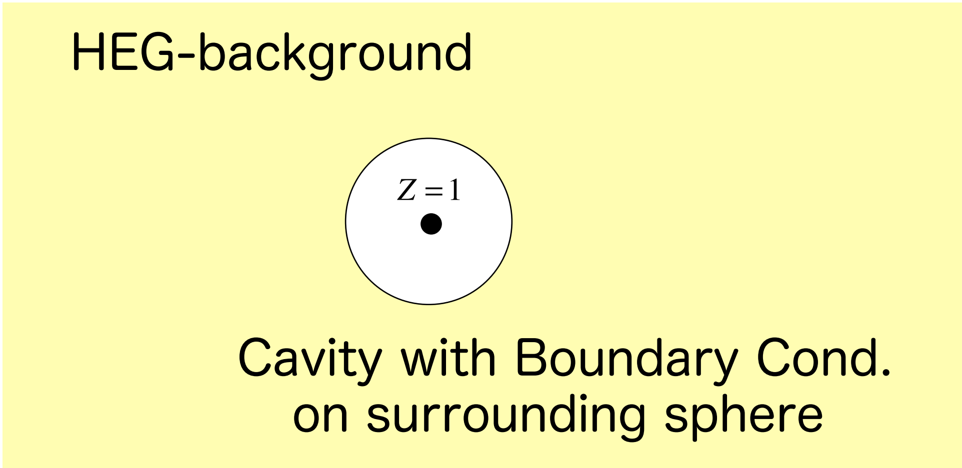
Z.D. Popovic and M.J. Scott, PRL 33, 1164 (1974).
C.O. Almbaldh, U. von Barth, Z.D. Popovic, and M.J. Stott, PRB14, 2250, (1976).

Interpretation of Affinity in DFT

D. Lee,* F. Furche, and K. Burke, J. Phys. Chem. Lett. 1, 2124 (2010).
J.M. Galbraith, H.F. Schaefer, J. Chem. Phys. 105, 862 (1996).
N. Rosch, S.B. Trickey, J. Chem. Phys. 106, 8940 (1997).

LDA studies

- J-H. Song, PhD thesis, Oregon State Univ. (2004).
- M. Shimomoto , K. Yoshizawa, Y. Takada (since 2006).
- A.I. Duff and J.F. Annett, Phys. Rev. B 76, 115113 (2007).



Phase shift in asymptotic behavior of KS orb.

$$\phi_l(r) = kr \cdot j_l(kr) \to \frac{1}{kr}\exp\left[kr + \delta_l(k) - \frac{l\pi}{2}\right]$$

LDA studies

Historically...

- Almbladh, von Barth, Popovic, Stott, PRB14, 2250 (1976).
- Zaremba, Sander, Shore, Rose, J. Phys. F: Met. Phys. 7, 1763 (1977).

Concept of embedding energy/Framework

Essentially...

- Norskov, PRB20, 446 (1979).

LDA results almost clarified.

Later...

- Puska, Nieminen & Manninen, PRB24, 3037 (1981).

Systematic database (rs = 2–8)

- J.-H. Song, Ph. D Thesis (Oregon State, supervisor: Jansen)(2004).

Best accurate results so far.

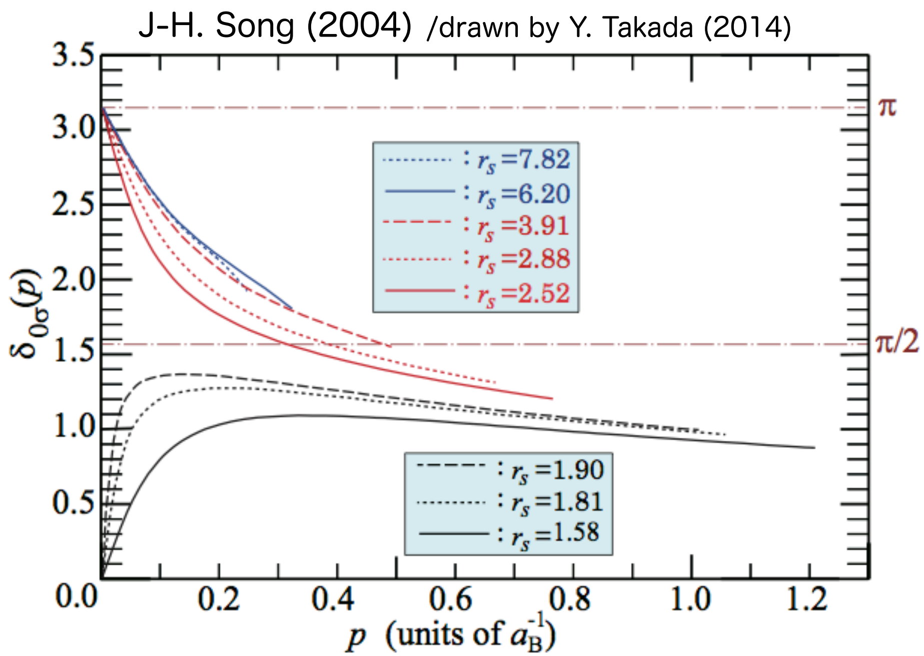
Kondo resonance

- Norskov, PRB20, 446 (1979).
- J.-H. Song, Ph. D Thesis (Oregon State, 2004)

- M. Shimomoto , K. Yoshizawa, Y. Takada (since 2006).
- A.I. Duff and J.F. Annett, Phys. Rev. B 76, 115113 (2007).

drawn by Y. Takada (2014)

Phase Shift



Sign of scattering pot.

$$a = -\left[\frac{d}{dp}\delta'_{l=0}(p)\right]_{p=0}$$

'slope of phase shift'

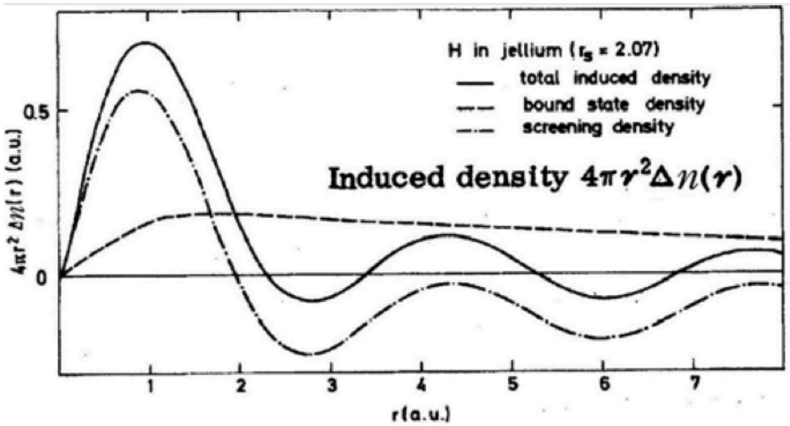
High density ; Attractive/corresponding to H^+

Low density ; Repulsive/H^- or Kondo?

More than one e^- around H^+ seen from far outside

Kondo captured by DFT?

DFT/Z=1 embedded in jellium /Norskov, PRB20, 446 (1979)



r_s > 2 ; KS level giving 'shallow & broad bound state'

- J-H. Song, PhD thesis, Oregon State Univ. (2004).
- M. Shimomoto , K. Yoshizawa, Y. Takada (since 2006).
- A.I. Duff and J.F. Annett, Phys. Rev. B 76, 115113 (2007).

Kondo (Model Treatment)

Elementary... / Not considering resonance between
free electron bath and an impurity

$$\delta n(r) \sim \left[\cos\left(2p_F r - \frac{\pi D}{2} + 2\delta_0 \right) - \cos\left(2p_F r - \frac{\pi D}{2} \right) \right]$$

... Conventional form of the phase shift.

Considering the resonance...

I. Affleck, L. Borda, and H. Saleur, Phys. Rev. B 77, 180404(R) (2008).

Resonance → extension with imaginary part

$$\delta n(r) \sim \left[\cos\left(2p_F r - \frac{\pi D}{2} + 2\delta_0 \right) \cdot F\left(r/\xi_K \right) - \cos\left(2p_F r - \frac{\pi D}{2} \right) \right]$$

short-range ; $F\left(r/\xi_K\right) = \exp\left[i \cdot 0\right] \cdots \quad r << \xi_K$

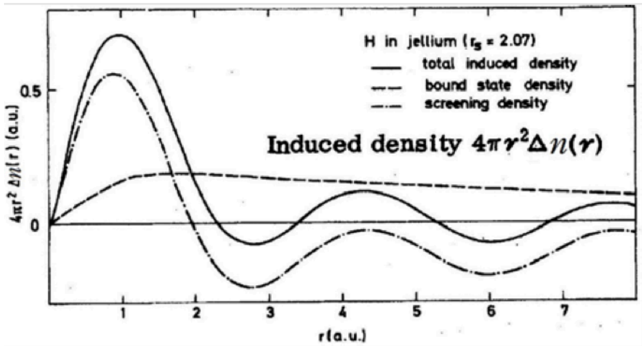
Long-range ; $F\left(r/\xi_K\right) = \exp\left[i \cdot \pi\right] \cdots \quad r >> \xi_K$

$\delta_0 \to \left(\delta_0 + \frac{\pi}{2} \right)$; one more electron bound by
the attracting potential.

Kondo captured by DFT?

$r_s > 2$; KS level giving 'shallow&broad bound state'

- KS orbital/non-physical entity
- DFT/its charge density is meaningful quantity



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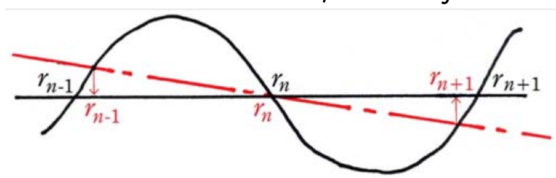


concerned KS orb. contribution

→ occurring so that phase shift reproduces.

QMC calculation

More reliable treatment of electronic correlation.

- Calibration of LDA

  Justification of DFT applied to metallic hydrogen

- QMC charge densities

  also reproduce the phase shift captured by DFT?

QMC studies

For Z=0 upto N=106 (Jellium sphere)

- 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

For Z=1

- Sugiyama, Terray & Alder, J. Stat. Phys. 52, 1211 (1988) ; VMC

  N=54 with PBC on a cubic supercell (3x3x3x2(spin))

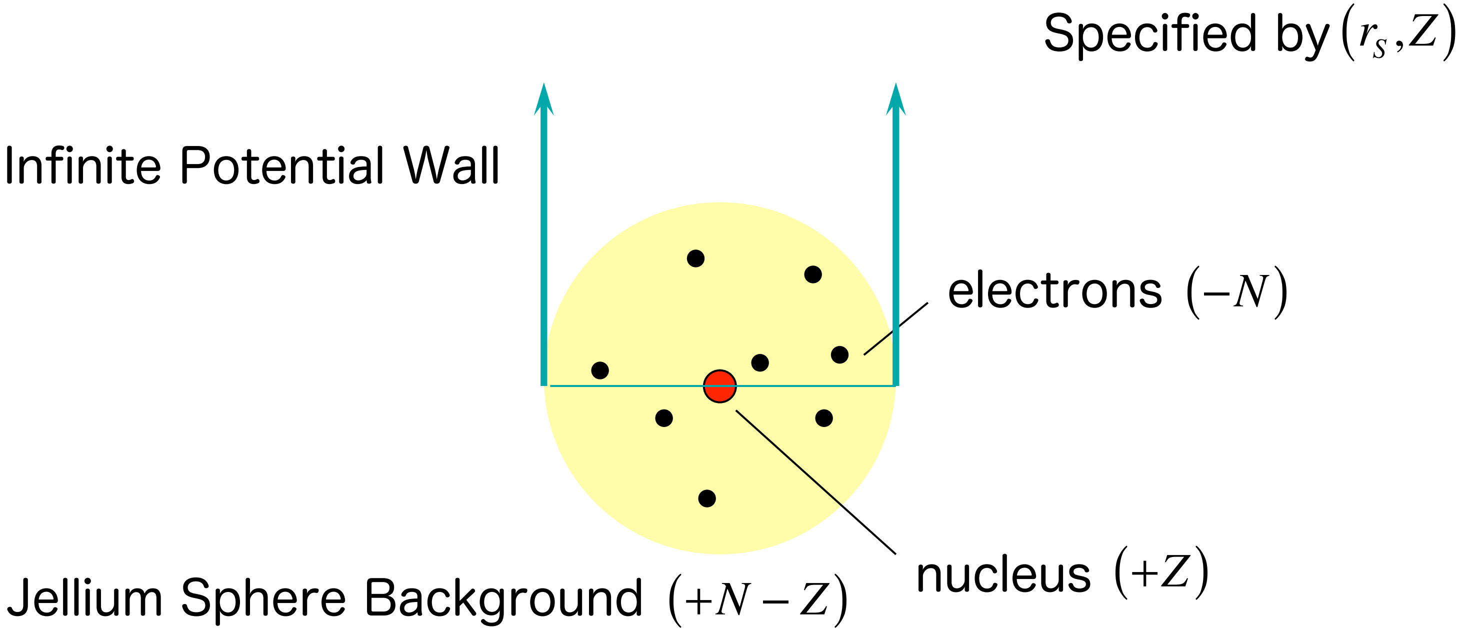
  $3 < r_s < 7$ is reported as the region of repulsive/attractive transition

- A.I. Duff and J.F. Annett, Phys. Rev. B 76, 115113 (2007).

  N=10 with fixed BC (i.e., solve in a finite-size sphere)

  Friedel oscillation evaluated by $\delta n(r)$

Present System

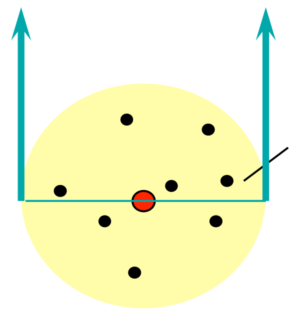


Present study ; Z=1, upto N=170

Friedel Oscillation

Density difference from Z=0

finite size err. partly removed



$(+N-Z)$

Scattering by the sphere edge is common for Z=0 and Z≠0

→ eliminated by taking the difference to extract genuine scattering nature by Z.

$\lambda = \left(\frac{N-1}{N-2}\right)^{\frac{1}{3}}$; scaling factor

adjusting sphere scale $R_B \propto N^{\frac{1}{3}}$

$$\delta n(\vec{r}) = n(\vec{r})_{Z,N} - \lambda^3 \cdot n(\lambda\vec{r})_{Z=0,N-2}$$

adjusting the normalization

Technical stuff

to be prepared

Generate Trial Node by LDA

↓ Trial/Guiding WaveFunction

DMC by CHAMP

- **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)

Calibration

w/o Potential Wall

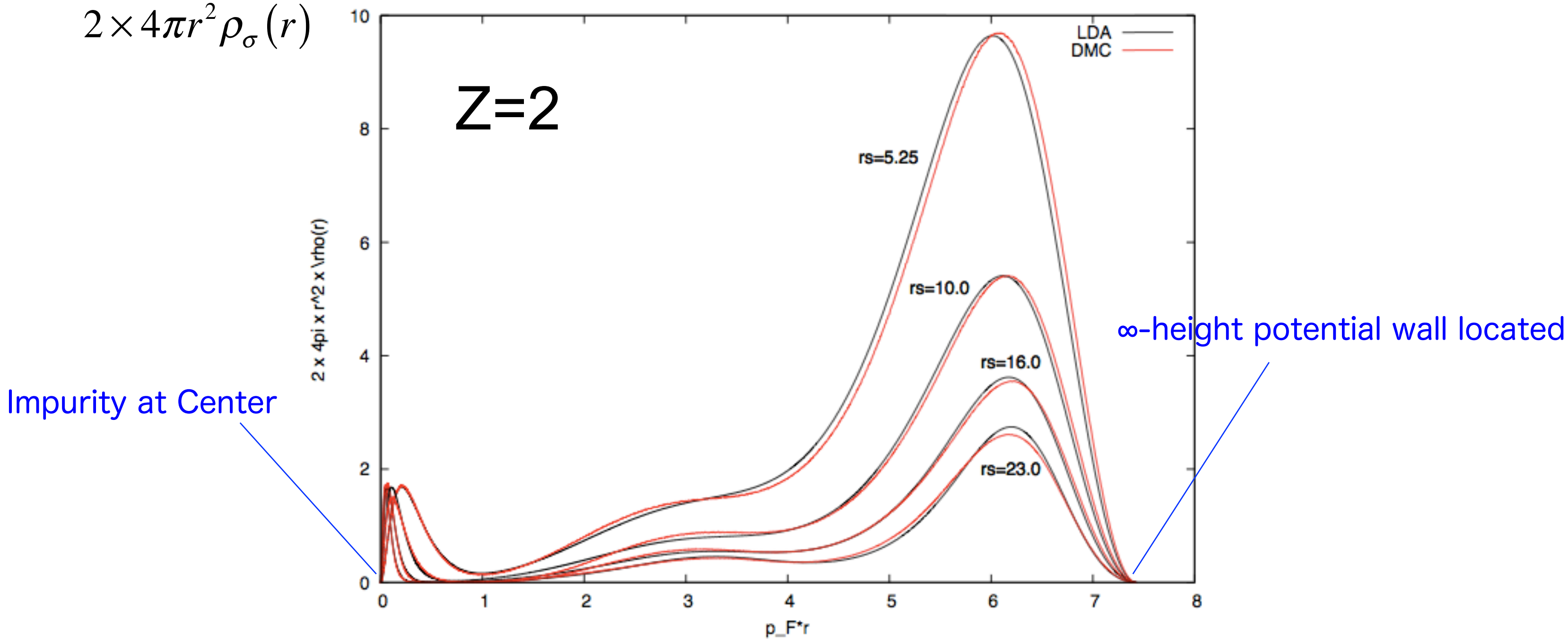
GS energy for Z=0, N=106, rs=1.0.

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)

Charge densities

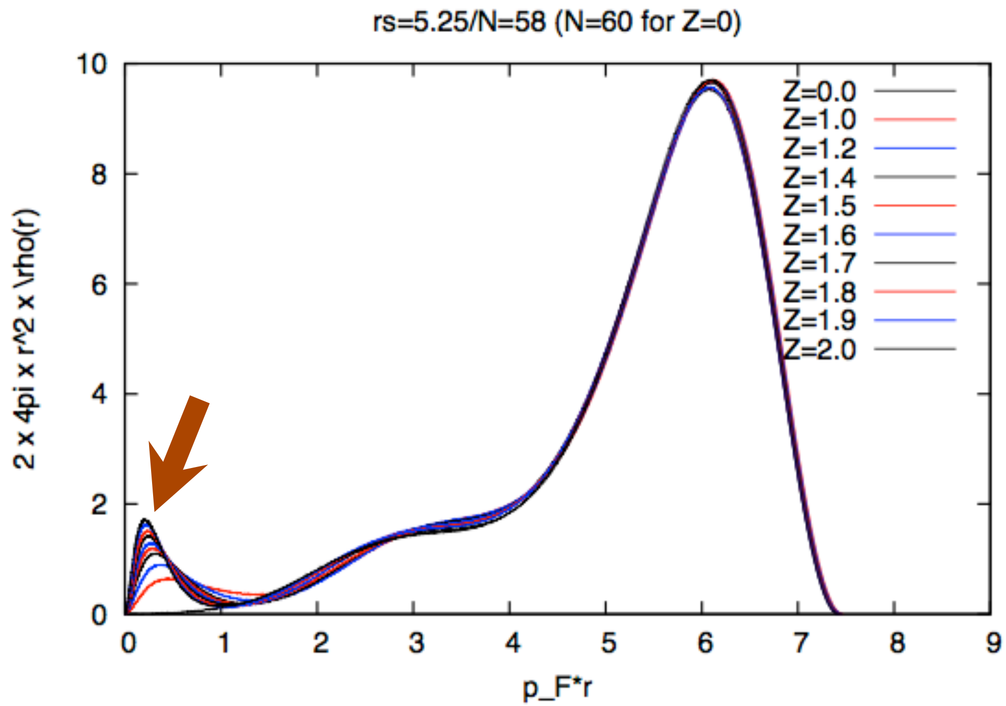
$2 \times 4\pi r^2 \rho_\sigma(r)$



Dual peak feature

How LDA and DMC differ

Cusp and 1st peak

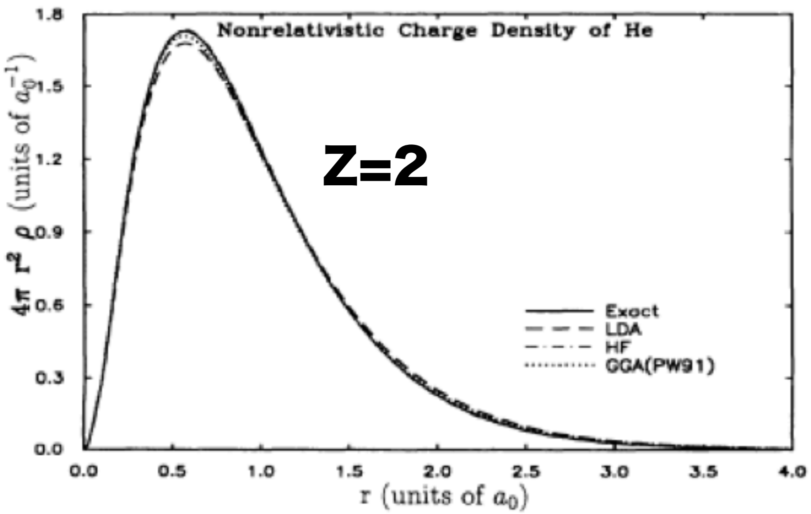


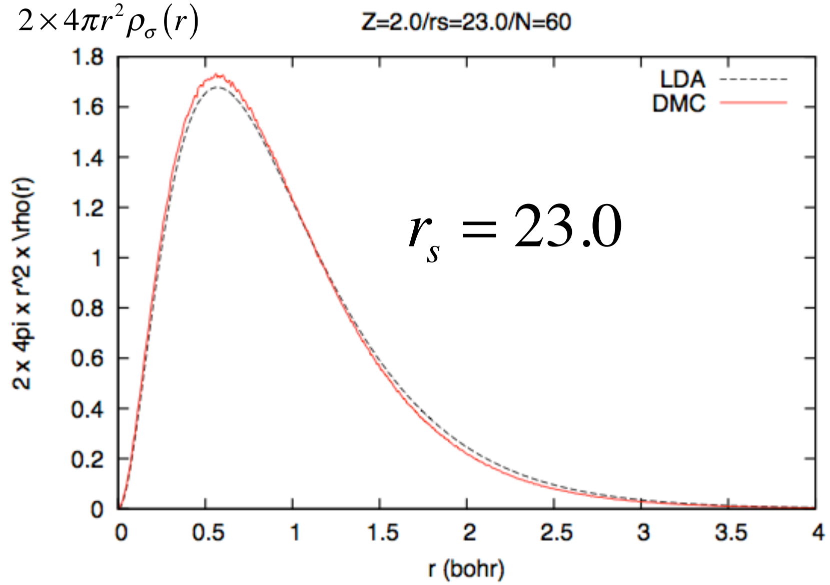
identified coming from $n(r) = n(0) \cdot \exp[-2Z \cdot r]$

→ then it should converges the atomic density when $r_s \to \infty$

Z=2/He Atom

Umrigar and Gonze, PRA50, 3827 (1994)

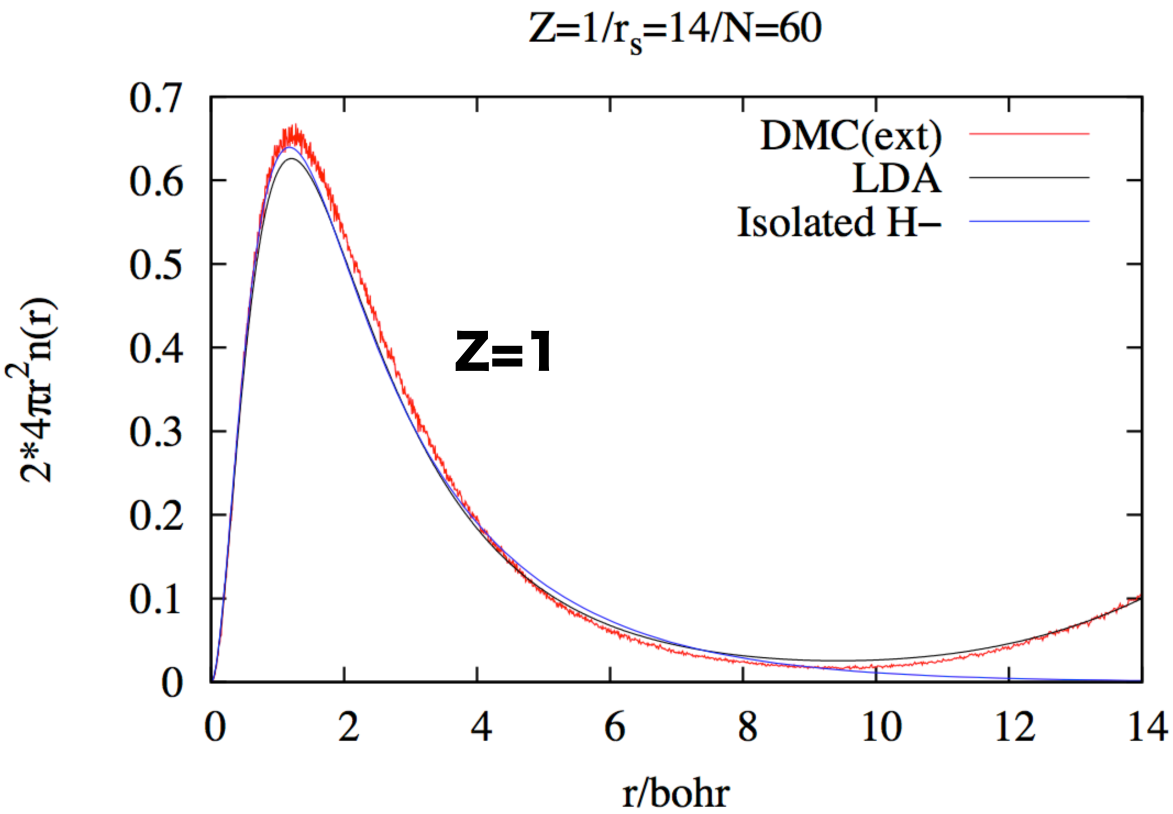




Coincides each other in dilute limit

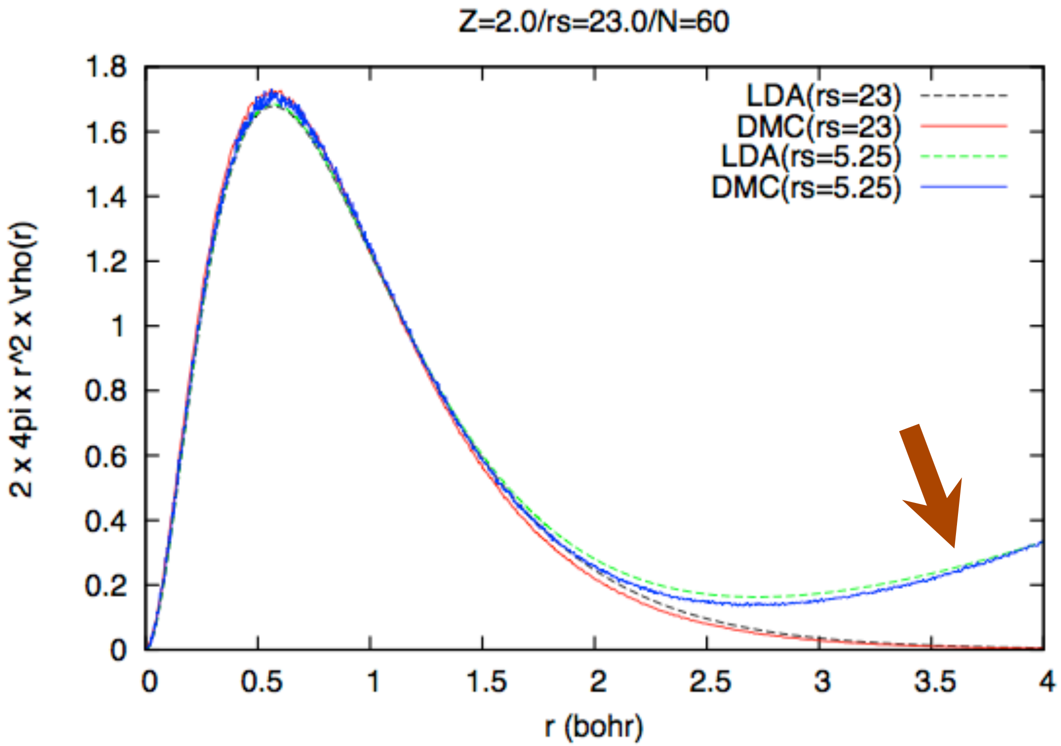
Same tendency in LDA/DMC difference

Dilute limit/Z=1



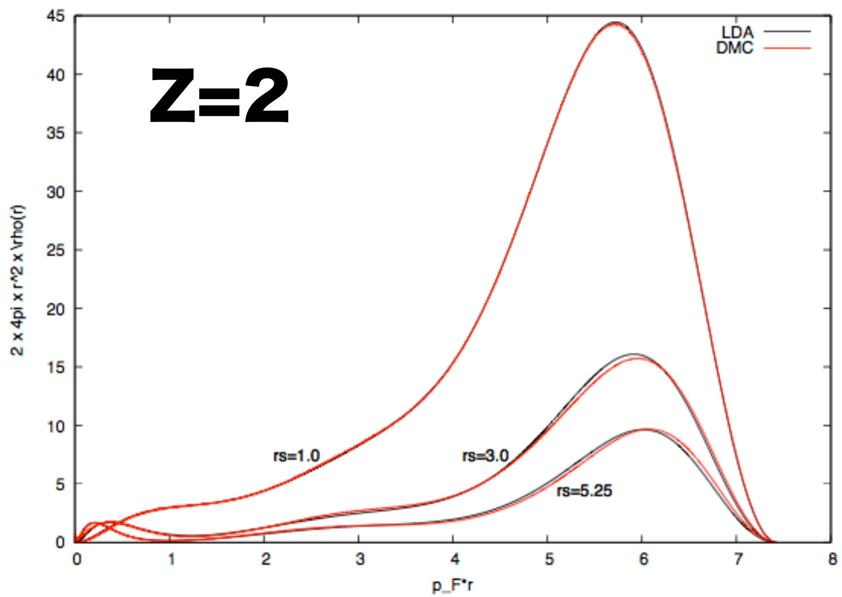
C.J. Umrigar and X. Gonze, Phys. Rev. A 50, 3827 (1994).

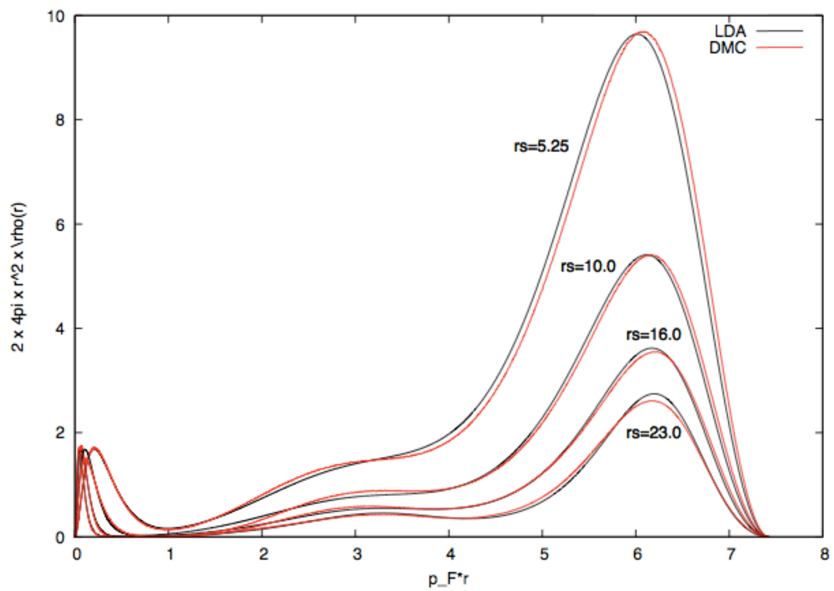
$Z=2/r_s$ dependence



increases as system becomes dense

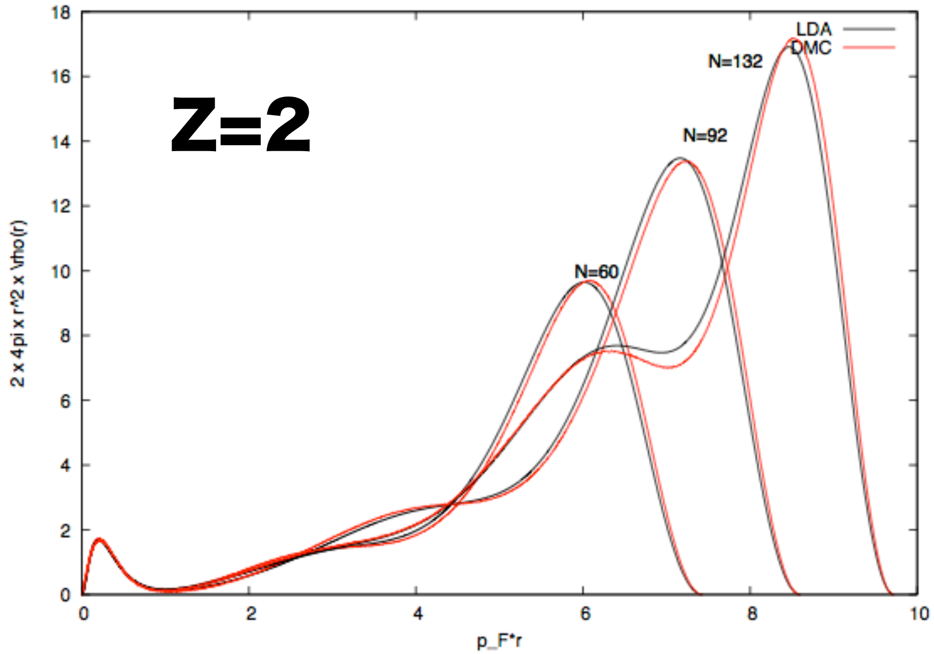
Diff. between LDA





The thicker the better agreements.

N-dependence

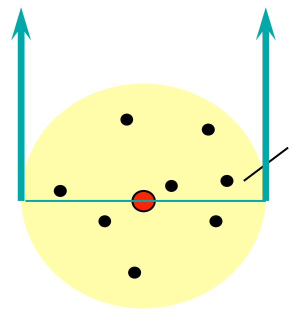


The more N, the more layered shell structure

Friedel Oscillation

Density difference from Z=0

finite size err. partly removed



Scattering by the sphere edge is common for Z=0 and Z≠0

→ eliminated by taking the difference to extract genuine scattering nature by Z.

$$\lambda = \left(\frac{N-1}{N-2}\right)^{\frac{1}{3}}$$; scaling factor

adjusting sphere scale $R_B \propto N^{\frac{1}{3}}$

$$\delta n(\vec{r}) = n(\vec{r})_{Z,N} - \lambda^3 \cdot n(\lambda \vec{r})_{Z=0,N-2}$$

adjusting the normalization

Typical occupation

to realize the stable calculation

s orbital subject to the resonance

r_s=1 (N=58)	r_s=4 (N=60)	r_s=4 (N=170)
4d	4d	5d
3s	11n	9l
6h	6h	6g
------ Fermi level	------------	------------
	3s	4s
5g	3p	4p
3p	5g	8k
4f	4f	5f
2s	3d	7i
3d	2s	6h
2p	2p	4d
1s	1s	5g
		3s
		3p
		4f
		3d
		2s
		2p
		1s

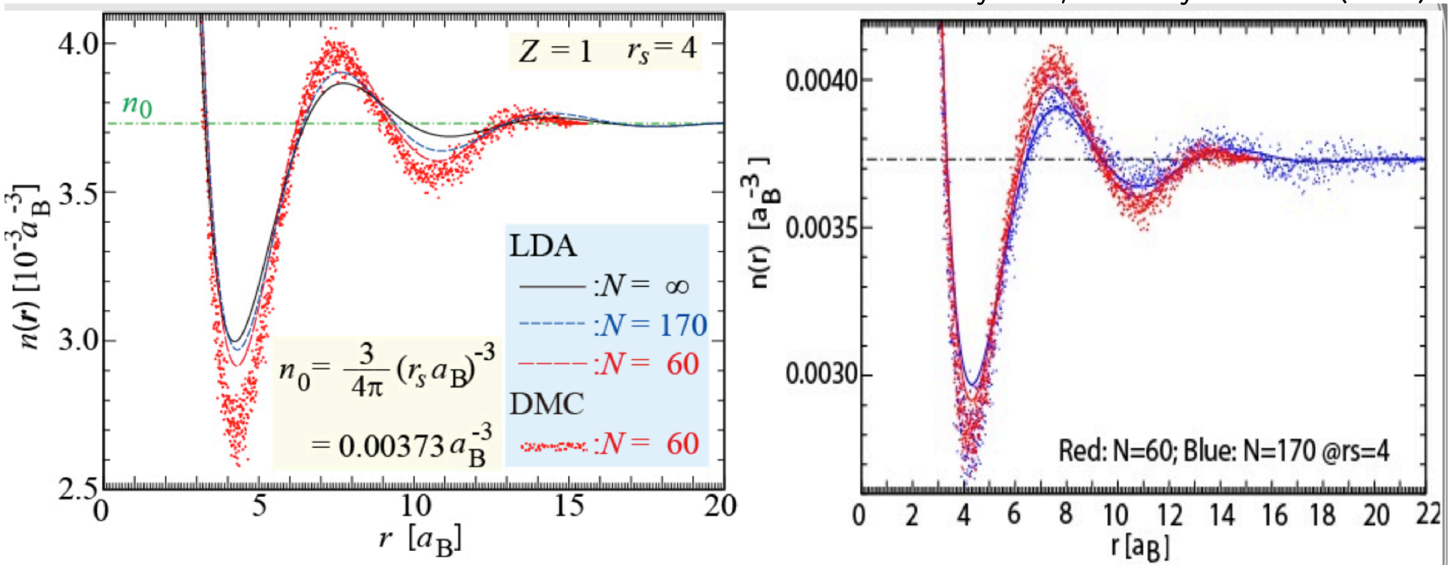
/drawn by Y. Takada (2014)

※Orbital name such as '1p', '1d' originates from Sottile et.al.

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

Friedel Ocsilation

DMC by R.M./drawn by Y. Takada (2014)

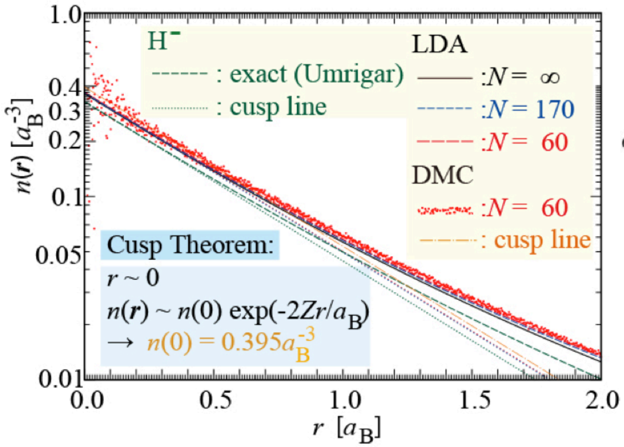


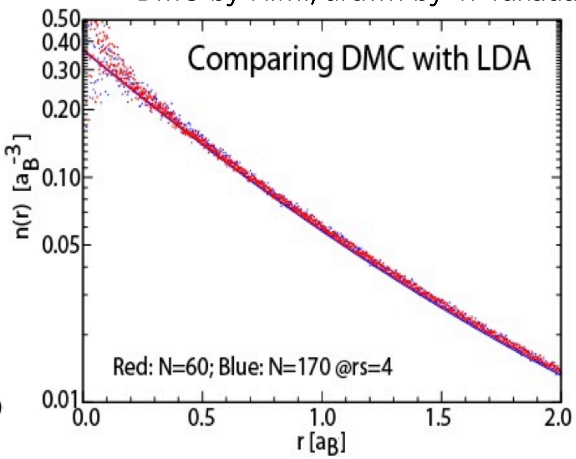
QMC almost similar to DFT

A bit stronger attraction in QMC

Cusp description

DMC by R.M./drawn by Y. Takada (2014)





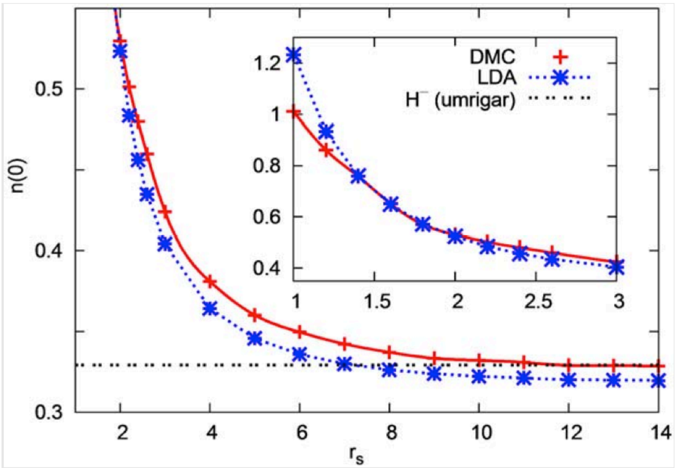
Diff. btwn DMC and LDA (almost similar in Friedel Osc.)

→ Diff. matters almost only on Cusp Intercept $n(0)$

$$n(r) = n(0)\cdot\exp[-2Z\cdot r]$$

Possible calibration ; $n_{LDA}(0) \to n_{DMC}(0)$

Cusp intercept



Cross-over around rs~2

[c.f., Hydrogen metal region (rs ≦ 2.0)

over-estimation by $n_{LDA}(0)$

Summary by DMC

Charge density difference btwn DMC and LDA

- Friedel Oscillation

  Reproduced the Kondo resonance DFT captured with slight stronger attraction.

- Cusp-intercept

  Correction to $n_{LDA}(0)$