Is the *homogeneous* electron gas *homogeneous*?

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Outline

- Electron gas (jellium): simplest way to view a metal
  - 'homogeneous' and 'normal' ⟸
- Hartree-Fock: simplest method for many-electron systems
  - a single Slater determinant wf --- self-consistent mean-field solution
  - conventional solution (**restricted** HF): foundation for Fermi liquid th. ⟸
- **R**HF is not true HF ground state (Overhauser, 1962)
- **What is the HF ground state of jellium?**
  - numerical --- full **unrestricted** HF solution
  - Broken spin symmetry, but different from Overhauser state
- An analytic model --- novel pairing mechanism (instability @ FS)

Collaborator:

- David Ceperley (UIUC)

Thanks:

- Henry Krakauer (W&M)
- Richard Martin (UIUC)

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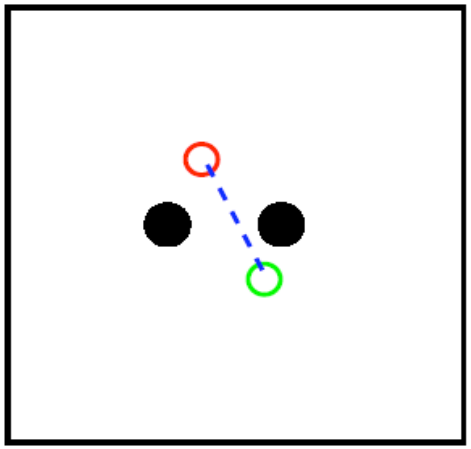
References: (http://physics.wm.edu/~shiwei)

- Zhang & Ceperley, PRL, 100, 236404 (2008)

Electron gas – simplest model for metal

Focus on ground state:

Illustrative example: "toy system" for molecule or solid



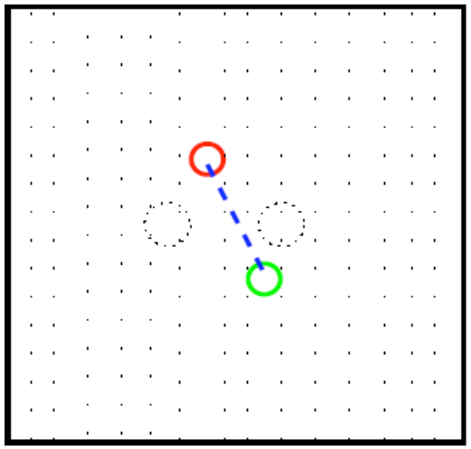
Periodic box (supercell)

ion, fixed, +1 charge

electron, spin ↑

electron, spin ↓

⇓ smear out ions → jellium



Periodic box (supercell)

ion −−> uniform positive backgroun

electron, spin ↑

electron, spin ↓

Good model for metals:

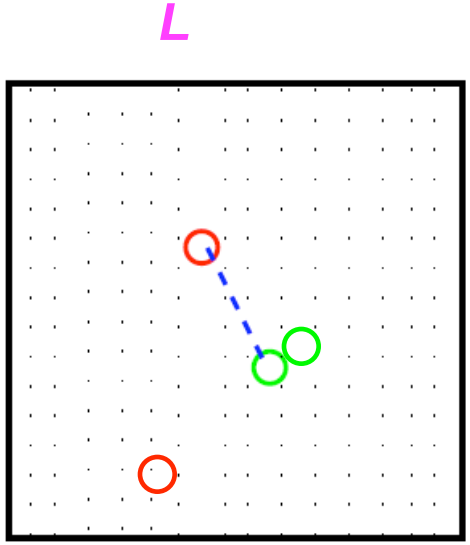
Na, Al, ….

Electron gas – simplest model for metal

- Investigated for >70 years:

  Wigner, Bloch, …

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j}^{N}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \text{cnst}$$



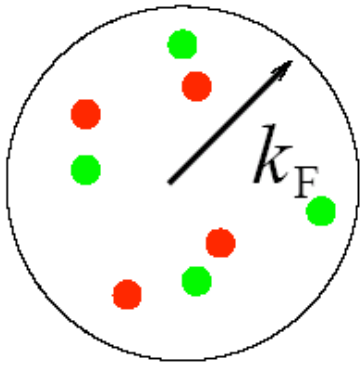
Periodic box (supercell)

electron, spin ↑

electron, spin ↓

- Non-interacting solution:

  Fermi sphere



$$N = N_\uparrow + N_\downarrow$$

r_s : average dist. between 2 electrons

$$4\pi {r_s}^3/3 \equiv L^3/N$$

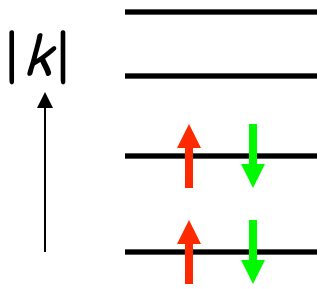
defines density

- Focus on
  - r_s < 5a.u. (high to medium density --- real materials)
  - Unpolarized: $N_\uparrow = N_\downarrow$

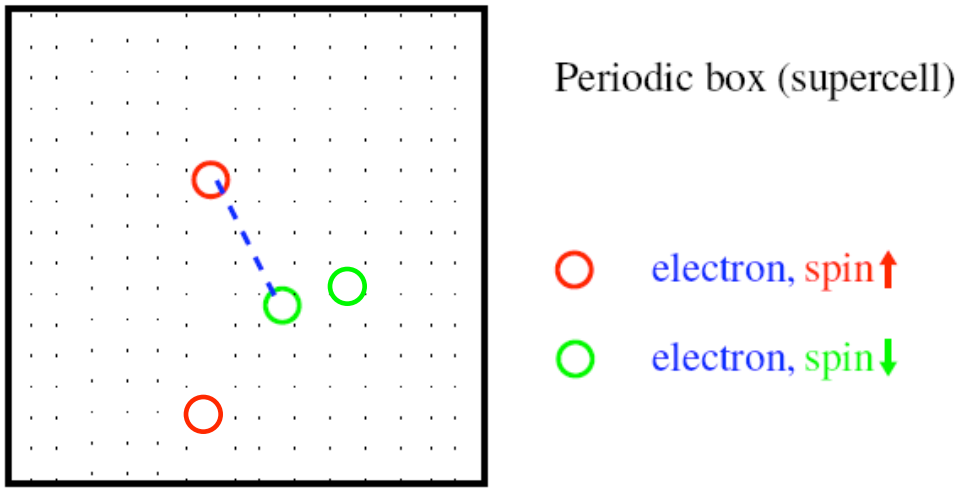
The challenge of non relativistic QM

High density: wave-like

→ Fermi liquid (?)



jellium



Low density: particle-like

→ Wigner crystal

r_s : average distance bt. electrons

$\varepsilon_K \sim 1/r_s^2$; $\varepsilon_P \sim 1/r_s$

Often system is at neither limit

Quantum Monte Carlo (QMC) results (Ceperley & Alder)

→ foundation of modern electronic structure calc's

"The standard model" in condensed matter

- Density functional theory (DFT) with local-density types of approximate functionals: LDA, GGA, …. (Nobel, **Kohn'** 98)
- Many applications
- Independent-electron framework:

Electronic Hamiltonian: (Born-Oppenheimer)

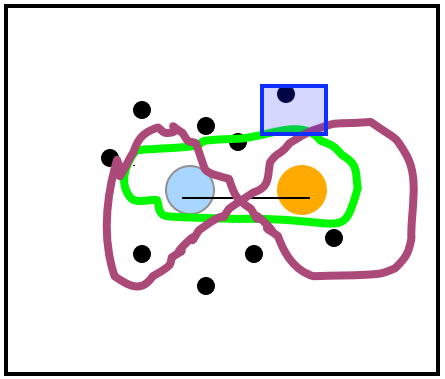
$$H = H_{1-\mathrm{body}} + H_{2-\mathrm{body}} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} V_{\mathrm{ext}}(\mathbf{r}_i) + \sum_{i<j}^{N} V_{\mathrm{int}}(|\mathbf{r}_i - \mathbf{r}_j|)$$

$$H_{\mathrm{LDA}} = H_{1-\mathrm{body}} + \sum_{i=1}^{N} f_{\mathbf{c}}(n(r_i))$$

LDA

jellium!

MnO



- Almost "routine" tool:

ABINIT, ESPRESSO, GAMESS, Gaussian, VASP, ….

"The standard model" in condensed matter

- Jellium is routinely used as a reference state in modern electronic structure calculations
- Jellium 'correlation energy' $f_c(n)$ is a fundamental concept
- But its definition is in terms of the Hartree-Fock energy

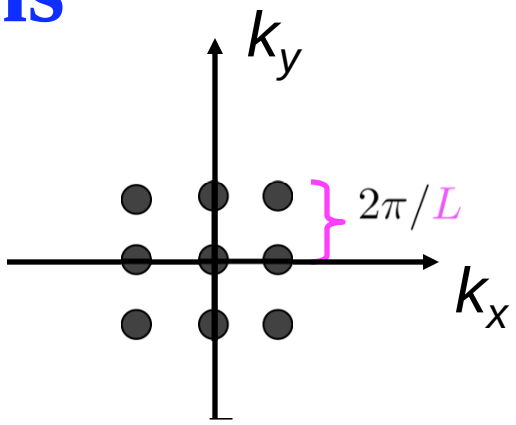
--- What's the HF energy? What's the HF state?

Many works, e.g. recently by Trail & Needs: Wigner

We will focus on high to intermediate density

Hartree-Fock solutions

- Choose plane-wave basis: |*k*>



- In 2nd quantization:

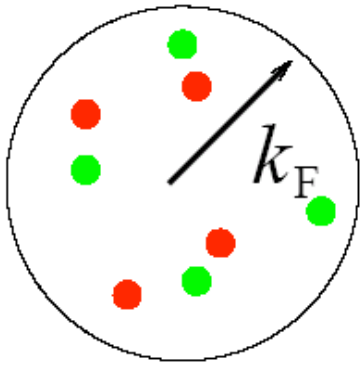
$$\hat{H} = \sum_{\sigma,\mathbf{k}} \frac{1}{2}\mathbf{k}^2 c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \frac{1}{2}\frac{4\pi}{L^3} \sum_{\sigma,\sigma'} \sum_{\mathbf{k},\mathbf{k}',\mathbf{Q}} \frac{1}{\mathbf{Q}^2} c^\dagger_{\mathbf{k}-Q,\sigma} c^\dagger_{\mathbf{k}'+Q,\sigma'} c_{\mathbf{k}',\sigma'} c_{\mathbf{k},\sigma}$$

- Energy:

$$K + (V_{\text{Hartree}} + V_{\text{exchange}})$$

- Wave function – single Slater determinant

$$|\Phi\rangle = |\Phi_\uparrow\rangle \otimes |\Phi_\downarrow\rangle$$



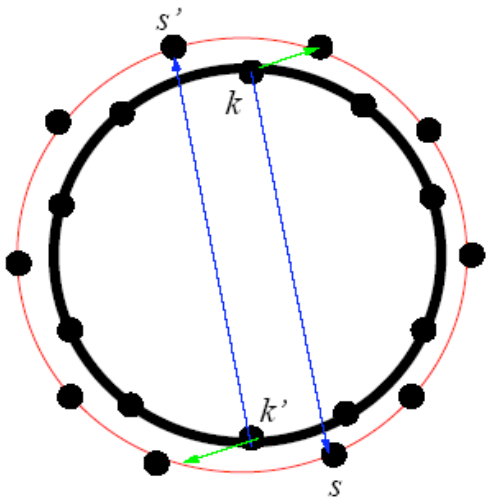
- Textbook solu$|\Phi_\uparrow\rangle = |\phi_1, \phi_2, \cdots, \phi_{N_\uparrow}\rangle$
  - $|\Phi_\uparrow\rangle = |\Phi_\downarrow\rangle = |\mathrm{FS}\rangle$ homogeneous in real space
  - *E*=*K*-|V_{exchange}| $|\phi_1\rangle = \sum_k c_1(k)|k\rangle$ $\sum_{k,k`}1/|k-k'|^2$

Hartree-Fock solutions

- Textbook solution is not **the** HF ground state
- Hand-waving: how to have a Slater det with $E<E_{RHF}$?
- Consider pairing state:

$$c_k^2 + c_s^2 = 1$$

$$\begin{aligned} |\uparrow\rangle &= c_k|k\rangle + c_s|s\rangle \\ |\downarrow\rangle &= c_k|k\rangle - c_s|s\rangle \end{aligned}$$



- 2 pairs {k,s}, {k',s'} at FS: s-k=-(k'-s')

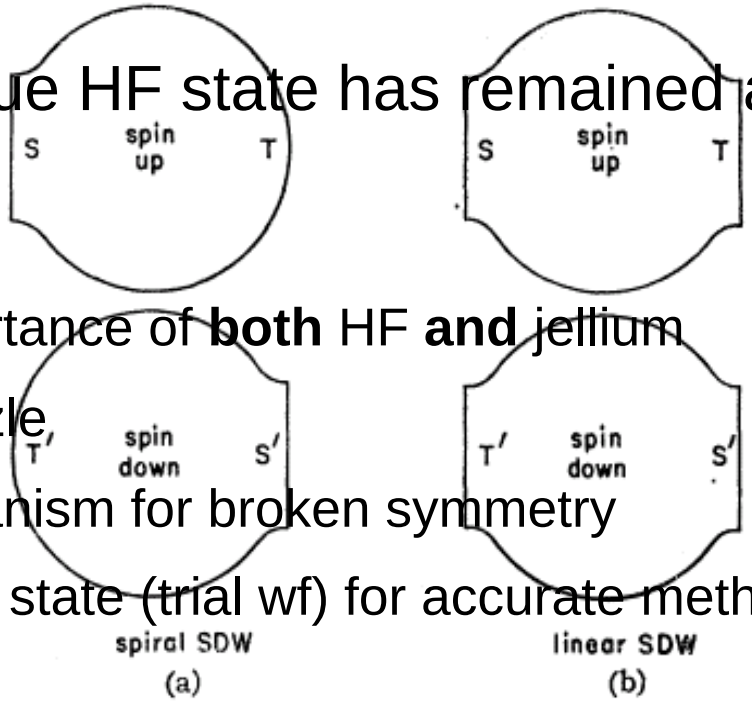
K	$V_{Hartree}$	$V_{exchange}$
higher	=0	**higher** & **lower**

Interference bt. 2 parallel pairs

$$\hat{H} = \sum_{\sigma,\mathbf{k}} \frac{1}{2}\mathbf{k}^2 c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \frac{1}{2}\frac{4\pi}{L^3} \sum_{\sigma,\sigma'} \sum_{\mathbf{k},\mathbf{k}',\mathbf{Q}} \frac{1}{\mathbf{Q}^2} c^\dagger_{\mathbf{k}-Q,\sigma} c^\dagger_{\mathbf{k}'+Q,\sigma'} c_{\mathbf{k}',\sigma'} c_{\mathbf{k},\sigma}$$

Hartree-Fock solutions

- Overhauser states:
  - proved (1962) there exists spin-density wave states with $E<E_{RHF}$
  - Spiral or linear SDWs
  - Wave vector of SDW=$2k_F$
  - **Not** a self-consistent HF solution, just an example determinant
- Determining the true HF state has remained a challenge
- Why bother?
  - fundamental importance of **both** HF **and** jellium
  - mathematical puzzle
  - understand mechanism for broken symmetry
  - suggest candidate state (trial wf) for accurate methods (e.g., QMC)



Finding the unrestricted HF solution

Iterative projection:

$$e^{-\tau \hat{H}_{\rm HF}(\Phi^{(n)})} |\Phi^{(n)}\rangle \;\rightarrow\; |\Phi^{(n+1)}\rangle$$

$|\Phi_\uparrow\rangle \otimes |\Phi_\downarrow\rangle$

$\hat{H}_{\rm HF}(\Phi^{(n)})$ is a one-body Hamiltonian:

$c^\dagger c^\dagger c\, c$ in $\hat{H} \;\rightarrow\; c^\dagger c \,\langle c^\dagger c\rangle_{\Phi^{(n)}} + \cdots$

$|\Phi_\uparrow\rangle \neq |\Phi_\downarrow\rangle$

unrestricted

$$\hat{H} = \sum_{\sigma,\mathbf{k}} \frac{1}{2}\mathbf{k}^2 c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \frac{1}{2}\frac{4\pi}{L^3} \sum_{\sigma,\sigma'} \sum_{\mathbf{k},\mathbf{k}',\mathbf{Q}} \frac{1}{\mathbf{Q}^2} c^\dagger_{\mathbf{k}-Q,\sigma} c^\dagger_{\mathbf{k}'+Q,\sigma'} c_{\mathbf{k}',\sigma'} c_{\mathbf{k},\sigma}$$

- For small τ, guaranteed to reach a minimum
- We use different choices (random) of initial $|\Phi^{(0)}\rangle$ to avoid local minima
- True UHF solution! (**But** spiral SDW solutions excluded)
- Tricks (FFT, etc)

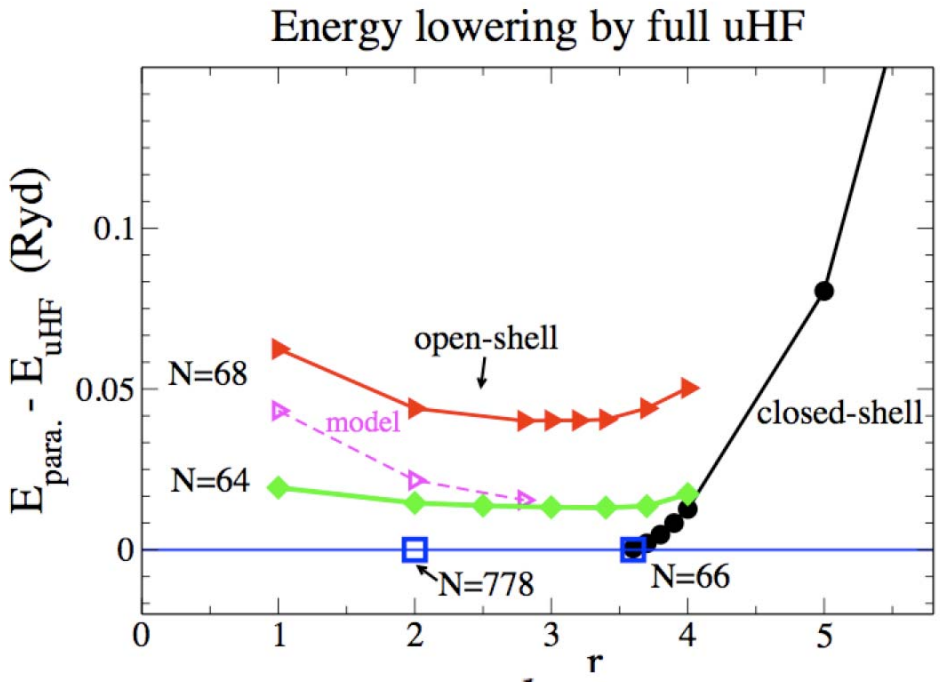
Unrestricted HF (UHF) solution

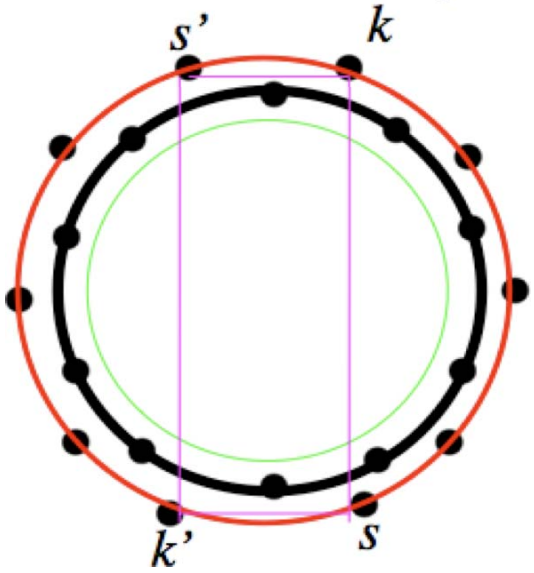
For finite-size (L):

- Closed-shell:
  - ➢ UHF exist for $r_s > r_s^c(L)$
- Open-shell:
  - ➢ UHF always exists

    pairing at no cost

How to approach the thermodynamic limit?





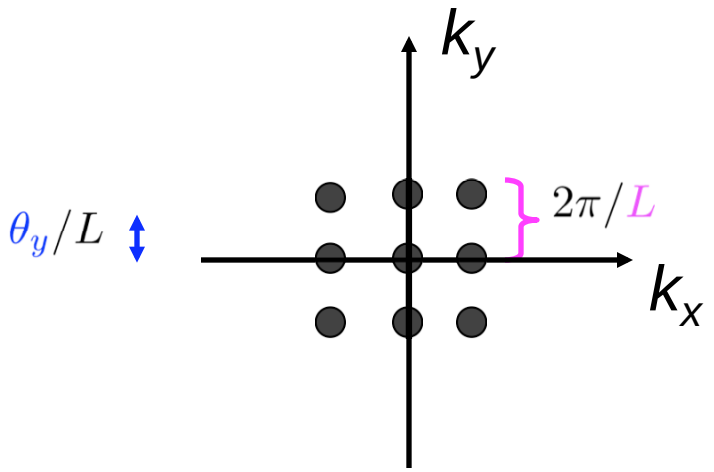
Twist averaged boundary conditions (TABC)

- TABC widely used in band structure methods; recently in many-body calculations
  (Lin, Zhong & Ceperley; Kwee, Zhang, Krakauer; Chang & Zhang; ….)

- A phase when electron goes around the lattice:

$$\Psi(x+L) = e^{i\theta_x}\,\Psi(x)$$

  – Shifts plane-wave vectors in |k>:



- Breaks degeneracy in free-particle spectrum

- Averaging results over twist θ greatly reduces finite-size effects

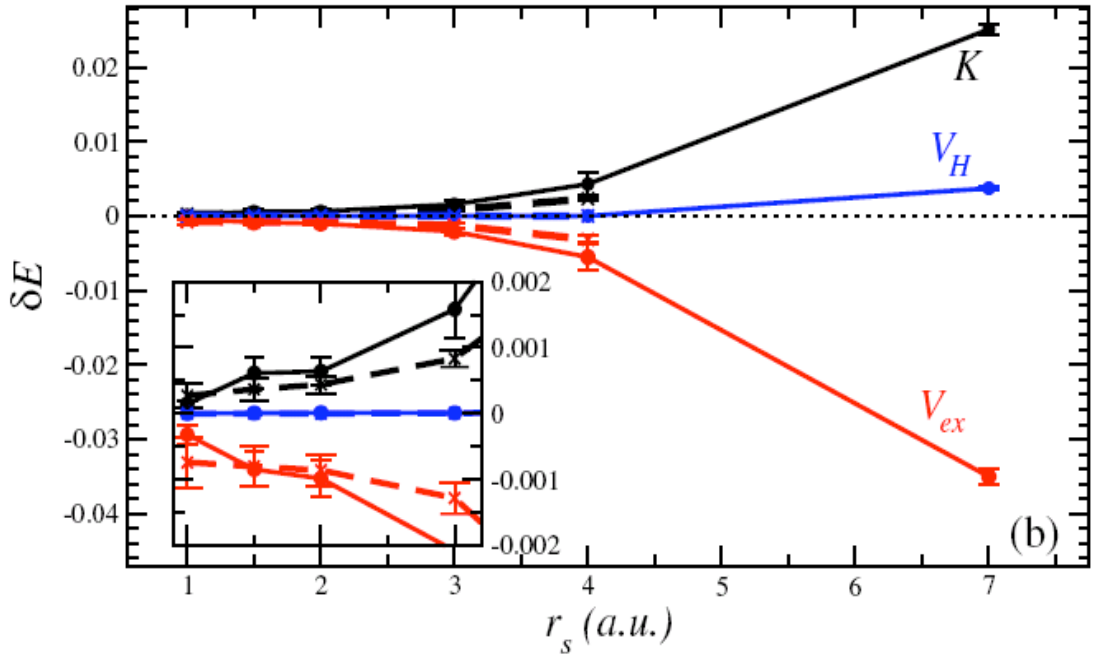
The unrestricted HF solution

Energy lowering from RHF:

- UHF for **all** r_s
- δE is tiny at low r_s:

  Recall

$$E_{\mathrm{RHF}} = \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} \right) \mathrm{Ry}$$



- UHF broken symmetry state:

  - lowering **exchange** at cost of **kinetic**

  - **Hartree** unchanged at low r_s → uniform charge density

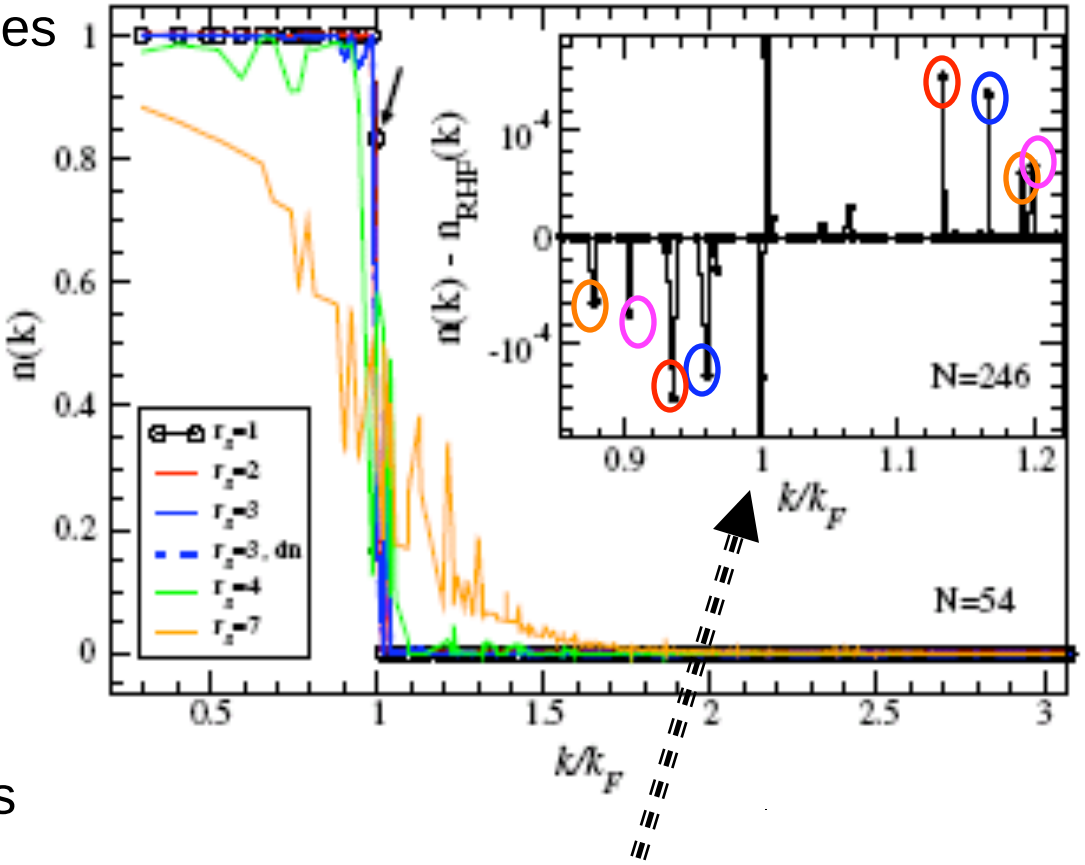
The unrestricted HF solution

Momentum distribution *n(k)* :

- Modification to FS decreases with r_s
  limited to near FS
- n(k) spin-indep. --- spin-symmetry always holds:

$$n_\uparrow(k) = n_\downarrow(k)$$

  e.g., no spiral
- Inset:
  - Primary spike at k_F
  - Paired “satellite” spikes (small, equal length)



The unrestricted HF solution

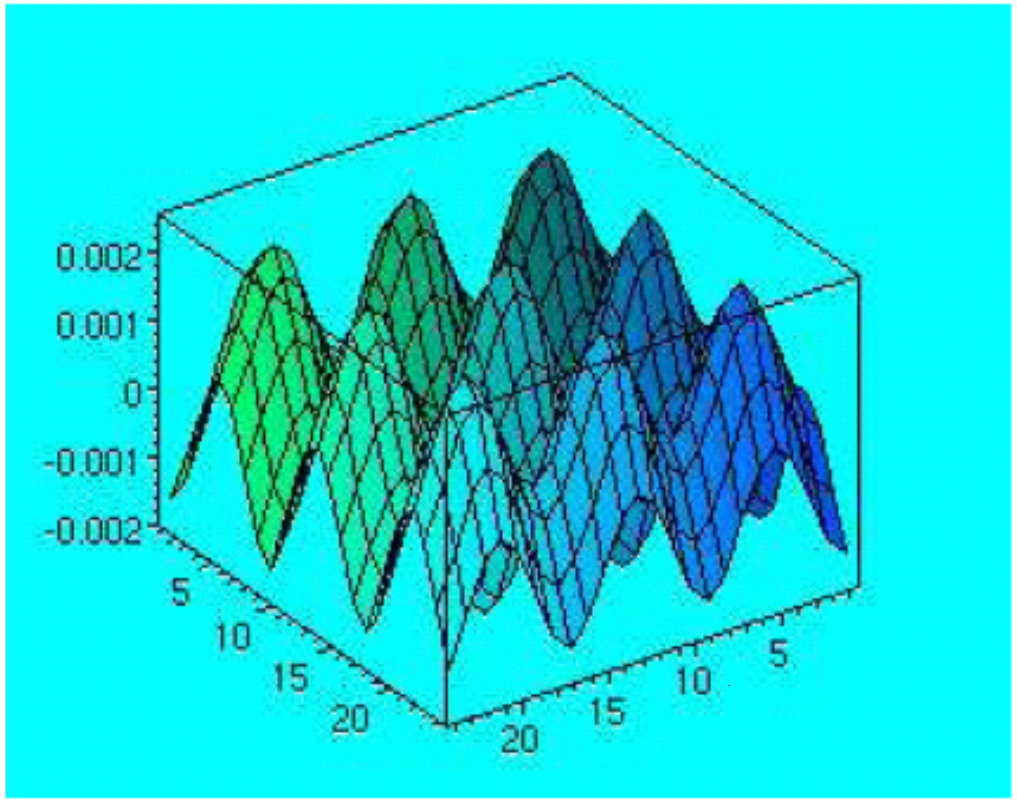
Spin density:

- Waves w/ amplitude

  ~ 10% of density

r_s=4, N=54

$$n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r}) \text{ in the } x\text{-}y \text{ plane } (z = 0)$$



The unrestricted HF solution

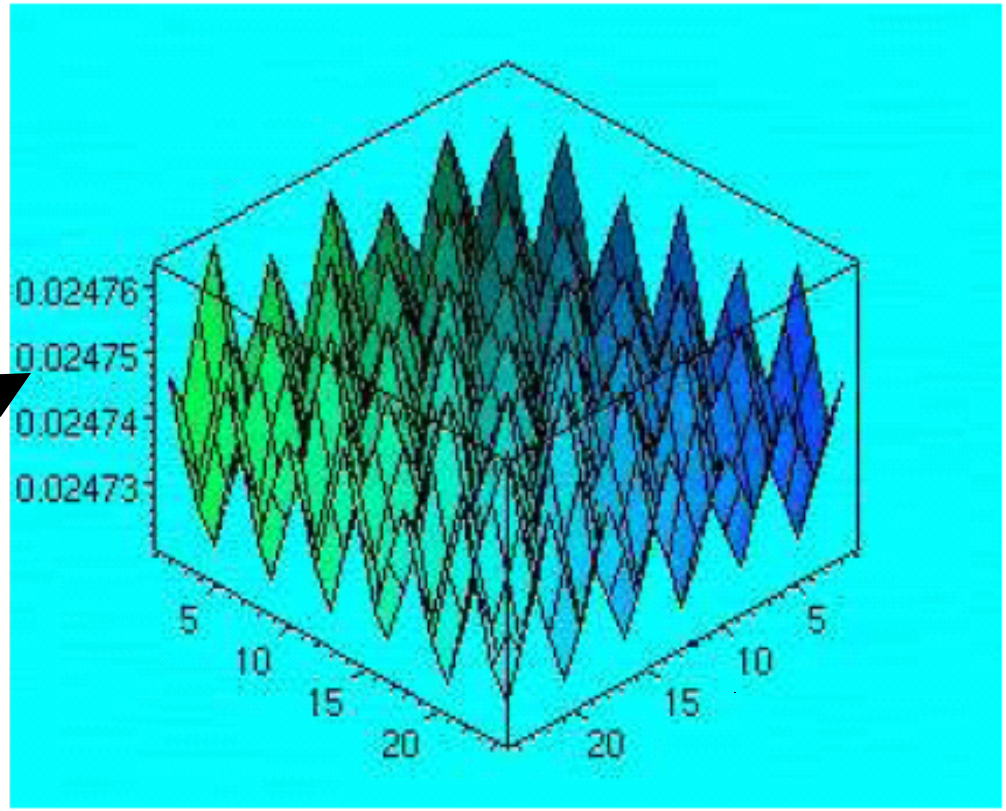
Charge density:

- Fluctuation is only

  ~ 0.1% of density

r_s=4, N=54

$n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r})$ in the x-y plane $(z = 0)$



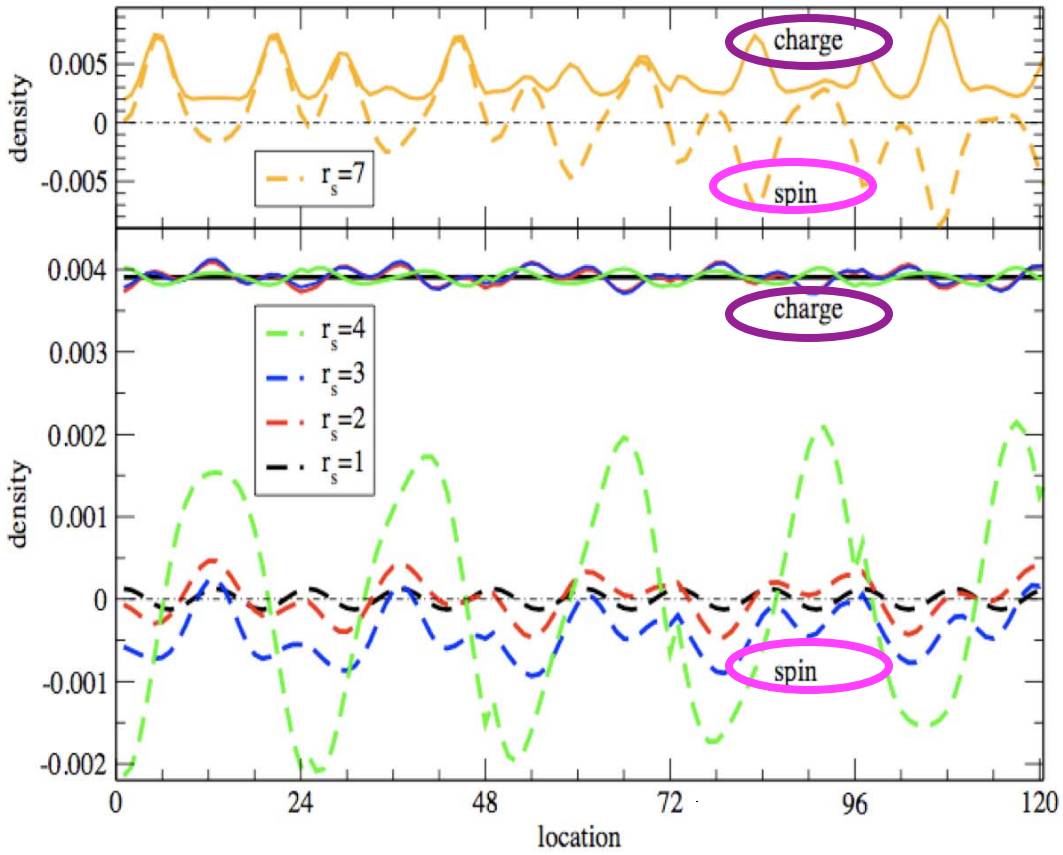
different scale

The unrestricted HF solution

Spin & Charge densities:

- r_s =7 is fundamentally different:
  - Wigner crystal
  - Particle-like (spin & charge similar fluct.)
- Below r_s=4:
  - Charge and spin different
  - Wave-like (large “double-occupancy”)

A line cut *(N=54)*



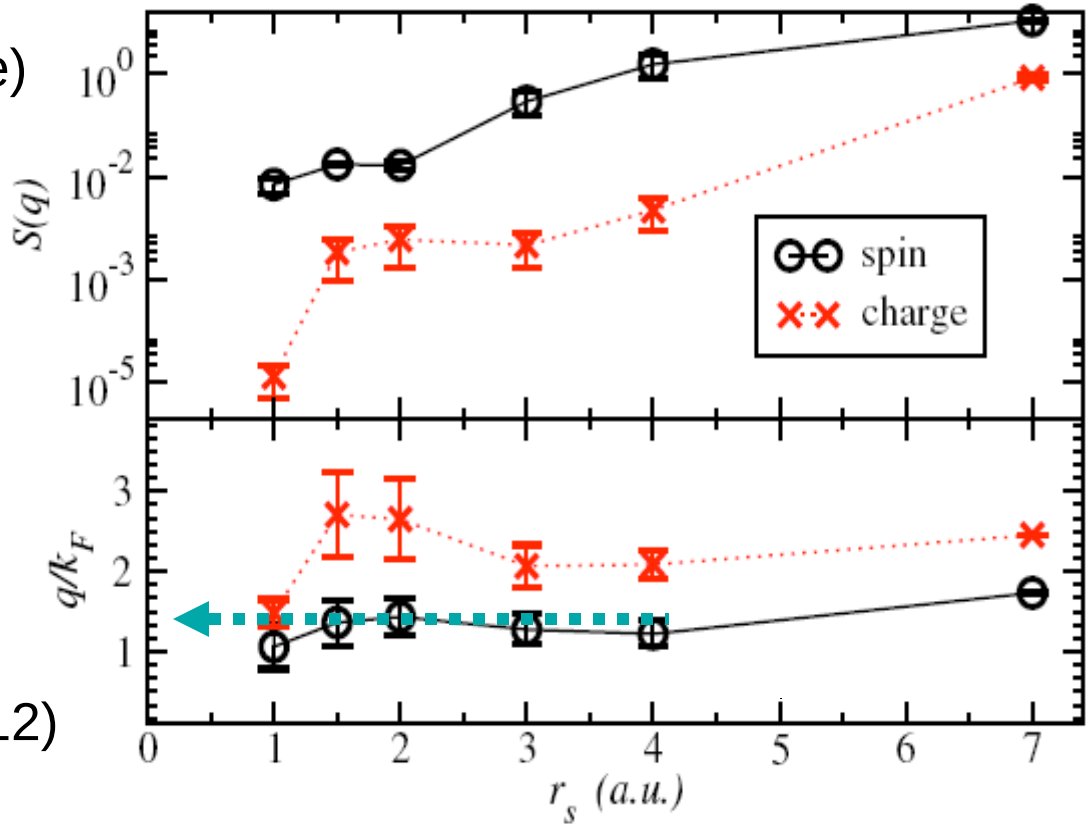
size of supercell

The unrestricted HF solution

S-S & C-C correlations:

- Peak value:
  - S_{sp} >> S_{ch} (log scale)
  - Decays with r_s
- Peak position
  - Peak of S_{sp} at q:
    q is **not** $2k_F$
    $q \sim 1.5(2)\ k_F$
  - Consistent (N=54 to 512)
  - **Not compatible with Overhauser state**

Structure factor peak value S(q) & position q



Understanding the UHF solution

- Broken-symmetry SDW-like, with wave vector q~1.5k_F:
  - Overhauser model:
    - pairing across FS
    - requires q=2k_F; smaller q cannot exist (higher K, less V_{ex} interf)?
- What is the mechanism for the UHF solution?
  - Not interf. bt. **"primary"** pairs
  - "satellite" pairing:

$$c_k|k\rangle \pm c_{k'}|k'\rangle$$

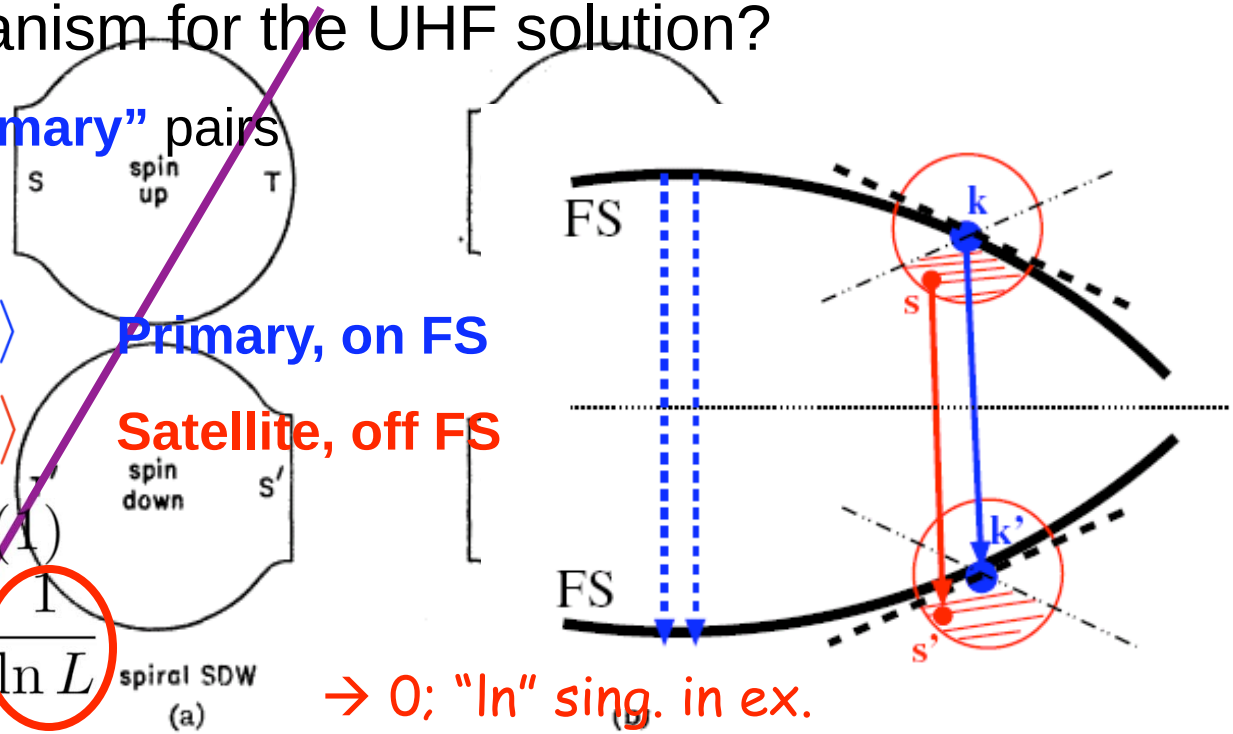
Primary, on FS

$$c_s|s\rangle \pm c_{s'}|s'\rangle$$

Satellite, off FS

$$c_k \sim c_{k'} \sim \mathcal{O}(1)$$

$$c_s \sim 1; c_{s'} \sim \frac{1}{\ln L}$$

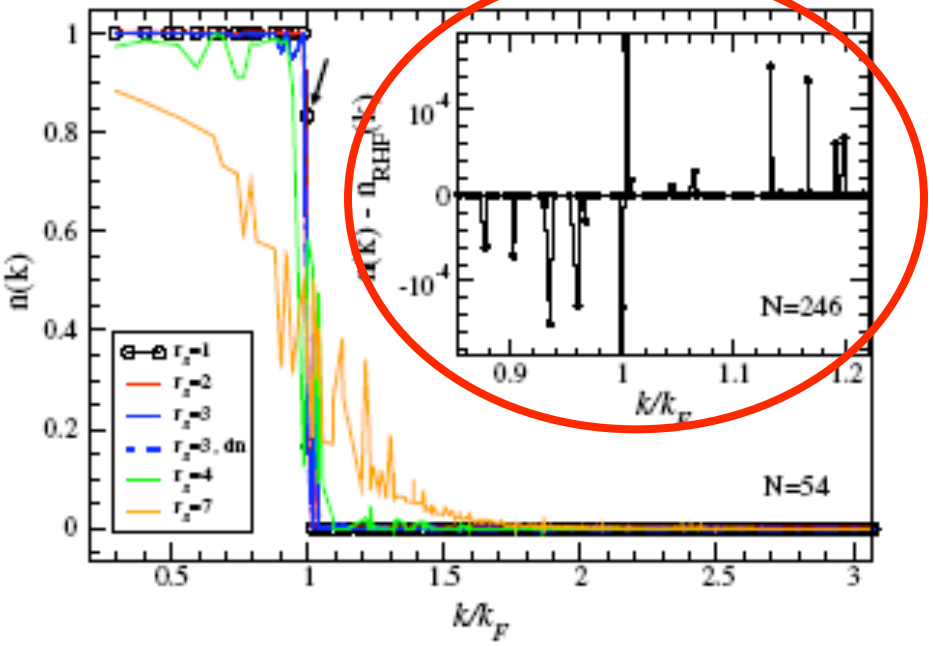


→ 0; "ln" sing. in ex.

Understanding the UHF solution

- What is the mechanism for the UHF solution?
  - “satellite” pairing:
  - interference between **primary** and **satellite** pairs is key

$$c_s|s\rangle \pm c_{s'}|s'\rangle \qquad c_s \sim 1; c_{s'} \sim \frac{1}{\ln L}$$



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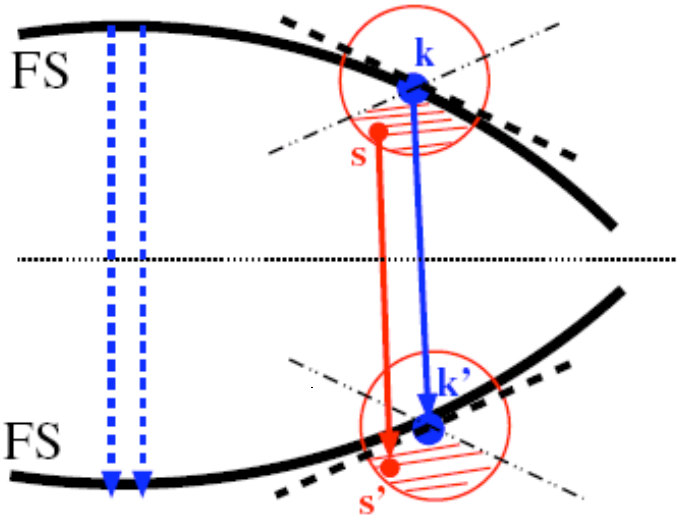
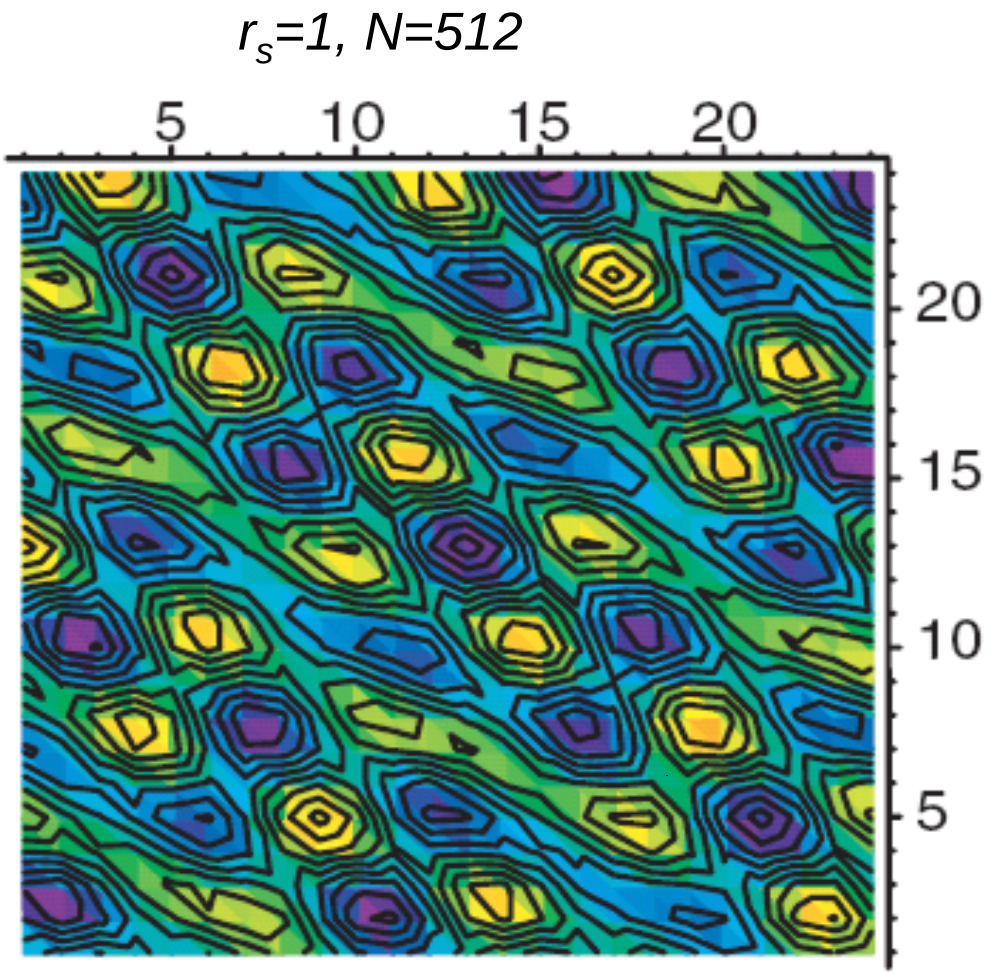


The unrestricted HF solution

What does the spin density look like at small r_s ?

- Delicate balance
  - confined to near FS
  - sensitive to FS typology



- Spatial symmetry further broken
- An-isotropic (spin stripes?)

Summary

- The conventional paramagnetic solution is not the true HF ground state of the 3-D electron gas
- Combined approach to obtain HF ground state:
  - Iterative numerical solution
  - Analytic pairing model
- The HF ground state:
  - Broken spin symmetry at all densities, $n_\uparrow(k) = n_\downarrow(k)$
  - Realistic densities: wave-like; almost cnst charge, SDW;
  - Spatially anistropic (spin stripes) at high density?
  - SDW with q~1.5(2)k_F, not $2k_F$
  - Mechanism --- pairing (Tuscany lattitude, not North-pole)
    + sattelites at Fermi surface