Is the \textit{homogeneous} electron gas \textit{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 \textit{wf} --- self-consistent mean-field solution
  - conventional solution (\textbf{restricted} HF): foundation for Fermi liquid th.
- \textbf{RHF} is not true HF ground state (Overhauser, 1962)
- \textbf{What is the HF ground state of jellium?}
  - numerical --- full \textbf{unrestricted} HF solution
  - Broken spin symmetry, but different from Overhauser state
- An analytic model --- novel pairing mechanism (instability @ FS)
Collaborator:
- David Ceperley (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

↓ smear out ions → jellium

Good model for metals:

Na, Al, ….
Electron gas – simplest model for metal

- Investigated for >70 years: Wigner, Bloch, …

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

- Non-interacting solution: Fermi sphere

\[N = N_\uparrow + N_\downarrow\]

\[\mathbf{r}_s: \text{ average dist. between 2 electrons}\]

\[4\pi r_s^3 / 3 \equiv L^3 / N\]

- Focus on
  - \(r_s < 5\text{a.u.}\) (high to medium density --- real materials)
  - Unpolarized: \(N_\uparrow = N_\downarrow\)
The challenge of non relativistic QM

High density: wave-like
→ Fermi liquid

Low density: particle-like
→ Wigner crystal

Often system is at neither limit

Quantum Monte Carlo (QMC) results

\[ r_s : \text{average distance bt. electrons} \]
\[ \varepsilon_K \sim \frac{1}{r_s^2} ; \quad \varepsilon_P \sim \frac{1}{r_s} \]
“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)
  
  \[
  H = H_{1\text{-body}} + H_{2\text{-body}} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V_{\text{ext}}(r_i) + \sum_{i<j}^{N} V_{\text{int}}(|r_i - r_j|)
  \]

  \[
  H_{\text{LDA}} = H_{1\text{-body}} + \sum_{i=1}^{N} f_{\text{c}}(n(r_i))
  \]

  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: $|k\rangle$

- In 2$\text{nd}$ quantization:

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

- Energy:

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

- Wave function – single Slater determinant

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

- Textbook solution:

  - $|\Phi_{\uparrow}\rangle = |\phi_1, \phi_2, \cdots, \phi_{N_\uparrow}\rangle$ homogeneous in real space
  - $$E = K - |V_{\text{exchange}}|$$
  - $$|\Phi_1\rangle = \sum_{k} c_1(k)|k\rangle \quad \sum_{k,k'} \frac{1}{|k-k'|^2}$$
Hartree-Fock solutions

- Textbook solution is not the HF ground state
- Hand-waving: how to have a Slater det with $E < E_{\text{RHF}}$?
- Consider pairing state:
  \[ c_k^2 + c_s^2 = 1 \]
  \[ |\uparrow\rangle = c_k |k\rangle + c_s |s\rangle \]
  \[ |\downarrow\rangle = c_k |k\rangle - c_s |s\rangle \]

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

\[ H = \sum_{\sigma, k} \frac{1}{2} k^2 c_{k, \sigma}^\dagger c_{k, \sigma} + \frac{1}{2} \frac{4\pi}{L^3} \sum_{\sigma, \sigma'} \sum_{k, k', Q} \frac{1}{Q^2} c_{k-Q, \sigma}^\dagger c_{k', \sigma'}^\dagger c_{k', \sigma'} c_{k, \sigma} \]

Interference bt. 2 parallel pairs
Hartree-Fock solutions

- Overhauser states:
  - proved (1962) there exists spin-density wave states with $E < E_{\text{RHF}}$
  - 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:

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

\[ \hat{H}_{HF}(\Phi^{(n)}) \text{ is a one-body Hamiltonian:} \]

\[ c^\dagger c^\dagger c c \text{ in } \hat{H} \rightarrow c^\dagger c \langle c^\dagger c \rangle_{\Phi^{(n)}} + \cdots \]

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

- For small \( \tau \), 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 \( \theta \) greatly reduces finite-size effects
The unrestricted HF solution

Energy lowering from RHF:

- UHF for all $r_s$
- $\delta E$ is tiny at low $r_s$:
  
  Recall
  
  $$E_{\text{RHF}} = \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s}\right) \text{Ry}$$

- UHF broken symmetry state:
  - lowering **exchange** at cost of **kinetic**
  - **Hartree** unchanged at low $r_s \rightarrow$ 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 with amplitude
  - ~10% of density

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

\( r_s = 4, \ N = 54 \)
The unrestricted HF solution

Charge density:
- Fluctuation is only 
  $\sim 0.1\%$ of density

\[ n_\uparrow(r) + n_\downarrow(r) \text{ in the } x-y \text{ plane (} z = 0) \]

\( r_s=4, \ N=54 \)

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:
  - $S_{sp} \gg S_{ch}$ (log scale)
  - Decays with $r_s$

- Peak position
  - Peak of $S_{sp}$ at $q$: $q$ is not $2k_F$
  - $q \approx 1.5(2) k_F$
  - Consistent ($N=54$ to 512)
  - Not compatible with Overhauser state
Understanding the UHF solution

• Broken-symmetry SDW-like, with wave vector $q \sim 1.5k_F$:
  - 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:
    - $c_k \ket{k} \pm c_{k'} \ket{k'}$
    - $c_s \ket{s} \pm c_{s'} \ket{s'}$
    - $c_k \sim c_{k'} \sim \mathcal{O}(1)$
    - $c_s \sim 1; c_{s'} \sim \frac{1}{\ln L}$
    - $\Rightarrow 0$; “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

\[ c_S |S\rangle \pm c_{S'} |S'\rangle \]
\[ c_S \sim 1; \quad c_{S'} \sim \frac{1}{\ln L} \]

\[ q = (k' - k) \] can thus be anything on (0, 2kF)

Optimizing \((\# \text{ of } \{k, k'\} \times \# \text{ of } \{s, s'\})\)

Exact UHF (numerical results) will do better
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 $q \sim 1.5(2)k_F$, not $2k_F$
  - Mechanism --- pairing (Tuscany lattitude, not North-pole) + sattelites at Fermi surface