Spin-density wave in the electron gas in Hartree-Fock, Reduced Density-Matrix Functional Theory, and Exact-Exchange Spin-DFT

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Outline

- Overhauser’s spiral spin density wave (SSDW)
- Reduced Density Matrix Functional Theory (RDMFT)
- Numerical results: HF and RDMFT
- SSDW in exact-exchange spin-DFT
Uniform electron gas in Hartree-Fock approximation

Classic papers by Overhauser (PRL (1960), PR (1962)):

Overhauser's theorem (analytical proof)

In the HF approximation, the paramagnetic state of the uniform electron gas is unstable w.r.t. formation of spin- or charge-density waves for all electron densities.

Ansatz for HF orbitals in SSDW state:

\[
\Phi_{1k}(r) = \frac{1}{\sqrt{\Omega}} \exp(ik \cdot r) \begin{pmatrix} 
\cos(\theta_k) \\
\sin(\theta_k) \exp(iq \cdot r)
\end{pmatrix}
\]

\[
\Phi_{2k}(r) = \frac{1}{\sqrt{\Omega}} \exp(ik \cdot r) \begin{pmatrix} 
-\sin(\theta_k) \\
\cos(\theta_k) \exp(iq \cdot r)
\end{pmatrix}
\]
SSDW for uniform electron gas in Hartree-Fock

ansatz provides HF solution with total HF energy lower than paramagnetic state if following self-consistency are satisfied

HF self-consistency conditions for SSDW

\[
\tan(2\theta_k) = \frac{2g_k}{\varepsilon_{\uparrow k} - \varepsilon_{\downarrow k+q}} \\
\varepsilon_{\sigma k} = \frac{k^2}{2} - V_\sigma(k)
\]

\[
V_{\uparrow}(k) = \int \frac{d^3k'}{(2\pi)^3} \frac{4\pi}{|k - k'|} \left( n_{1k} \cos^2(\theta_k) + n_{2k} \sin^2(\theta_k) \right)
\]

\[
V_{\downarrow}(k + q) = \int \frac{d^3k'}{(2\pi)^3} \frac{4\pi}{|k - k'|} \left( n_{1k} \sin^2(\theta_k) + n_{2k} \cos^2(\theta_k) \right)
\]

\[
2g_k = \int \frac{d^3k'}{(2\pi)^3} \frac{4\pi}{|k - k'|} \left( n_{1k} - n_{2k} \right) \sin(2\theta_k)
\]
SSDW for uniform electron gas in Hartree-Fock

ansatz leads to constant density $n$ and spin-spiral density wave for magnetization density $\mathbf{m}(\mathbf{r})$ (use $\mathbf{q} = (0, 0, q)$)

$$
\mathbf{m}(\mathbf{r}) = \begin{pmatrix}
    m_0 \cos(qz) \\
    m_0 \sin(qz) \\
    0
\end{pmatrix}
$$

and

$$
m_0 = -\frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} (n_{1k} - n_{2k}) \sin(2\theta_k)
$$

although a simple model, no numerical solution of SSDW in HF for 3-D electron gas has been given!!

often assumed: optimal wavevector for SSDW $q \lesssim 2k_F$
Reduced Density Matrix Functional Theory

One-particle reduced density matrix (1-RDM)

\[ \gamma(r, r') = N \int d^3r_2 \ldots \int d^3r_N \psi^*(r', r_2, \ldots, r_N) \psi(r, r_2, \ldots, r_N) \]

spectral decomposition:

\[ \gamma(r, r') = \sum_i n_i \Phi_i(r) \Phi_i^\dagger(r') \]

\( n_i \): occupation numbers
\( \Phi_i(r) \): natural orbitals (Pauli spinors)
Gilbert Theorem

Ground state $\Psi_0^N$ and ground state energy of system of $N$ interacting electrons is functional of 1-RDM

**Ground state energy**


**kinetic energy (exact):**

$$T[\gamma] = \frac{1}{2} \sum_\sigma \int d^3 r \lim_{r \to r'} \nabla' \nabla \gamma_{\sigma \sigma}(r, r')$$

**potential energy (exact):**

$$V[\gamma] = \sum_\sigma \int d^3 r V(r) \gamma_{\sigma \sigma}(r, r)$$

**Interaction energy (approximation needed):**

$$W[\gamma] = \sum_{\sigma_1 \sigma_2} \int d^3 r_1 \int d^3 r_2 P_{\sigma_1 \sigma_2}[\gamma](r_1, r_2) \frac{P_{\sigma_1 \sigma_2}(r_1, r_2)}{|r_1 - r_2|}$$

with ground state pair density $P_{\sigma_1 \sigma_2}[\gamma](r_1, r_2)$
use density matrix power functional 
(Sharma et al, PRB 78, 201103(R) (2008))

\[
P_{\sigma\sigma'}[\gamma](r, r') = \frac{1}{2} \gamma_{\sigma\sigma}(r, r) \gamma_{\sigma'\sigma'}(r', r') - \frac{1}{2} \gamma_\alpha(r, r') \gamma_\alpha(r', r) \\
\gamma_\alpha(r, r') = \sum_i n^\alpha_i \Phi_i(r) \Phi_i^\dagger(r') \quad \text{and} \quad 0.5 \leq \alpha < 1
\]

limiting cases:
\[\alpha = 1: \text{Hartree-Fock}\]
\[\alpha = 0.5: \text{Müller or Buijse-Baerends functional}\]

for SSDW: use spinors of the form of Overhauser’s HF spinors
Numerical Procedure

total energy per particle is functional of occupation numbers \( n_{1k} \), \( n_{2k} \) and of angle \( \theta_k \)

discretize \( k \)-space with points \( k_i \) \( \rightarrow \) total energy becomes high-dimensional function of \( n_{1k_i}, n_{2k_i} \) and \( \theta_{k_i} \)

\( \rightarrow \) optimization with steepest descent

details in: F.G. Eich et al, cond-mat/0910.0534
HF total energies and phase diagram

HF total energy per electron as function of $q$ for various $r_s$

HF total energy of PM, FM, and SSDW phases
inset: SSDW amplitude
Optimal SSDW wavevector and HF single-particle bands

optimal SSDW wavevector

HF energy bands at $r_s = 5$

note: $q$ not necessarily close to $2k_F$!
RDMFT total energy and energy contributions

RDMFT total energy per electron for $r_s = 5.0$ and different values of $\alpha$

corelation destroys SSDW!

energy contributions for $r_s = 5.0$ and different $\alpha$

S. Kurth

Spin-density wave in the electron gas in HF, RDMFT, and EXX
Spin-density wave in non-collinear spin-DFT

Ref: S. Kurth, F.G. Eich, PRB 80, 125120 (2009)

Kohn-Sham equation of non-collinear spin-DFT

\[
\left( -\nabla^2 + v_s(r) + \mu_B \sigma \mathbf{B}_s(r) \right) \phi_i(r) = \varepsilon_i \phi_i(r)
\]

here: assume form of KS potentials:

\[ v_s(r) = 0 \]

\[ \mathbf{B}_s(r) = (B \cos(qz), B \sin(qz), 0) \]
analytic solution: Kohn-Sham orbitals and orbital energies

\[ \Phi_{1k}(r) = \frac{1}{\sqrt{\Omega}} \exp(i kr) \begin{pmatrix} \cos(\theta_k) \\ \sin(\theta_k) \exp(i q z) \end{pmatrix} \]

\[ \Phi_{2k}(r) = \frac{1}{\sqrt{\Omega}} \exp(i kr) \begin{pmatrix} -\sin(\theta_k) \\ \cos(\theta_k) \exp(i q z) \end{pmatrix} \]

\[ \varepsilon_{1k} = \frac{k_x^2 + k_y^2}{2} + \varepsilon^{(-)} \]

\[ \varepsilon_{2k} = \frac{k_x^2 + k_y^2}{2} + \varepsilon^{(+)} \]

\[ \varepsilon^{(\pm)} = \frac{k^2}{2} + \frac{q^2}{8} \pm \sqrt{\frac{q^2}{4} k^2 + \mu_B^2 B^2}, \quad \kappa = k_z + \frac{q}{2} \]

\[ \tan(\theta_\kappa) = \frac{1}{2\alpha} (1 - \sqrt{1 + 4\alpha^2}), \quad \alpha = \frac{\mu_B B}{q\kappa} \]

total energy per particle \( E_{EXX}^{tot}(q, B) \) \( \longrightarrow \) minimize w.r.t. \( q \) and \( B \)
Energy minimization: occupied states in two KS bands

total energy per electron as function of $q$ for various $B$
for $r_s = 5.4$

HF and KS bands for optimal $q = 1.68 \ k_F$
and $\mu_B B = 0.011 \ \text{a.u.}$

![Graph showing total energy per electron as function of $q$ for various $B$.]

![Graph showing energies of different bands as a function of $\kappa/k_F$.]
Energy minimization: occupied states in one KS band

total energy per electron as function of $q$ for various $B$
for $r_s = 5.4$

HF and KS bands for optimal $q = 1.33 \ k_F$
and $\mu_B B = 0.020 \ \text{a.u.}$
Phase diagram and optimal parameters: 1 and 2 bands

Phase diagram: PM, FM and SSDW (occupations in 1 and 2 bands)

optimal values of $q$ and $B$ and SSDW amplitude
OEP equations in non-collinear spin-DFT

four OEP equations

\[
\sum_{i}^{\text{occ}} \left( \Phi_{i}^{\dagger}(r) \Psi_{i}(r) + h.c. \right) = 0
\]

\[
-\mu_B \sum_{i}^{\text{occ}} \left( \Phi_{i}^{\dagger}(r) \sigma \Psi_{i}(r) + h.c. \right) = 0
\]

\( \Psi_{i}(r) \): orbital shifts (see Txema’s talk last week)

for SSDW: first and last OEP eqs. exactly satisfied
2nd and 3rd OEP eq. equivalent

\[
J(q, B) \cos(qz) = 0 \quad J(q, B) \sin(qz) = 0
\]
is OEP equation satisfied?

prefactor of OEP eq. for \( r_s = 5.4 \) as function of \( q \) for various \( B \)

upper panel: two-band case, lower panel: one-band case

only for one-band case OEP eq. is satisfied for the parameter values minimizing the total energy!
Collaborators:

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- C.R. Proetto, Free Univ. Berlin, Germany, and Centro Atomico Bariloche, Argentina
- S. Sharma and E.K.U. Gross, MPI Halle, Germany
Summary

- SSDW instability in the uniform electron gas in HF, RDMFT, EXX-SDFT
- HF: optimal wavevector can be far from $2k_f$
- RDMFT: correlation destroys SSDW
- EXX-SDFT: SSDW stable over smaller range of $r_s$ than HF
- EXX-SDFT: occupation in one band with holes below the Fermi energy gives lower energy than two-band case and is consistent with OEP equations