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:

$$\Phi_{1\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{k}\cdot\mathbf{r}) \begin{pmatrix} \cos(\theta_{\mathbf{k}}) \\ \sin(\theta_{\mathbf{k}}) \exp(i\mathbf{q}\cdot\mathbf{r}) \end{pmatrix}$$

$$\Phi_{2\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{k}\cdot\mathbf{r}) \begin{pmatrix} -\sin(\theta_{\mathbf{k}}) \\ \cos(\theta_{\mathbf{k}}) \exp(i\mathbf{q}\cdot\mathbf{r}) \end{pmatrix}$$

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

$$\tan(2\theta_{\mathbf{k}}) = \frac{2g_{\mathbf{k}}}{\varepsilon_{\uparrow\mathbf{k}} - \varepsilon_{\downarrow\mathbf{k}+\mathbf{q}}} \qquad \varepsilon_{\sigma\mathbf{k}} = \frac{\mathbf{k}^2}{2} - V_\sigma(\mathbf{k})$$

$$V_\uparrow(\mathbf{k}) = \int \frac{\mathrm{d}^3k'}{(2\pi)^3} \frac{4\pi}{|\mathbf{k}-\mathbf{k}'|} \left(n_{1\mathbf{k}} \cos^2(\theta_{\mathbf{k}}) + n_{2\mathbf{k}} \sin^2(\theta_{\mathbf{k}})\right)$$

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

$$2g_{\mathbf{k}} = \int \frac{\mathrm{d}^3k'}{(2\pi)^3} \frac{4\pi}{|\mathbf{k}-\mathbf{k}'|} \left(n_{1\mathbf{k}} - n_{2\mathbf{k}}\right) \sin(2\theta_{\mathbf{k}})$$

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

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

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)

$$\gamma(\mathbf{r},\mathbf{r}') = N \int \mathrm{d}^3 r_2 \ldots \int \mathrm{d}^3 r_N \Psi^*(\mathbf{r}',\mathbf{r}_2,\ldots,\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)$$

spectral decomposition:

$$\gamma(\mathbf{r},\mathbf{r}') = \sum_i n_i \Phi_i(\mathbf{r})\Phi_i^\dagger(\mathbf{r}')$$

n_i: occupation numbers
$\Phi_i(\mathbf{r})$: natural orbitals (Pauli spinors)

Gilbert Theorem

Ground state Ψ_0^N and ground state energy of system of N interacting electrons is functional of 1-RDM

Ground state energy

$$E_V[\gamma] = T[\gamma] + V[\gamma] + W[\gamma]$$

kinetic energy (exact):

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

potential energy (exact): $V[\gamma] = \sum_\sigma \int \mathrm{d}^3r V(\mathbf{r})\gamma_{\sigma\sigma}(\mathbf{r},\mathbf{r})$

Interaction energy (approximation needed):

$$W[\gamma] = \sum_{\sigma_1\sigma_2} \int \mathrm{d}^3r_1 \int \mathrm{d}^3r_2 \frac{P_{\sigma_1\sigma_2}[\gamma](\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}$$

with ground state pair density $P_{\sigma_1\sigma_2}[\gamma](\mathbf{r}_1,\mathbf{r}_2)$

Approximation for energy functional

use density matrix power functional
(Sharma et al, PRB **78**, 201103(R) (2008))

$$P_{\sigma\sigma'}[\gamma](\mathbf{r},\mathbf{r}') = \frac{1}{2}\gamma_{\sigma\sigma}(\mathbf{r},\mathbf{r})\gamma_{\sigma'\sigma'}(\mathbf{r}',\mathbf{r}') - \frac{1}{2}\gamma^{\alpha}_{\sigma\sigma'}(\mathbf{r},\mathbf{r}')\gamma^{\alpha}_{\sigma'\sigma}(\mathbf{r}',\mathbf{r})$$

$$\gamma^{\alpha}(\mathbf{r},\mathbf{r}') = \sum_i n_i^{\alpha}\Phi_i(\mathbf{r})\Phi_i^{\dagger}(\mathbf{r}') \quad \text{and} \quad 0.5 \le \alpha < 1$$

limiting cases:
$\alpha = 1$: Hartree-Fock
$\alpha = 0.5$: Müller or Buijse-Baerends functional
(Müller, Phys. Lett. (1984), Buijse, Baerends, Mol. Phys. (2002))

for SSDW: use spinors of the form of Overhauser's HF spinors

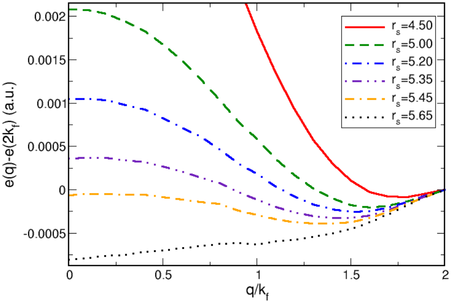
Numerical Procedure

total energy per particle is functional of occupation numbers $n_{1\mathbf{k}}$, $n_{2\mathbf{k}}$ and of angle $\theta_{\mathbf{k}}$
discretize k-space with points $k_i \longrightarrow$ total energy becomes high-dimensional function of $n_{1\mathbf{k}_i}$, $n_{2\mathbf{k}_i}$ and $\theta_{\mathbf{k}_i}$
$\longrightarrow$ optimziation with steepest descent

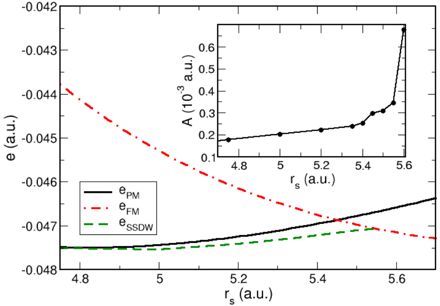
details in: F.G. Eich et al, cond-mat/0910.0534

HF total energies and phase diagram

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

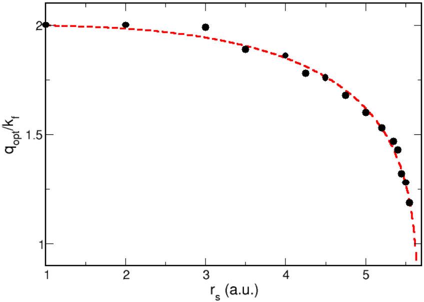


HF total energy of PM, FM, and SSDW phases
inset: SSDW amplitude

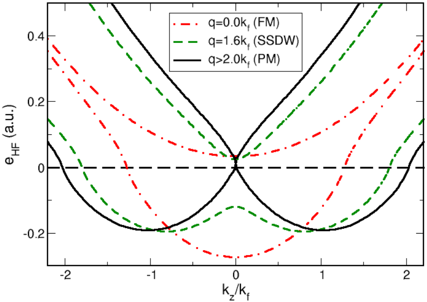


Optimal SSDW wavevector and HF single-particle bands

optimal SSDW wavevector



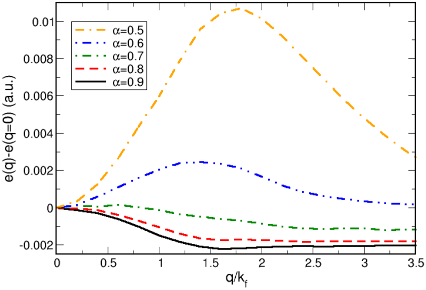
HF energy bands at $r_s = 5$



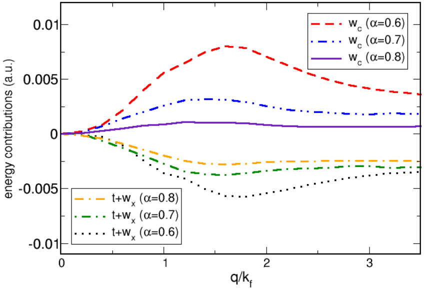
note: q not necessarily close to $2k_F$!

RDMFT total energy and energy contributions

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



energy contributions for $r_s = 5.0$ and different α



corelation destroys SSDW !

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

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}) + \mu_B \boldsymbol{\sigma} \mathbf{B}_s(\mathbf{r})\right) \Phi_i(\mathbf{r}) = \varepsilon_i \Phi_i(\mathbf{r})$$

here: *assume* form of KS potentials:

$$v_s(\mathbf{r}) = 0$$

$$\mathbf{B}_s(\mathbf{r}) = (B\cos(qz), B\sin(qz), 0)$$

analytic solution: Kohn-Sham orbitals and orbital energies

$$\Phi_{1\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{kr}) \begin{pmatrix} \cos(\theta_k) \\ \sin(\theta_k)\exp(iqz) \end{pmatrix}$$

$$\Phi_{2\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{kr}) \begin{pmatrix} -\sin(\theta_k) \\ \cos(\theta_k)\exp(iqz) \end{pmatrix}$$

$$\varepsilon_{1\mathbf{k}} = \frac{k_x^2 + k_y^2}{2} + \varepsilon_\kappa^{(-)} \qquad \varepsilon_{2\mathbf{k}} = \frac{k_x^2 + k_y^2}{2} + \varepsilon_\kappa^{(+)}$$

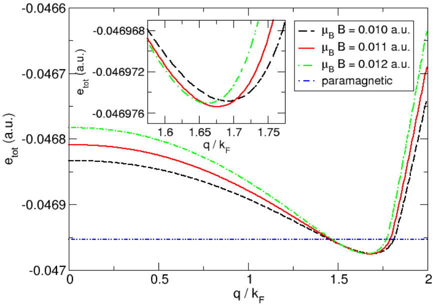
$$\varepsilon_\kappa^{(\pm)} = \frac{\kappa^2}{2} + \frac{q^2}{8} \pm \sqrt{\frac{q^2}{4}\kappa^2 + \mu_B^2 B^2}, \qquad \kappa = k_z + \frac{q}{2}$$

$$\tan(\theta_\kappa) = \frac{1}{2\alpha}\left(1 - \sqrt{1 + 4\alpha^2}\right), \qquad \alpha = \frac{\mu_B B}{q\kappa}$$

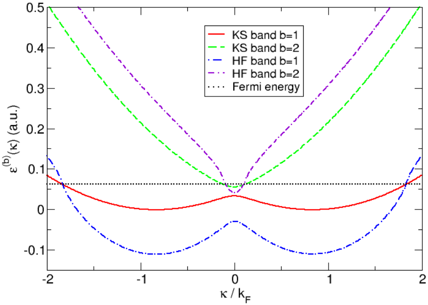
total energy per particle $e_{EXX}^{tot}(q, B) \longrightarrow$ minimize w.r.t. q and B

Energy minimization: occupied states in two KS bands

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



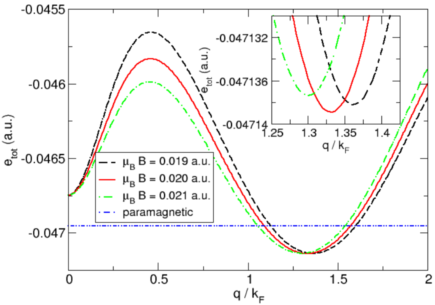
HF and KS bands
for optimal $q = 1.68\ k_F$
and $\mu_B B = 0.011$ a.u.

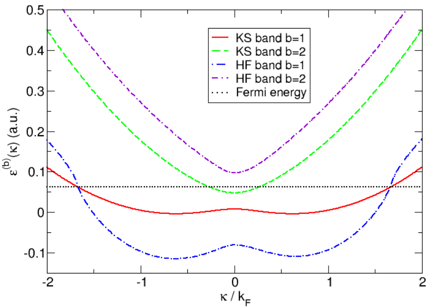


Energy minimization: occupied states in one KS band

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 $\mu_B B = 0.020$ a.u.

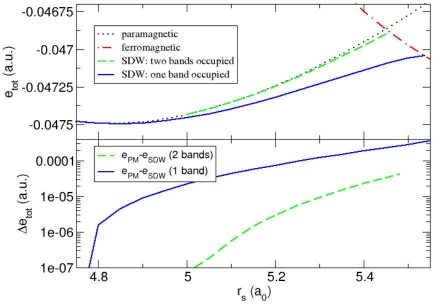


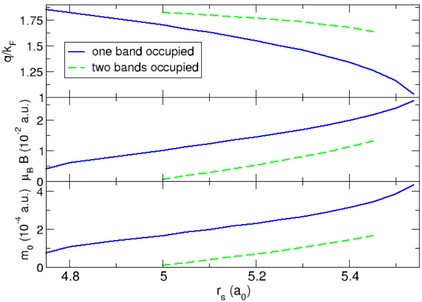


Phase diagram and optimal parameters: 1 and 2 bands

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

$$\sum_i^{occ} \left(\Phi_i^\dagger(\mathbf{r})\Psi_i(\mathbf{r}) + h.c. \right) = 0$$

$$-\mu_B \sum_i^{occ} \left(\Phi_i^\dagger(\mathbf{r})\boldsymbol{\sigma}\Psi_i(\mathbf{r}) + h.c. \right) = 0$$

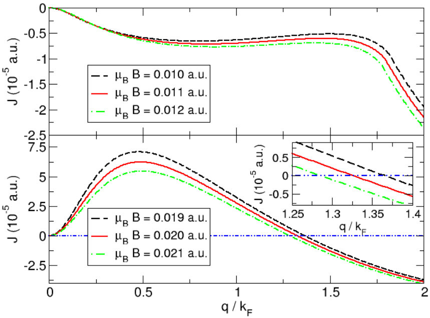
$\Psi_i(\mathbf{r})$: orbital shifts (see Txema's talk last week)

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

$$J(q,B)\cos(qz) = 0 \qquad\qquad J(q,B)\sin(qz) = 0$$

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:

- F.G. Eich, MPI Halle, Germany
- 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