Noncollinear spins in QMC: spiral Spin Density Waves in the HEG

Zoltán Radnai

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Overview

- What are noncollinear spin systems and why are they interesting?
- How does the DFT community deal with it?
- Implementation of noncollinear spins in Variational Monte Carlo
- Application to spiral Spin Density Waves in the Homogeneous Electron Gas
- Current questions and problems

Introduction to noncollinear spins

Physical definition:

- In a *collinear* system, every particle has a definite spin orientation, either up or down, with respect to a global quantization axis.
- In a *noncollinear* system, the particles can have spin directions that are not parallel to the global quantization axis and/or the spin direction can vary with position in space.

Examples of noncollinear systems:

- Frustrated (e.g. triangular) antiferromagnetic lattices
- Spiral magnetic structures in crystals such as γ phase of Fe and Cr compounds
- Spin wave excitations
- Spiral Spin Density Waves in the Homogeneous Electron Gas

Mathematical approach:

Total wavefunction of a system of N particles is $\Psi(\mathbf{X}) = \Psi(\mathbf{x}_1, ..., \mathbf{x}_N)$ and depends on both position and spin. For a *collinear* system Ψ is an eigenfunction of the total $\widehat{S}_z$ operator, but this is not exact enough definition.

In practice a collinear system is one where

- The spin-dependence of the wavefunction can be eliminated and Ψ treated as function of position coordinates ($\mathbf{R}$) only.
- Particles with up and down spin are considered distinguishable.
- Expectation values (energy, density etc.) can be obtained using $\Psi(\mathbf{R})$ only.

This happens in all the familiar methods, e.g. standard HF, DFT, VMC/DMC etc.

Familiar example: determinant of single-particle orbitals

$$\Psi(\mathbf{X}) = \begin{vmatrix} \psi_1(\mathbf{x}_1) & \cdots & \psi_1(\mathbf{x}_N) \\ \vdots & & \vdots \\ \psi_N(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix}, \tag{1}$$

where each orbital is of the form $\psi_i(\mathbf{x}) = \phi_i(\mathbf{r})\chi_i(s)$, with $\chi_i(s) = \delta_{\sigma_i,s}$ a spin eigenstate.

In case of determinant, following form is used instead:

$$\Psi(\mathbf{R}) = \begin{vmatrix} \phi_1^{\uparrow}(\mathbf{r}_1) & \cdots & \phi_1^{\uparrow}(\mathbf{r}_{N_\uparrow}) \\ \vdots & & \vdots \\ \phi_{N_\uparrow}^{\uparrow}(\mathbf{r}_1) & \cdots & \phi_{N_\uparrow}^{\uparrow}(\mathbf{r}_{N_\uparrow}) \end{vmatrix} \begin{vmatrix} \phi_1^{\downarrow}(\mathbf{r}_{N_\uparrow+1}) & \cdots & \phi_1^{\downarrow}(\mathbf{r}_N) \\ \vdots & & \vdots \\ \phi_{N_\downarrow}^{\downarrow}(\mathbf{r}_{N_\uparrow+1}) & \cdots & \phi_{N_\downarrow}^{\downarrow}(\mathbf{r}_N) \end{vmatrix} \tag{2}$$

with $N_\uparrow$ up-spin particles and $N_\downarrow = N - N_\uparrow$ down-spin particles.

For a *noncollinear* system such a separation is not possible and explicit spin dependence must be included.

- Can either consider the single-particle orbitals to explicitly depend on spin coordinates and write them as $\psi(\mathbf{x})$ or treat them as two-component spinors and write them as $\psi_\alpha(\mathbf{r})$. Physical *direction* of spin depends on relationship of the two components.

- **Magnetization density**: $\mathbf{m}(\mathbf{r})$ is the net magnetic moment (a physical observable) in the three spatial directions at point $\mathbf{r}$ in space. Similar to density $n(r)$ and important in describing noncollinear structures.

A collinear system is one where $m_x(\mathbf{r}) = m_y(\mathbf{r}) = 0$ and $m_z(\mathbf{r})$ is the spin density.

Noncollinear DFT

- Hohenberg-Kohn theorem originally developed for spinless case. Exchange correlation energy functional of density only ($E_{xc}[n(r)]$).

- Von Barth and Hedin developed the general spin dependent version, which was originally noncollinear in formulation. They suggested that E_{xc} should really depend on spin density matrix $\rho_{\alpha\beta}(\mathbf{r})$ (see below). Yet most DFT calculations are restricted to collinear, possibly spin-polarized case.

- The **spin density matrix** is defined in unfamiliar 2nd quantized notation:

$$\rho_{\alpha\beta}(\mathbf{r}) = \langle \widehat{\psi}^{\dagger}_{\beta}(\mathbf{r})\widehat{\psi}_{\alpha}(\mathbf{r})\rangle$$

- In DFT context, in terms of the occupied single-particle spinors

$$\rho_{\alpha\beta}(\mathbf{r}) = \sum_{n} f_n \psi_{n,\alpha}(\mathbf{r})\psi^{*}_{n,\beta}(\mathbf{r})$$

- It can be related to the density and magnetization density by

$$\begin{aligned} n(\mathbf{r}) &= Tr\rho \\ \mathbf{m}(\mathbf{r}) &= \sum_{\alpha\beta} \rho_{\alpha\beta}\sigma_{\beta\alpha} \\ \rho_{\alpha\beta}(\mathbf{r}) &= \frac{1}{2}n(\mathbf{r})\delta_{\alpha\beta} + \frac{1}{2}\mathbf{m}(\mathbf{r})\cdot\sigma_{\alpha\beta}(\mathbf{r}) \end{aligned}$$

- Saying that $E_{xc} = E_{xc}[\rho_{\alpha\beta}(\mathbf{r})]$ is equivalent to saying $E_{xc} = E_{xc}[n(\mathbf{r}), \mathbf{m}(\mathbf{r})]$.

- Collinear DFT within the Local Spin Density Approximation assumes that there is a global quantization axis, and $\mathbf{m}$ points along that everywhere. Hence $E_{xc} = E_{xc}[n(\mathbf{r}), |\mathbf{m}(\mathbf{r})|]$ or equivalently $E_{xc} = E_{xc}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})]$. This does away with the need to use spinor orbitals.

- In noncollinear DFT $\mathbf{m}(\mathbf{r})$ is allowed to point in any direction. Spinor orbitals are now needed, and the Kohn-Sham equations become 2x2 matrix equations. Formally, the exchange-correlation potential is given by

$$V_{xc}^{\alpha\beta}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho_{\alpha\beta}(\mathbf{r})} = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}\delta_{\beta\alpha} + \sum_i \frac{\delta E_{xc}}{\delta m_i(\mathbf{r})}\sigma_{i\beta\alpha}.$$

- Even in the case of fully unconstrained noncollinear calculations, it is assumed that $E_{xc} = E_{xc}[n(\mathbf{r}), |\mathbf{m}(\mathbf{r})|, \nabla|\mathbf{m}(\mathbf{r})|, etc.]$. This means that in most actual DFT codes,

$$V_{xc}^{\alpha\beta}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}\delta_{\beta\alpha} + \frac{\delta E_{xc}}{\delta |\mathbf{m}(\mathbf{r})|}\widehat{\mathbf{m}}(\mathbf{r}) \cdot \sigma_{\beta\alpha}.$$

(this is the case in ABINIT and VASP).

- *Even in fully unconstrained noncollinear calculations involving complicated functionals, changes in the magnetization direction are neglected!*

Noncollinear Variational Monte Carlo

- Standard collinear VMC calculations evaluate quantities such as

$$E = \frac{\left\langle \Psi(\mathbf{R}) | \widehat{H} | \Psi(\mathbf{R}) \right\rangle}{\langle \Psi(\mathbf{R}) | \Psi(\mathbf{R}) \rangle} = \frac{\int |\Psi(\mathbf{R})|^2 E_L(\mathbf{R}) \, d\mathbf{R}}{\int |\Psi(\mathbf{R})|^2 \, d\mathbf{R}} \tag{3}$$

- Metropolis Monte Carlo is used to sample $|\Psi(\mathbf{R})|^2$, often using an electron-by-electron algorithm.

- In noncollinear calculation we need to use $\Psi(\mathbf{X}) = \Psi(\mathbf{R}, \mathbf{S})$ to evaluate quantities such as

$$E = \frac{\sum_{\mathbf{S}} \int |\Psi(\mathbf{R}, \mathbf{S})|^2 E_L(\mathbf{R}, \mathbf{S}) \, d\mathbf{R}}{\sum_{\mathbf{S}} \int |\Psi(\mathbf{R}, \mathbf{S})|^2 \, d\mathbf{R}} \tag{4}$$

- The form of the expression is the same, so extend the standard method to include the spin coordinates $s_1, ..., s_N$ in the process.

- This approach is ideally suited for evaluation of *spin-dependent* operators (for example spin-density matrix)

Pseudocode for noncollinear VMC

An extension of the standard electron-by-electron algorithm for a Slater-Jastrow wavefunction of the form

$$\Psi(\mathbf{X}) = \exp(J(\mathbf{R}))D(\mathbf{X})$$

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Loop over time steps.
  Loop over electrons in configuration.
     - Propose move of electron:  $\mathbf{r}_i \rightarrow \mathbf{r}'_i$.  This changes single column of D.
     - Calculate ratio $\Psi(\mathbf{R}_{\text{new}},\mathbf{S})/\Psi(\mathbf{R}_{\text{old}},\mathbf{S})$.
     - Perform Metropolis accept/reject step.
     - If move is accepted update cofactor matrix and determinant.
     - Propose spin flip of electron:  $s_i \rightarrow s'_i$.  This changes single column of D.
     - Calculate ratio $\Psi(\mathbf{R},\mathbf{S}_{\text{new}})/\Psi(\mathbf{R},\mathbf{S}_{\text{old}})$.
     - Perform Metropolis accept/reject step.
     - If move is accepted update cofactor matrix and determinant.
  End loop over electrons in configuration.
  - Accumulate local energy and other observables, if required.
End loop over time steps.
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(This is the current implementation in CASINO)

- Position and spin moves are separated for sake of efficiency

- The position moves are proposed and accepted using ordinary two-level sampling

- Only position moves change the Jastrow factor

- Spin "flips" are (currently) proposed as: 50% chance to change spin and 50% chance to keep current spin. This could be improved, but some chance to keep current spin is necessary for *ergodicity*.

- The Metropolis acceptance ratio for spin flips is

$$A(s_i \rightarrow s_i') = \text{min}\left\{1, \frac{|\Psi(\mathbf{R}, \mathbf{S}_{\text{new}})|^2}{|\Psi(\mathbf{R}, \mathbf{S}_{\text{old}})|^2}\right\} = \text{min}\left\{1, \frac{|D(\mathbf{S}_{\text{new}})|^2}{|D(\mathbf{S}_{\text{old}})|^2}\right\} \tag{5}$$

- Sherman-Morrison formula, use of cofactor matrix etc. all hold for spin flips too

Jastrow factor and cusp conditions

- Power of QMC is that correlation effects can be directly incorporated into the wavefunction. In VMC this is achieved via the Jastrow factor.

- In the collinear case the Jastrow factor is introduced in the wavefunction as $\Psi(\mathbf{R}) = \exp(J(\mathbf{R}))D^{\uparrow}D^{\downarrow}$. The terms in J are different depending on the assigned spins of the (distinguishable) up- and down-spin electrons.

- J is chosen so that Ψ obeys electron-electron cusp conditions. These conditions are different when two parallel-spin or anti-parallel spin electrons meet.

How to include the Jastrow factor in the noncollinear wavefunction?

- We could attempt to include a spin-dependent $J(\mathbf{R}, \mathbf{S})$. This could satisfy the cusp conditions. Unfortunately this would alter the physical spin directions represented by the spin-dependent orbitals.

- We can instead include a spin-independent $J(\mathbf{R})$. Since all electrons are indistinguishable, all quantities such as r_{ij} appear with equal status. Use the form usually used for anti-parallel spin pairs.

- Cusp conditions are not completely satisfied.

We can test the seriousness of disobeying cusp conditions:

- Do a collinear calculation involving unpolarized HEG
- Alter the Jastrow factor to obey anti-parallel cusp conditions, even for parallel spins.
- See how much difference this makes:

System	Energy
HF	0.6480
Normal J in VMC	0.5932(2)
Altered J in VMC	0.5939(2)
DMC	0.5819(5)

(N=102 electrons, density parameter $r_s = 1.0$, single adjustable parameter A using old form of Jastrow factor)

It might be possible to come up with something better for noncollinear case?

Spin-density matrix in noncollinear VMC

The definition of the spin-density matrix most useful for VMC calculations is

$$\begin{aligned}
\rho_{\alpha\beta}(\mathbf{r}) &= \sum_i \frac{\sum_{\mathbf{S}/s_i} \int \Psi^*(\mathbf{r}_1, s_1, ..., \mathbf{r}, \beta, ..., \mathbf{r}_N, s_n)\Psi(\mathbf{r}_1, s_1, ..., \mathbf{r}, \alpha, ..., \mathbf{r}_N, s_n) d\mathbf{R}/\mathbf{r}_i}{\sum_{\mathbf{S}} \int |\Psi(\mathbf{R}, \mathbf{S})|^2 d\mathbf{R}} \\
&= \sum_i \frac{\sum_{\mathbf{S}} \int |\Psi(\mathbf{R}, \mathbf{S})|^2 \delta(\mathbf{r} - \mathbf{r}_i)\delta_{s_i\beta} \frac{\Psi(..., \mathbf{r}_i, \alpha, ...)}{\Psi(..., \mathbf{r}_i, \beta, ...)} d\mathbf{R}}{\sum_{\mathbf{S}} \int |\Psi(\mathbf{R}, \mathbf{S})|^2 d\mathbf{R}} \\
&= \left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta_{s_i\beta} \frac{\Psi(..., \mathbf{r}_i, \alpha, ...)}{\Psi(..., \mathbf{r}_i, \beta, ...)} \right\rangle \qquad (6)
\end{aligned}$$

This is very similar to how the ordinary density, spin density or pair correlation function is usually evaluated. It's customary to accumulate the Fourier components of such quantities. For the spin-density matrix, we have

$$\tilde{\rho}_{\alpha\beta}(\mathbf{G}) = \frac{1}{\Omega} \left\langle \sum_i \exp(-i\mathbf{G} \cdot \mathbf{r}_i)\delta_{s_i\beta} \frac{\Psi(..., \mathbf{r}_i, \alpha, ...)}{\Psi(..., \mathbf{r}_i, \beta, ...)} \right\rangle \qquad (7)$$

which can be readily accumulated in the course of the simulation in bins, along with other quantities such as density and pair correlation function.

Fourier components of magnetization density follow as before:

$$\tilde{\mathbf{m}}(\mathbf{G}) = \sum_{\alpha\beta} \tilde{\rho}_{\alpha\beta}(\mathbf{G})\sigma_{\beta\alpha}$$

where σ is the vector of Pauli matrices.

Noncollinear Applications

People are interested in

- **Spin waves**: Low-energy excited states of the system. Possible with collinear (e.g. ferromagnetic) ground state too.
- For spin waves, want to know spin wave spectrum: dispersion relation $\omega(\mathbf{q})$. It is known that for $q \to 0$, $\omega \to cq^2$.
- **Spin Density Waves**: Static, noncollinear configurations of the magnetization density, possibly even in ground-state.

Experimental evidence for existence of such phenomena come from neutron scattering.

Different forms of attempts for spin wave spectrum:

- Electronic structure calculations relying on mapping to Heisenberg model: $H = \sum_{i,j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$
- Time-dependent DFT
- Theoretical calculations to evaluate the dynamical response function $\chi(\omega, \mathbf{q})$

Can draw some analogy with phonons, but it's not perfect!

- Phonon spectrum can be derived from energies of *static* arrangements of atoms.
- Spin wave spectrum can't be easily derived from energies of SDWs.

With phonons, the form of the *dynamics* is explicitly known, with spin waves it's not.

VMC in it's current form is not suited for dynamics, so concentrate on SDWs.

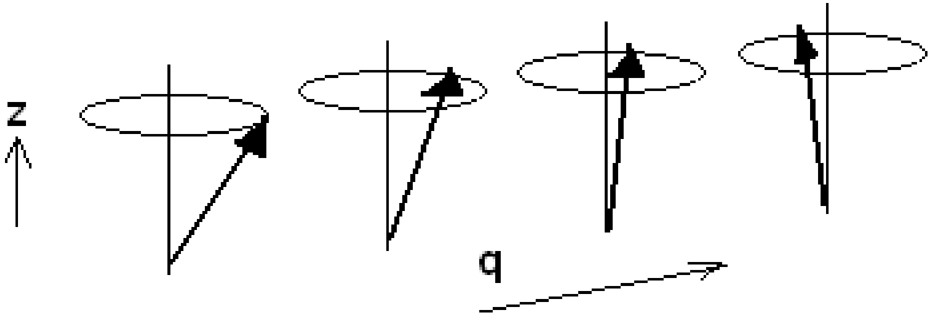
Question: is there a way to relate energies of SDWs to spin wave spectrum? Possible limiting cases such as long-wavelength regime?

Spiral Spin Density Waves

Magnetization density vector $\mathbf{m}$ varies in helical fashion,

- From site to site in a crystal
- Smoothly in a homogeneous system (e.g. HEG)

Characterised by a wavevector $\mathbf{q}$: direction and wave-length



This covers a wide class of problems. Examples of occurences in literature:

- Overhauser: HF ground-state of 3D HEG is giant SDW
- Herring: Energy of the Bloch wall using HF
- Some DFT applications to ground-state of Fe crystals

Wavefunction for spiral SDW in HEG

Construct determinant of single-particle spinors:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \begin{pmatrix} \cos(\tfrac{1}{2}\theta(\mathbf{k}))\, e^{-i\frac{1}{2}\phi(\mathbf{r})} \\ \sin(\tfrac{1}{2}\theta(\mathbf{k}))\, e^{+i\frac{1}{2}\phi(\mathbf{r})} \end{pmatrix} \tag{8}$$

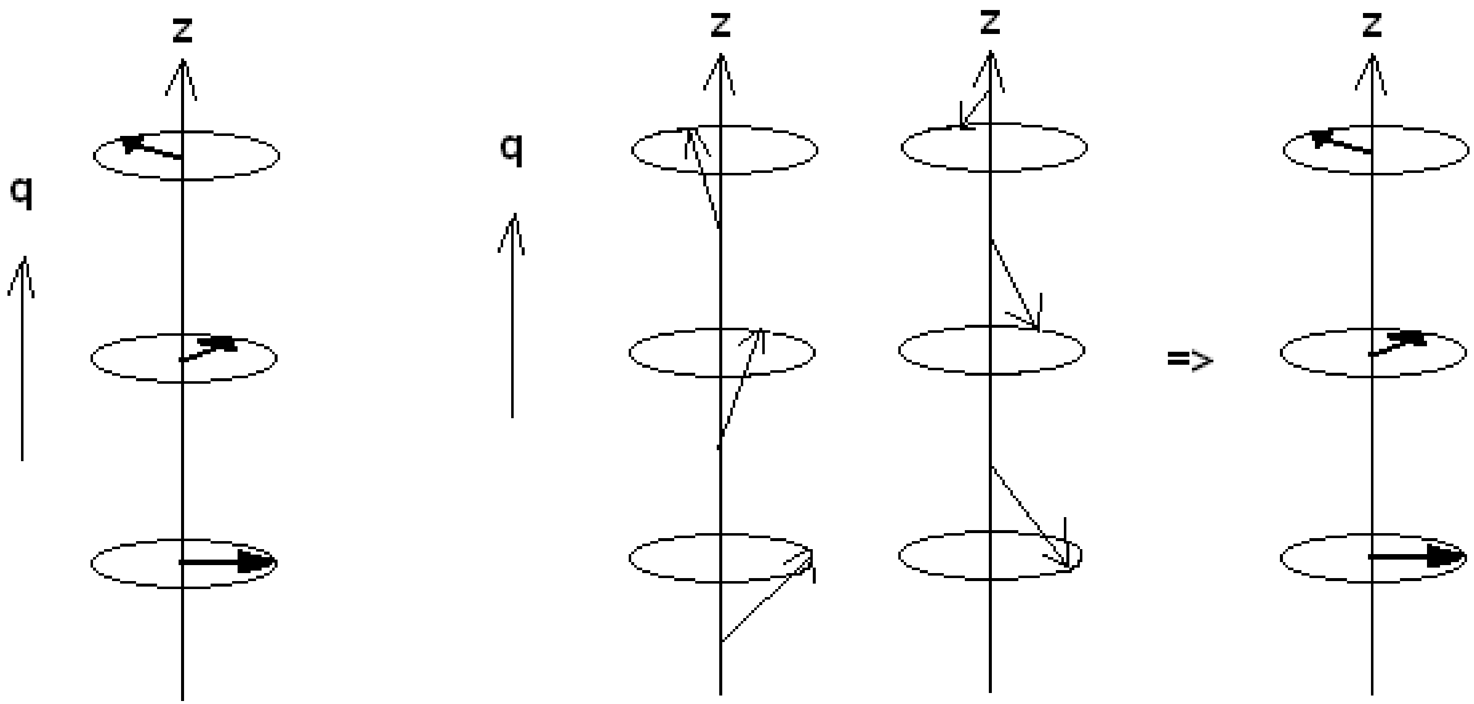
where $\phi(\mathbf{r}) = \mathbf{q}\cdot\mathbf{r}$.

- $\mathbf{k}$ is the plane-wave vector
- $\mathbf{q}$ is the magnetization wave vector (constant)
- the orbital represents a spin pointing in (θ, ϕ) direction
- θ is constant for each particle, but in general different for each $\mathbf{k}$
- ϕ varies with position
- For each $\mathbf{k}$, there are *two* orthogonal orbitals, the other obtained by $\theta(\mathbf{k}) \to \pi + \theta(\mathbf{k})$.

Add Jastrow to form complete wavefunction.

Determinant of such orbitals can describe several *qualitatively* different systems and problems.

Ferromagnetic case: (picture earlier) almost all spins point in z-direction, small spiral about z-direction. Large m_z, small m_x and m_y.



(*Left*) Plane spiral: Spins are almost exactly in the x-y plane. Large amplitude spiral, with large m_x and m_y, and $m_z = 0$. (see Herring: Bloch Wall)

(*Right*) Paramagnetic spiral: Almost all individual spins are parallel to or opposite to z-direction, some of them with deviation from z-direction. $m_z = 0$, smaller m_x and m_y. (see Overhauser: giant SDWs)

For such a determinant, we can *analytically* find the magnetization density:

- $m_x(\mathbf{r}) = \frac{1}{\Omega}\sum_{\mathbf{k}} \sin(\theta(\mathbf{k}))\cos(\mathbf{q}\cdot\mathbf{r}) = m_t\frac{1}{\Omega}\cos(\mathbf{q}\cdot\mathbf{r})$
- $m_y(\mathbf{r}) = \frac{1}{\Omega}\sum_{\mathbf{k}} \sin(\theta(\mathbf{k}))\sin(\mathbf{q}\cdot\mathbf{r}) = m_t\frac{1}{\Omega}\sin(\mathbf{q}\cdot\mathbf{r})$
- $m_z(\mathbf{r}) = \frac{1}{\Omega}\sum_{\mathbf{k}} \cos^2(\frac{1}{2}\theta(\mathbf{k})) - \sin^2(\frac{1}{2}\theta(\mathbf{k})) = m_l\frac{1}{\Omega}$

Aim: Minimize the energy expectation E subject to constraints $\mathbf{q}$, m_t and m_l. Variational freedom is in:

- Choice of wave vectors $\mathbf{k}$ to occupy
- Choice of occupation of 1 or 2 orbitals for each wave vector $\mathbf{k}$
- Function $\theta(\mathbf{k})$
- Parameters in Jastrow

With this, provide data for construction of DFT functional dependent not just on $n(r)$ and $\nabla|\mathbf{m}|$, but also on changes in *direction* of $\mathbf{m}$.

Energy of Bloch Wall

Bloch Wall: Transition layer between two oppositely aligned ferromagnetic domains.

Question: What is the lowest variational energy of a ferromagnetic HEG where magnetization varies smoothly in x-y plane, along z-direction?

Herring considered it in Hartree-Fock: Variational parameters $\theta(\mathbf{k})$, all close to $\pi/2$.

Can get exact analytical result for special case when $\theta(\mathbf{k}) = \pi/2 \, \forall \, \mathbf{k}$ (i.e. no variational freedom). Energy per electron (in atomic units) varies as

$$\Delta E = E(q) - E(0) = \frac{1}{8}q^2 \tag{9}$$

Result using CASINO, $N = 19$, $r_s = 1.0$, for 5 different values of q, constant $q_0 = 1.4607$, best fit quadratic:

$$E(q) = 1.0621 - 7.3997 * 10^{-17}(q/q_0) + 0.26673(q/q_0)^2$$

Effect of Jastrow

When Jastrow is included with determinant of spiral SDW orbitals

- Magnetization density remains spiral
- It can be proved that $\mathbf{q}$ is unaffected
- We hoped that amplitudes m_t and m_l are unaffacted: but not true. This makes it hard to enforce constraint during optimization.

Calculation with 19 electron spiral SDW HEG at $r_s = 1.0$, $\mathbf{k}$ occupying those 19 as in a ferromagnet (i.e. spherically about $\mathbf{k} = 0$), with arbitrary set of $\theta(\mathbf{k})$. Magnetization wave vector $\mathbf{q}$ chosen arbitrarily in x-y plane. q comparable to reciprocal lattice vectors.

A deliberately unoptimized and bad Jastrow was added to the wave function.

	m_t : x,y component	m_l : z component
Analytical	11.759	13.774
Without Jastrow	11.757(5)	13.775(5)
With Jastrow	11.288(5)	13.125(5)

Presence of Jastrow alters amplitudes noticably, but not significantly.

Assorted Energies

Calculations with 19 electrons at $r_s = 1.0$, set of $\mathbf{k}$ chosen as for ferromagnet.

Type		Total	PE	KE	(HF KE)
HF		1.0599	-0.6246	1.6845	1.6845
	±	0.0024	0.0024		
x-y spiral		1.5943	-0.6236	2.2179	2.2179
	±	0.0024	0.0024		
Arbitrary		1.6077	-0.6069	2.2146	2.2144
	±	0.0004	0.0003	0.0003	
Arbitrary + Jastrow		2.1708	-0.4000	2.5708	2.2144
	±	0.0020	0.0006	0.0016	

- HF: standard collinear HF ferromagnetic HEG
- x-y spiral: All 19 spins spiral in the x-y plane
- Arbitrary: 19 arbitrarily chosen $\theta(\mathbf{k})$
- Arbitrary + Jastrow: Same with an arbitrary unoptimized Jastrow factor.

$\mathbf{q} = \mathbf{b}_x + \mathbf{b}_\mathbf{y}$, where $\mathbf{b}_i$ are the reciprocal vectors of the simulation cell.

Conclusions

- Noncollinear VMC is implemented and functioning in CASINO.
- Spiral Spin Density Waves in the Homogeneous Electron Gas are implemented and functioning.
- We can handle arbitrary spin orientations, orbital occupations and calculate the actual magnetization density. Therefore we can study of a variety of spiral SDW problems.
- Jastrow affects magnetization density so constraining it is difficult.

Further work and questions

- How to optimize the parameters $\theta(\mathbf{k})$ subject to constraints? This is potentially doable in variance minimization.
- How to optimize occupation of orbitals?
- What type of spiral SDW is of the most interest and worth studying?