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

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Overview

• What are noncollinear spin systems and why are they interesting?
• Relevant Hartree-Fock theory
• Implementation of noncollinear spins in Variational Monte Carlo
• Application to spiral Spin Density Waves in the Homogeneous Electron Gas
• Spin-density matrix
• Summary
Introduction to noncollinear spins

Physical approach:

- 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 the spin direction can vary with position.

Examples of noncollinear problems:

- Frustrated (e.g. triangular) antiferromagnetic lattices

- Spiral magnetic structures in crystals such as $\gamma$ phase of Fe and Cr compounds

- Spiral Spin Density Waves in the Homogeneous Electron Gas

- Spin wave excitations (a dynamical problem)

Experimental evidence comes from neutron scattering
Mathematical approach:

Total wavefunction of a system of $N$ particles is $\Psi(X) = \Psi(x_1, ..., x_N)$. For a collinear system $\Psi$ is an eigenfunction of the total $\hat{S}_z$ operator.

In a collinear system

- The spin-dependence of the wavefunction can be eliminated and $\Psi$ 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 is used in all the standard methods: HF, DFT, VMC/DMC
Familiar example: determinant of single-particle orbitals

\[ \Psi(X) = \begin{vmatrix} \psi_1(x_1) & \cdots & \psi_1(x_N) \\ \vdots & \ddots & \vdots \\ \psi_N(x_1) & \cdots & \psi_N(x_N) \end{vmatrix}, \]  

(1)

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

In actual calculations, following form is used instead:

\[ \Psi(R) = \begin{vmatrix} \phi_1^\uparrow(r_1) & \cdots & \phi_1^\uparrow(r_N) \\ \vdots & \ddots & \vdots \\ \phi_N^\uparrow(r_1) & \cdots & \phi_N^\uparrow(r_N) \\ \phi_1^\downarrow(r_{N+1}) & \cdots & \phi_1^\downarrow(r_N) \\ \vdots & \ddots & \vdots \\ \phi_N^\downarrow(r_{N+1}) & \cdots & \phi_N^\downarrow(r_N) \end{vmatrix} \]  

(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 retained.

- Can consider the orbitals to explicitly depend on spin coordinates and write them as $\psi(x)$. Equivalently, treat them as two-component spinors and write them as $\psi_\alpha(r)$.

- Physical *direction* of spin depends on relationship of the two components.

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

In a collinear system $m_x(r) = m_y(r) = 0$ and $m_z(r)$ is the spin density.
Generalized Hartree-Fock theory

- Extension of HF theory to noncollinear spins. Determinant made up of spinor orbitals $\psi_i$

$$\Psi = \frac{1}{\sqrt{N!}} \det |\psi_i(r_j)|$$

- Total energy is $E = \langle \Psi | \hat{H} | \Psi \rangle$. Evaluate variation with respect to orbitals, subject to orthonormality constraint. Gives single-particle HF equation (depending on form of $\hat{H}$) such as:

$$(\hat{K} + \hat{U} + \hat{V} - \hat{J})\psi_k(r) = \epsilon_k \psi_k(r)$$

- This is a 2x2 matrix equation. $\hat{K}$ (kinetic energy), $\hat{U}$ (external potential), $\hat{V}$ (direct term) and $\hat{J}$ (exchange term) are 2x2 matrices of operators. $\hat{J}$ can have off-diagonal components, giving rise to noncollinearity.

- Collinear case is special case with $\psi(r) = \phi(r)\chi$, where $\chi$ is a spin eigenstate. Reduces problem to Unrestricted HF theory.

- HF equation needs to be solved self-consistently.
Noncollinear Variational Monte Carlo

• Standard collinear VMC calculations evaluate expectation values such as

\[ E = \frac{\langle \psi(R)|\hat{H}|\psi(R) \rangle}{\langle \psi(R)|\psi(R) \rangle} = \frac{\int |\psi(R)|^2 E_L(R) \, dR}{\int |\psi(R)|^2 \, dR} \]  

(5)

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

• In noncollinear calculation use $\psi(X) = \psi(R, S)$ to evaluate quantities such as

\[ E = \frac{\sum_S \int |\psi(R, S)|^2 E_L(R, S) \, dR}{\sum_S \int |\psi(R, S)|^2 \, dR} \]  

(6)

• 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 (over the alternatives) is ideally suited for evaluation of spin-dependent operators (e.g. spin-density matrix)
Pseudocode for noncollinear VMC

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

\[ \Psi(X) = \exp(J(R))D(X) \]

Loop over time steps.
Loop over electrons in configuration.
Propose move of electron: \( r_i \rightarrow r'_i \). This changes single column of D.
Calculate ratio \( \Psi(R_{\text{new}}, S)/\Psi(R_{\text{old}}, S) \).
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 \( \Psi(R, S_{\text{new}})/\Psi(R, S_{\text{old}}) \).
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.

(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 proposed as: 50% chance to change spin and 50% chance to keep current spin. Some chance to keep current spin is necessary for *ergodicity*.

• The Metropolis acceptance ratio for spin flips is

\[
A(s_i \rightarrow s'_i) = \min \left\{ 1, \frac{|\psi(R, S_{\text{new}})|^2}{|\psi(R, S_{\text{old}})|^2} \right\} = \min \left\{ 1, \frac{|D(S_{\text{new}})|^2}{|D(S_{\text{old}})|^2} \right\}
\] (7)

• Sherman-Morrison formula, use of cofactor matrix etc. all hold for spin flips too
Jastrow factor and cusp conditions

• In QMC correlation effects can be directly incorporated into the wavefunction. In VMC this is achieved via the Jastrow factor.

• In the collinear case Jastrow factor appears as \( \Psi(R) = \exp(J(R))D^\uparrow D^\downarrow \). Terms in \( J \) depend on the spins of the (distinguishable) up- and down-spin electrons.

• \( J \) is chosen so that \( \Psi \) obeys electron-electron cusp conditions. These conditions are different when two parallel-spin or anti-parallel spin electrons meet.

Introducing the Jastrow factor in the noncollinear wavefunction:

• We could attempt to include a spin-dependent \( J(R, S) \) to satisfy the cusp conditions. This alters the physical spin directions represented by the spin-dependent orbitals.

• Instead include a spin-independent \( J(R) \), treating all electrons indistinguishable. Use the form usually used for anti-parallel spin pairs.

• Cusp conditions are not completely satisfied.
Test the seriousness of disobeying cusp conditions:

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

<table>
<thead>
<tr>
<th>System</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.6480</td>
</tr>
<tr>
<td>Normal $J$ in VMC</td>
<td>0.5932(2)</td>
</tr>
<tr>
<td>Altered $J$ in VMC</td>
<td>0.5939(2)</td>
</tr>
<tr>
<td>DMC</td>
<td>0.5819(5)</td>
</tr>
</tbody>
</table>

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

Static, noncollinear system where magnetization density varies in helical fashion. Site to site in a crystal, smoothly in a homogeneous system (e.g. HEG).

Characterised by a wavevector $q$: direction and wave-length

![Diagram of spiral spin density waves]

“Frozen magnon”

This covers a wide range of problems. Examples in literature:

- Overhauser: HF ground-state of 3D HEG is giant SDW instead of paramagnet
- Herring: Energy of Bloch wall
- DFT applications to ground-state of Fe crystals
- Spin wave spectrum by mapping to Heisenberg model: $H = \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$
Wavefunction for spiral SDW in HEG

Construct determinant of single-particle spinors:

\[
\psi_k(r) = e^{i k \cdot r} \begin{pmatrix} \cos \left( \frac{1}{2} \theta_k \right) e^{-i \frac{1}{2} \phi(r)} \\ \sin \left( \frac{1}{2} \theta_k \right) e^{+i \frac{1}{2} \phi(r)} \end{pmatrix}
\]  

(8)

where \( \phi(r) = q \cdot r \).

- \( k \) is the plane-wave vector
- \( q \) is the magnetization wave vector (constant)
- the orbital represents a spin pointing in \((\theta, \phi)\) direction
- \( \theta \) is constant for each particle, but in general different for each \( k \)
- \( \phi \) varies with position
- For each \( k \), there are two orthogonal orbitals, the other obtained by \( \theta_k \rightarrow \pi + \theta_k \).

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:

- \( m_x(r) = \frac{1}{\Omega} \sum_k \sin \theta_k \cos(q \cdot r) = \frac{1}{\Omega} m_l \cos(q \cdot r) \)
- \( m_y(r) = \frac{1}{\Omega} \sum_k \sin \theta_k \sin(q \cdot r) = \frac{1}{\Omega} m_l \sin(q \cdot r) \)
- \( m_z(r) = \frac{1}{\Omega} \sum_k \cos^2(\frac{1}{2} \theta_k) - \sin^2(\frac{1}{2} \theta_k) = \frac{1}{\Omega} m_l \)

**Aim:** Minimize the energy expectation \( E \) subject to constraints on \( q, m_l \) and \( m_l \).

Variational freedom is in:

- Choice of wave vectors \( k \) to occupy
- Choice of occupation of 1 or 2 orbitals for each wave vector \( k \) ("bands")
- Function \( \theta_k \)
- Parameters in Jastrow

Noncollinear DFT calculations usually neglect variation in direction of magnetization. Can potentially construct better functionals based on QMC results.
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 $\theta_k$, all close to $\pi/2$.

- Can get exact analytical result for special case when $\theta_k = \pi/2$ (i.e. no variational freedom). Energy per electron (in a.u.) varies as

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

- Result using CASINO, $N = 19$, $r_s = 1.0$, best fit quadratic:

$$ E(q) = 1.0621 - 5.0659 \times 10^{-17} q + 0.12501 q^2 $$

- Improve Herring’s results by including correlation in VMC.
Giant Spin Density Waves

- Ground state of HEG was believed to be paramagnet or ferromagnet, depending on $r_s$.

- Overhauser in 1950's proved that within HF, ground state is never a paramagnet in 3D. It's unstable to formation of sSDW ("giant" SDW).

  ![Fermi surface for giant SDW](image)

- It is believed that correlation effects make SDW unfavourable and make paramagnet the ground state again.
Hartree-Fock theory for spiral SDW

QMC calculations require starting wavefunction, usually supplied by other software.

- For collinear HEG, we know form explicitly: electrons in Fermi-sphere.

- For sSDW problems need HF theory to provide initial wavefunction: occupation of \( k \)-points and bands, and spin angles \( \theta_k \).

We developed a HF code specifically for sSDW. Analytical results are similar to the ordinary HEG.

- Total HF energy for any set of sSDW orbitals:

\[
E = \sum_{k} \frac{1}{2} \left\{ k^2 + \frac{1}{4} q^2 - k \cdot q \cos \theta_k \right\} - \frac{1}{2} \frac{1}{\Omega} \sum_{k, k' \neq k} \frac{4\pi}{|k - k'|^2} \cos \frac{1}{2} (\theta_k - \theta_{k'}) + \frac{1}{2} N \xi
\]

(\( \xi \) is the Ewald self-image term)

- Single-particle HF equation, solved self-consistently to minimize \( E \):

\[
\begin{bmatrix}
K_{k1} & 0 \\
0 & K_{k2}
\end{bmatrix} - \begin{bmatrix}
J_{k1} & J_{k0} \\
J_{k0} & J_{k2}
\end{bmatrix} \begin{bmatrix}
\cos(\frac{1}{2} \theta_k) \\
\sin(\frac{1}{2} \theta_k)
\end{bmatrix} = \epsilon_k \begin{bmatrix}
\cos(\frac{1}{2} \theta_k) \\
\sin(\frac{1}{2} \theta_k)
\end{bmatrix}
\]

(11)
Assorted Energies

Calculations in CASINO with 19 electrons at $r_s = 1.0$, set of $k$ chosen as for ferromagnet. Energies in a.u. per particle.

<table>
<thead>
<tr>
<th>Type</th>
<th>Total</th>
<th>PE</th>
<th>KE</th>
<th>HF result</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>1.0599</td>
<td>-0.6246</td>
<td>1.6845</td>
<td>1.0614</td>
</tr>
<tr>
<td>±</td>
<td>0.0024</td>
<td>0.0024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x-y spiral</td>
<td>1.5943</td>
<td>-0.6236</td>
<td>2.2179</td>
<td>1.5948</td>
</tr>
<tr>
<td>±</td>
<td>0.0024</td>
<td>0.0024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arbitrary</td>
<td>1.6077</td>
<td>-0.6069</td>
<td>2.2146</td>
<td>1.6071</td>
</tr>
<tr>
<td>±</td>
<td>0.0004</td>
<td>0.0003</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>Arbitrary + Jastrow</td>
<td>2.1708</td>
<td>-0.4000</td>
<td>2.5708</td>
<td>N/A</td>
</tr>
<tr>
<td>±</td>
<td>0.0020</td>
<td>0.0006</td>
<td>0.0016</td>
<td></td>
</tr>
</tbody>
</table>

- HF: standard collinear ferromagnetic HEG
- x-y spiral: All 19 spins spiral in the x-y plane
- Arbitrary: 19 arbitrarily chosen $\theta_k$
- Arbitrary + Jastrow: Same with an arbitrary unoptimized Jastrow factor.

$q = b_x + b_y$, where $b_i$ are the reciprocal vectors of the simulation cell.
Spin-density matrix

- The **spin-density matrix** is a 2x2 matrix, where each element depends on position. Defined in second quantized notation as

\[
\rho_{\alpha\beta}(r) = \langle \hat{\psi}_\beta^\dagger(r) \hat{\psi}_\alpha(r) \rangle
\]

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

\[
\rho_{\alpha\beta}(r) = \sum_n f_n \psi_{n,\alpha}(r) \psi_{n,\beta}^*(r)
\]

(see later for definition useful for QMC)

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

\[
\begin{align*}
n(r) &= Tr\rho \\
m(r) &= \sum_{\alpha\beta} \rho_{\alpha\beta} \sigma_{\beta\alpha} \\
\rho_{\alpha\beta}(r) &= \frac{1}{2} n(r) \delta_{\alpha\beta} + \frac{1}{2} m(r) \cdot \sigma_{\alpha\beta}(r)
\end{align*}
\]

- Some DFT codes can perform fully unconstrained noncollinear calculations, by considering \( E_{xc} = E_{xc}[\rho_{\alpha\beta}(r)] \). Specific form used however usually neglects changes in the *direction* of magnetization!
Spin-density matrix in noncollinear VMC

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

\[ \rho_{\alpha\beta}(r) = \sum_i \frac{\sum S/s_i \int \Psi^*(r_1, s_1, ..., r, \beta, ..., r_N, s_n) \psi(r_1, s_1, ..., r, \alpha, ..., r_N, s_n) dR/r_i}{\sum S \int |\psi(R, S)|^2 dR} \]

\[ = \left\langle \sum_i \delta(r - r_i) \delta_{s_i \beta} \frac{\psi(..., r_i, \alpha, ...) \psi(..., r_i, \beta, ...)}{\psi(..., r_i, \beta, ...)} \right\rangle \]  

(12)

This is similar to how the density, spin density or pair correlation function is usually evaluated. We accumulate the Fourier components:

\[ \tilde{\rho}_{\alpha\beta}(G) = \frac{1}{\Omega} \left\langle \sum_i \exp(-iG \cdot r_i) \delta_{s_i \beta} \frac{\psi(..., r_i, \alpha, ...) \psi(..., r_i, \beta, ...)}{\psi(..., r_i, \beta, ...)} \right\rangle \]  

(13)

Fourier components of magnetization density follow:

\[ \tilde{m}(G) = \sum_{\alpha\beta} \tilde{\rho}_{\alpha\beta}(G) \sigma_{\beta\alpha} \]

where \( \sigma \) is the vector of Pauli matrices.
Summary

- Noncollinear VMC is available in CASINO.

- Spiral Spin Density Waves in the Homogeneous Electron Gas are implemented.

- We can handle arbitrary spin orientations, orbital occupations and calculate the actual magnetization density within VMC.

- Specialized Hartree-Fock code provides initial wavefunction.

- We are applying it to study a variety of spiral SDW problems.

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