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 γ 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 $\Psi(\mathbf{X}) = \Psi(\mathbf{x}_1, ..., \mathbf{x}_N)$. For a *collinear* system Ψ is an eigenfunction of the total $\hat{S}_z$ operator.

In a collinear system

- 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 is used in all the standard methods: HF, DFT, VMC/DMC

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 actual calculations, 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 retained.

- Can consider the orbitals to explicitly depend on spin coordinates and write them as $\psi(\mathbf{x})$. Equivalently, 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.

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

Generalized Hartree-Fock theory

- Extension of HF theory to noncollinear spins. Determinant made up of spinor orbitals ψ_i

$$\Psi = \frac{1}{\sqrt{N!}} \det |\psi_i(\mathbf{r}_j)| \tag{3}$$

- 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:

$$(\hat{\mathbf{K}} + \hat{\mathbf{U}} + \hat{\mathbf{V}} - \hat{\mathbf{J}})\psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r}) \tag{4}$$

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

- Collinear case is special case with $\psi(\mathbf{r}) = \phi(\mathbf{r})\chi$, where χ 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

$$E = \frac{\left\langle \Psi(\mathbf{R}) | \hat{H} | \Psi(\mathbf{R}) \right\rangle}{\langle \Psi(\mathbf{R}) | \Psi(\mathbf{R}) \rangle} = \frac{\int |\Psi(\mathbf{R})|^2 E_L(\mathbf{R})\, d\mathbf{R}}{\int |\Psi(\mathbf{R})|^2\, d\mathbf{R}} \tag{5}$$

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

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

$$E = \frac{\sum_{\mathbf{S}} \int |\Psi(\mathbf{R}, \mathbf{S})|^2 E_L(\mathbf{R}, \mathbf{S})\, d\mathbf{R}}{\sum_{\mathbf{S}} \int |\Psi(\mathbf{R}, \mathbf{S})|^2\, d\mathbf{R}} \tag{6}$$

- 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

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

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Loop over time steps.
  Loop over electrons in configuration.
     Propose move of electron:  r_i → r'_i.  This changes single column of D.
     Calculate ratio Ψ(R_new, S)/Ψ(R_old, S).
     Perform Metropolis accept/reject step.
     If move is accepted update cofactor matrix and determinant.
     Propose spin flip of electron:  s_i → s'_i.  This changes single column of D.
     Calculate ratio Ψ(R, S_new)/Ψ(R, S_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 currentspin is necessary for *ergodicity*.
- The Metropolis acceptance ratio for spin flips is

$$A(s_i \to s_i') = \min\left\{1, \frac{|\Psi(\mathbf{R}, \mathbf{S}_{\text{new}})|^2}{|\Psi(\mathbf{R}, \mathbf{S}_{\text{old}})|^2}\right\} = \min\left\{1, \frac{|D(\mathbf{S}_{\text{new}})|^2}{|D(\mathbf{S}_{\text{old}})|^2}\right\} \tag{7}$$

- 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 $\Psi(\mathbf{R}) = \exp(J(\mathbf{R}))D^{\uparrow}D^{\downarrow}$. Terms in J depend on the spins of the (distinguishable) up- and down-spin electrons.

- J is chosen so that Ψ 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 $J(\mathbf{R}, \mathbf{S})$ to satisfy the cusp conditions. This alters the physical spin directions represented by the spin-dependent orbitals.

- Instead include a spin-independent $J(\mathbf{R})$, 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:

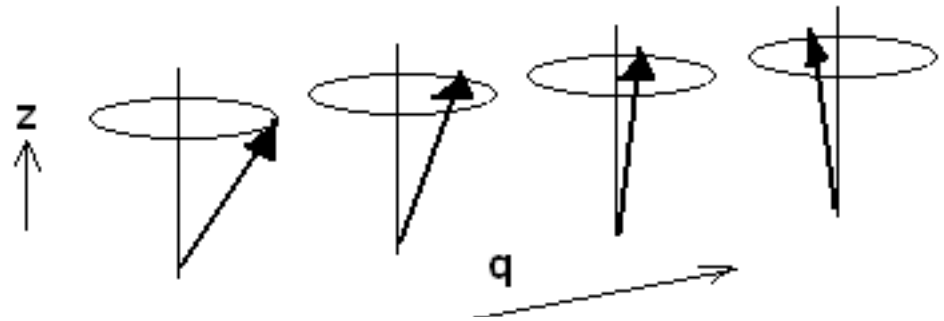
System	Energy
HF	0.6480
Normal J in VMC	0.5932(2)
Altered J in VMC	0.5939(2)
DMC	0.5819(5)

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

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 $\mathbf{q}$: direction and wave-length



"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:

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

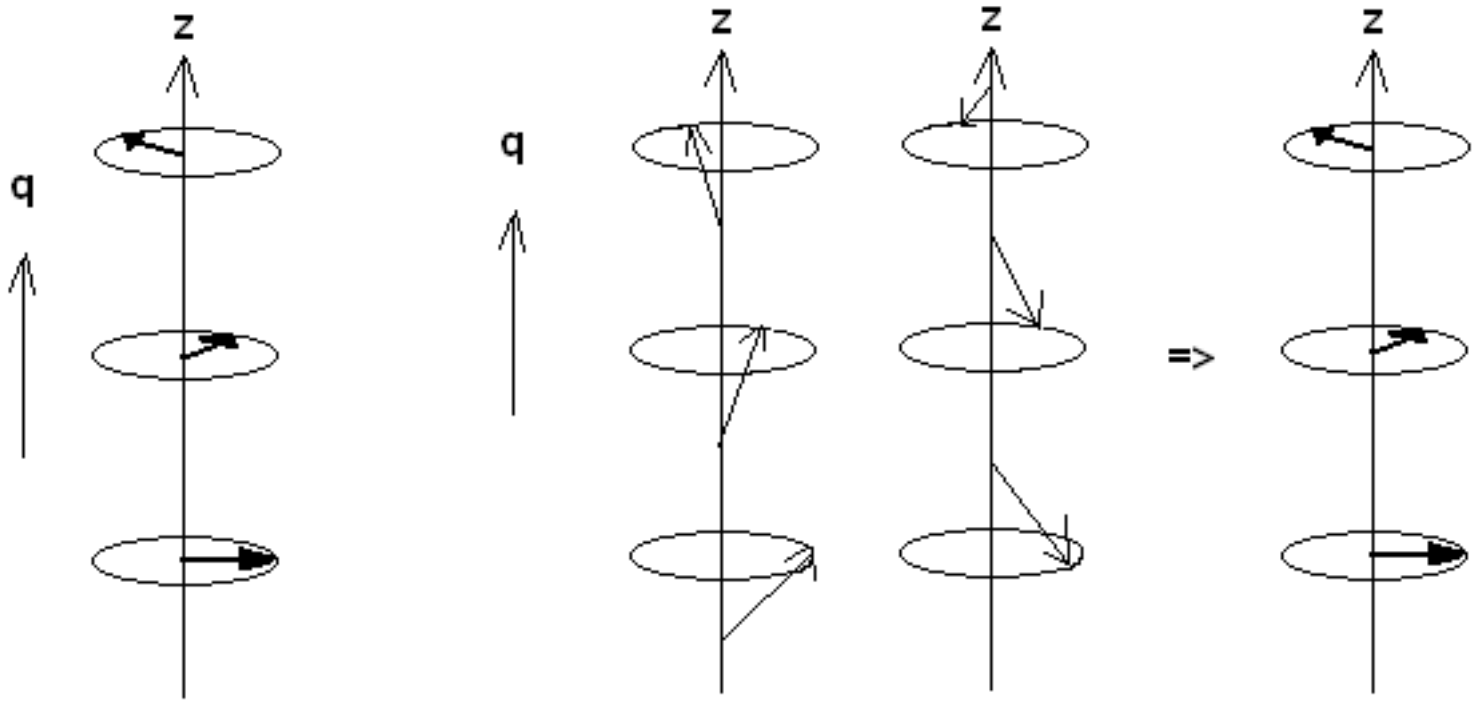
where $\phi(\mathbf{r}) = \mathbf{q}\cdot\mathbf{r}$.

- $\mathbf{k}$ 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 $\theta_{\mathbf{k}} \rightarrow \pi + \theta_{\mathbf{k}}$.

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:

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

Aim: Minimize the energy expectation E subject to constraints on $\mathbf{q}$, 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 $\mathbf{k}$ ("bands")
- Function $\theta_{\mathbf{k}}$
- 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 $\theta_{\mathbf{k}}$, all close to $\pi/2$.

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

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

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

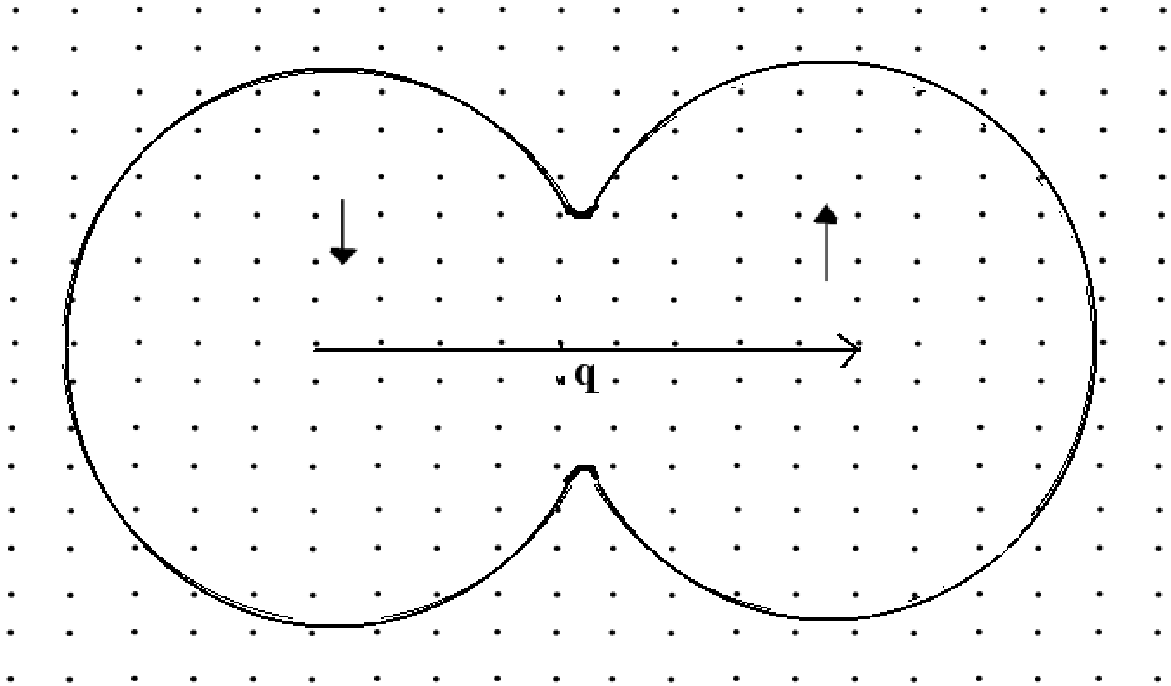
$$E(q) = 1.0621 - 5.0659 * 10^{-17}\, q + 0.12501\, q^2$$

- Improve Herring's results by including correlation in VMC.

Giant Spin Density Waves

- Ground state of HEG was beleived 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

- It is beleived 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 $\mathbf{k}$-points and bands, and spin angles $\theta_{\mathbf{k}}$.

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:

$$E = \sum_{\mathbf{k}} \frac{1}{2} \left\{ \mathbf{k}^2 + \frac{1}{4}\mathbf{q}^2 - \mathbf{k}\cdot\mathbf{q}\cos\theta_{\mathbf{k}} \right\} - \frac{1}{2}\frac{1}{\Omega} \sum_{\mathbf{k},\mathbf{k}'\neq\mathbf{k}} \frac{4\pi}{|\mathbf{k}-\mathbf{k}'|^2} \cos^2\frac{1}{2}(\theta_{\mathbf{k}} - \theta_{\mathbf{k}'}) + \frac{1}{2}N\xi \tag{10}$$

  (ξ is the Ewald self-image term)

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

$$\left[\begin{pmatrix} K_{\mathbf{k}1} & 0 \\ 0 & K_{\mathbf{k}2} \end{pmatrix} - \begin{pmatrix} J_{\mathbf{k}1} & J_{\mathbf{k}o} \\ J_{\mathbf{k}o} & J_{\mathbf{k}2} \end{pmatrix} \right] \begin{pmatrix} \cos(\frac{1}{2}\theta_{\mathbf{k}}) \\ \sin(\frac{1}{2}\theta_{\mathbf{k}}) \end{pmatrix} = \epsilon_{\mathbf{k}} \begin{pmatrix} \cos(\frac{1}{2}\theta_{\mathbf{k}}) \\ \sin(\frac{1}{2}\theta_{\mathbf{k}}) \end{pmatrix} \tag{11}$$

Assorted Energies

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

Type		Total	PE	KE	HF result
HF		1.0599	-0.6246	1.6845	1.0614
	$\pm$	0.0024	0.0024		
x-y spiral		1.5943	-0.6236	2.2179	1.5948
	$\pm$	0.0024	0.0024		
Arbitrary		1.6077	-0.6069	2.2146	1.6071
	$\pm$	0.0004	0.0003	0.0003	
Arbitrary + Jastrow		2.1708	-0.4000	2.5708	N/A
	$\pm$	0.0020	0.0006	0.0016	

- HF: standard collinear 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.

Spin-density matrix

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

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

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

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

  (see later for definition useful for QMC)

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

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

- Some DFT codes can perform fully unconstrained noncollinear calculations, by considering $E_{xc} = E_{xc}[\rho_{\alpha\beta}(\mathbf{r})]$. 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

$$\begin{aligned}\rho_{\alpha\beta}(\mathbf{r}) &= \sum_i \frac{\sum_{\mathbf{S}/s_i}\int \Psi^*(\mathbf{r}_1,s_1,...,\mathbf{r},\beta,...,\mathbf{r}_N,s_n)\Psi(\mathbf{r}_1,s_1,...,\mathbf{r},\alpha,...,\mathbf{r}_N,s_n)d\mathbf{R}/\mathbf{r}_i}{\sum_{\mathbf{S}}\int|\Psi(\mathbf{R},\mathbf{S})|^2 d\mathbf{R}} \\ &= \left\langle \sum_i \delta(\mathbf{r}-\mathbf{r}_i)\delta_{s_i\beta}\frac{\Psi(...,\mathbf{r}_i,\alpha,...)}{\Psi(...,\mathbf{r}_i,\beta,...)}\right\rangle \end{aligned} \tag{12}$$

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

$$\tilde{\rho}_{\alpha\beta}(\mathbf{G}) = \frac{1}{\Omega}\left\langle \sum_i \exp(-i\mathbf{G}\cdot\mathbf{r}_i)\delta_{s_i\beta}\frac{\Psi(...,\mathbf{r}_i,\alpha,...)}{\Psi(...,\mathbf{r}_i,\beta,...)}\right\rangle \tag{13}$$

Fourier components of magnetization density follow:

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

where σ is the vector of Pauli matrices.

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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