

Non-collinear spins in quantum Monte Carlo calculations

ESDG talk by Zoltán Radnai

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Introduction

- Most systems can be modelled in a *collinear* fashion, with every electron having a definite spin (up or down) with respect to a global quantization axis.
- There are some applications where such an approach is insufficient. Need to be able to deal with electron spin pointing in any direction, and potentially varying with position. In other words, *non-collinear* spin structures.

Examples:

- Frustrated (e.g. triangular) antiferromagnetic lattices
- Spiral or helical spin structures in materials such as fcc iron or chromium
- Spin Density Waves in the Homogeneous Electron Gas

Introducing spinor orbitals

- In standard collinear calculations (RHF, UHF, a lot of DFT, QMC), single-particle orbitals simply take the form of $\psi = \phi(\mathbf{r})\chi$, with χ being a spin-up or spin-down eigenfunction. The χ part of the orbital then plays little role.
- In the most general form, a particle with spin should really be described using a two-component spinor orbital, $\psi_\alpha(\mathbf{r})$.
- Example of use: General Unrestricted Hartree Fock theory. Form a determinant from spinor orbitals, the self-consistent Hartree-Fock equation is then really a 2x2 matrix equation:

$$F_{\alpha\beta}\psi_{i\beta}(\mathbf{r}) = \epsilon_i\psi_{i\alpha}(\mathbf{r}).$$

Non-collinear DFT

- Hohenberg-Kohn theorem originally developed for spinless case. Exchange correlation energy functional of density only ($E_{xc}[n]$).
- Von Barth and Hedin developed the general spin dependent version, which was originally non-collinear in formulation. They suggested that E_{xc} should really depend on spin density matrix $\rho_{\alpha\beta}(\mathbf{r})$.
- Most DFT calculations are restricted to collinear, possibly spin-polarized case.

Notations and definitions

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

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

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

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

- 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 non-collinear 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

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

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

$$V_{xc}^{\alpha\beta}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}}{\delta |\mathbf{m}(\mathbf{r})|} \hat{\mathbf{m}}(\mathbf{r}) \cdot \sigma^{\alpha\beta}.$$

(this is the case in ABINIT and VASP for example).

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

Failure of local approximations in DFT and beyond

- Antiferromagnetic/spiral spin configurations clearly depend on having non-local correlations between spin directions.
- The restrictions to the local approximations and the neglect of variation in magnetization direction mean that DFT still has notorious difficulty describing spin spiral ground states.
- Several approaches have been suggested to go beyond the simple local approximations.
- Capelle and Oliveira has suggested introducing another variable, called the staggered spin-density $\rho_s(\mathbf{r}, \mathbf{r}') = \langle (\hat{\Psi}_\uparrow^\dagger(\mathbf{r}) \hat{\Psi}_\downarrow^\dagger(\mathbf{r}')) \rangle$ to introduce one more explicit term in the energy expression, beyond T_s and U_H . ρ_s is non-local in nature.
- Recent paper by Katsnelson and Antropov suggested including spin angular gradient terms in E_{xc} , so that $E_{xc} = \int d\mathbf{r} \{ n \epsilon_{xc}(n_\uparrow, n_\downarrow) + \lambda(n_\uparrow, n_\downarrow) (\nabla_\alpha e_\beta) (\nabla_\alpha e_\beta) \}$, where $\mathbf{e} = \mathbf{m}/|\mathbf{m}|$. This includes terms dependent on the change in direction of \mathbf{m} . (They obtain λ from many-body theory calculations).

Non-collinear spins in QMC

Attempt 1 - VMC

- Compared to DFT, it is conceptually simple to have non-collinear spin configurations in QMC. In principle we can deal with an arbitrary many-body wave function directly, including its spin configuration.

- Introduce single-particle spinor orbitals directly in Variational Monte Carlo

$$\psi(\mathbf{r}, \sigma) = \phi^\alpha(\mathbf{r})\alpha(\sigma) + \phi^\beta(\mathbf{r})\beta(\sigma),$$

where α and β are the spin-up and spin-down eigenstates, relative to a fixed, global quantization axis.

- Construct a Slater determinant of these orbitals to form the trial wavefunction

$$\Psi_T(\mathbf{r}_1 \dots \mathbf{r}_N, \sigma_1 \dots \sigma_N) = \begin{vmatrix} \psi_1(\mathbf{r}_1, \sigma_1) & \dots & \psi_1(\mathbf{r}_N, \sigma_N) \\ \vdots & & \vdots \\ \psi_N(\mathbf{r}_1, \sigma_1) & \dots & \psi_N(\mathbf{r}_N, \sigma_N) \end{vmatrix}$$

- Any N-particle wavefunction can be rewritten as $\Psi = \sum_i D_i(\{\mathbf{r}\})\chi_i(\{\sigma\})$, if the spin functions χ_i are a complete set of eigenstates for the N-particle spin space. In the most general case, there are 2^N terms in the sum.

- In the case of Ψ_T , a typical term has the form

$$\chi_i = \alpha(\sigma_1)\alpha(\sigma_2)\beta(\sigma_3)\alpha(\sigma_4)\cdots\beta(\sigma_{N-1})\beta(\sigma_N)$$

$$D_i = \begin{vmatrix} \phi_1^\alpha(\mathbf{r}_1) & \phi_1^\alpha(\mathbf{r}_2) & \phi_1^\beta(\mathbf{r}_3) & \phi_1^\alpha(\mathbf{r}_4) & \cdots & \phi_1^\beta(\mathbf{r}_{N-1}) & \phi_1^\beta(\mathbf{r}_N) \\ \vdots & & & & & & \vdots \\ \phi_N^\alpha(\mathbf{r}_1) & \phi_N^\alpha(\mathbf{r}_2) & \phi_N^\beta(\mathbf{r}_3) & \phi_N^\alpha(\mathbf{r}_4) & \cdots & \phi_N^\beta(\mathbf{r}_{N-1}) & \phi_N^\beta(\mathbf{r}_N) \end{vmatrix}$$

- The expectation value of any spin-independent operator (such as \hat{H}) becomes

$$\langle \Psi_T | \hat{H} | \Psi_T \rangle = \sum_{\{\sigma\}} \int d\{\mathbf{r}\} \sum_i (D_i^* \chi_i^*) \hat{H} \sum_j (D_j \chi_j) = \int d\{\mathbf{r}\} \sum_i D_i^* \hat{H} D_i,$$

where we have used the orthogonality relation $\sum_{\{\sigma\}} \chi_i^* \chi_j = \delta_{ij}$.

- All the D_i containing the same number of α labels are identical up to a permutation of the labels α and β , or equivalently a permutation of the variables $\{\mathbf{r}\}$. When we perform $\int d\{\mathbf{r}\} D_i^* \hat{H} D_i$, all these terms give identical results. If there are m of the α labels within a single row of D , there are $\binom{N}{m}$ such D s.

- This makes the evaluation of $\langle \hat{H} \rangle$ a lot easier. We can replace the expectation value with

$$\langle \Psi_T | \hat{H} | \Psi_T \rangle = \int d\{\mathbf{r}\} \sum_{m=0}^N D_m^* \hat{H} D_m,$$

where

$$D_m = \binom{N}{m} \begin{vmatrix} \phi_1^\alpha(\mathbf{r}_1) & \cdots & \phi_1^\alpha(\mathbf{r}_m) & \phi_1^\beta(\mathbf{r}_{m+1}) & \cdots & \phi_1^\beta(\mathbf{r}_N) \\ \vdots & & & & & \vdots \\ \phi_N^\alpha(\mathbf{r}_1) & \cdots & \phi_N^\alpha(\mathbf{r}_m) & \phi_N^\beta(\mathbf{r}_{m+1}) & \cdots & \phi_N^\beta(\mathbf{r}_N) \end{vmatrix}.$$

- Different m correspond to different polarizations of the electrons. The number of columns in which D_m and $D_{m'}$ differ is $|m - m'|$. There are now only $N + 1$ terms instead of 2^N in the sum, and there are only $2N$ different columns that can appear in the D_m s.
- The normalized expectation value is

$$\begin{aligned} \frac{\langle \Psi_T | \hat{H} | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} &= \frac{\int d\{\mathbf{r}\} \sum_{m=0}^N D_m^* \hat{H} D_m}{\int d\{\mathbf{r}\} \sum_{m=0}^N |D_m|^2} = \frac{\int d\{\mathbf{r}\} \sum_{m=0}^N |D_m|^2 \frac{\hat{H} D_m}{D_m^*}}{\int d\{\mathbf{r}\} \sum_{m=0}^N |D_m|^2} \\ &= \int d\{\mathbf{r}\} \sum_{m=0}^N p_m(\{\mathbf{r}\}) E_{L,m}(\{\mathbf{r}\}) \end{aligned}$$

- The distribution $p_m(\{\mathbf{r}\})$ can be sampled using the standard Monte Carlo walk method. The electron-by-electron algorithm can be extended, so that the move of an electron $\mathbf{r} \rightarrow \mathbf{r}'$ may be accompanied by a flipping of its spin (changing $m \rightarrow m'$). This still results in just one column of D changing.

Collinear case is special case of non-collinear one

- Example two-electron system: Two up-spin electrons. Achieved by setting $\phi_1^\beta = \phi_2^\beta = 0$. Only the $m = 0$ term survives, with $D_0 = \begin{vmatrix} \phi_1^\alpha(\mathbf{r}_1) & \phi_1^\alpha(\mathbf{r}_2) \\ \phi_2^\alpha(\mathbf{r}_1) & \phi_2^\alpha(\mathbf{r}_2) \end{vmatrix}$.
- Example two-electron system: One up- and one down-spin electron. Achieved by setting $\phi_1^\beta = \phi_2^\alpha = 0$. Only the $m = 1$ term survives, with $D_1 = 2 \begin{vmatrix} \phi_1^\alpha(\mathbf{r}_1) & \phi_1^\beta(\mathbf{r}_2) \\ \phi_2^\alpha(\mathbf{r}_1) & \phi_2^\beta(\mathbf{r}_2) \end{vmatrix} = 2\phi_1^\alpha(\mathbf{r}_1)\phi_2^\beta(\mathbf{r}_2)$.
- In general, the collinear case corresponds to having a single term out of the sum over m .
- In the collinear case, it is usual to separate the determinant $D = D^\uparrow D^\downarrow$. This directly corresponds to collecting the terms of equal m in the non-collinear case, and lead to the same result.

Jastrow correlation factor

- So far, method is no different than poor version of GUHF.
- Power of QMC is in that correlation effects can be directly incorporated into the wavefunction.
- In the collinear case it is usual to introduce a Jastrow factor in the wavefunction $\Psi_T = e^J D^\uparrow D^\downarrow$, where J depends on $\{\mathbf{r}_{iI}\}$, $\{\mathbf{r}_{ij}\}$ and $\{\mathbf{r}_{ijI}\}$. In principle J is ought to be symmetric under the interchange of any pair of electrons. In practice it is chosen to be symmetric only under the interchange of up-spin and down-spin electrons among themselves.
- J is chosen so that Ψ_T obeys electron-electron cusp conditions. These conditions are different when two parallel-spin or anti-parallel spin electrons meet.
- In the construction of J , it is assumed that we have a fixed number of up- and down-spin electrons respectively.

How to include the Jastrow factor in the non-collinear trial function?

- One obvious attempt is to include a separate J with each term in sum over m , such as $\Psi_T = \sum_m e^{J_m} D_m \chi_m$. This would fail because the different J_m weight each D_m differently, and so alters the ratio between each term, altering the spin configuration we are trying to achieve.

- Solution is to have a single factor J for all terms: $\Psi_T = e^J \sum_m D_m \chi_m$. J now cannot depend on the spin of the electrons and must include identical terms for all pairs of electrons. **This will make Ψ_T disobey the cusp conditions in general.**
- This is not such a big problem however. We can choose J to obey the anti-parallel spin cusp conditions, making J largely right.
- We can test the seriousness of this alteration. Do a normal calculation involving unpolarized HEG, where the Jastrow factor is altered to obey anti-parallel cusp conditions only. 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)

- It might be possible to come up with something better.

Attempt 2 - DMC

- It appears to be much harder to introduce non-collinear spin in Diffusion Monte Carlo. As yet no solution, some of the problem is illustrated here.
- Try and maintain a fixed spin configuration and achieve the lowest energy state corresponding to that.
- Usual procedure is to start with the imaginary-time Schrödinger equation

$$(\hat{H} - E_T)\Psi = -\frac{\partial\Psi}{\partial\tau},$$

which has a formal solution

$$\Psi(\tau) = e^{-\tau(\hat{H}-E_T)}\Psi(0).$$

In the limit $\tau \rightarrow \infty$, the expression on the RHS projects out the ground state if $E_T = E_0$, the ground state energy, so that $\lim_{\tau \rightarrow \infty} \Psi(\tau) = \Psi_0$.

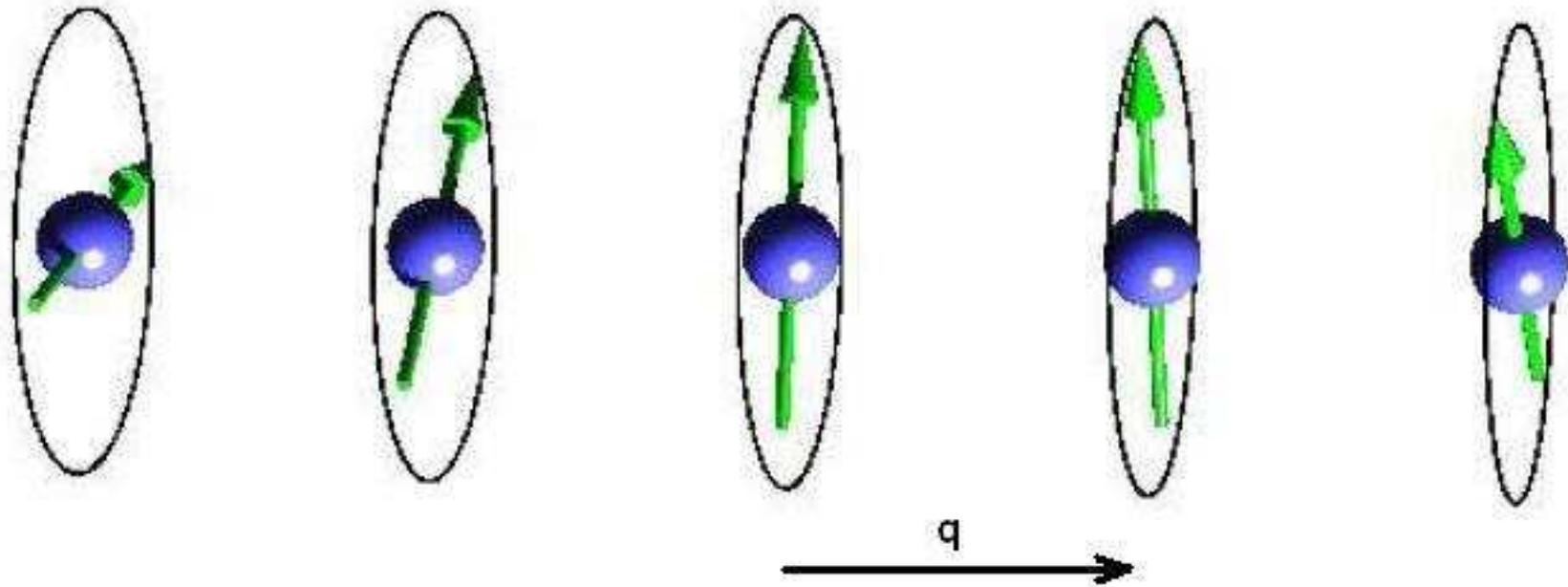
- Consider an initial wavefunction of the form $\Psi(0) = \sum_m D_m \chi_m$. Since \hat{H} is independent of spin, we obtain

$$\lim_{\tau \rightarrow \infty} e^{-\tau(\hat{H}-E_T)}\Psi(0) = \lim_{\tau \rightarrow \infty} \sum_m e^{-\tau(\hat{H}-E_T)} D_m \chi_m = \sum_m c_m \Psi_0 \chi_m,$$

provided that each of the D_m have a non-zero overlap with the ground-state Ψ_0 . The relationship between the D_m , responsible for maintaining a given spin configuration, is therefore destroyed.

Potential Application - SDW in HEG

- The phases of the Homogeneous Electron Gas have been extensively studied, including a plethora of QMC calculations. Comparisons have been made between unpolarized, partially polarized and fully polarized phases, crystalline phase etc.
- All the QMC calculations have been restricted to collinear calculations!
- Overhauser showed first that in the Hartree-Fock approximation, the lowest energy state of the fluid phase of HEG is neither polarized nor unpolarized, but in fact a spiral Spin Density Wave state.



- It is generally believed by many-body theorists that correlation effects beyond HF destroy the stability of the SDW and it ceases to be the ground state. Performing a QMC calculation with an SDW state could resolve that question.
- Aim is to obtain a description of the SDW spectrum, at least in the long-wavelength limit.
- If we can obtain a set of energies for different amplitudes and wavelengths of the SDW, we can potentially parameterize a new E_{xc} functional for non-collinear DFT, that could include effects of changes in magnetization direction.
- It should be possible to create for example a local approximation

$$E_{xc} = \int d\mathbf{r} \epsilon_{xc}(n(\mathbf{r}), |\mathbf{m}(\mathbf{r})|, \nabla|\mathbf{m}(\mathbf{r})|, \mathbf{q}(\mathbf{r})),$$

where \mathbf{q} would be a local wavevector representing the rate of change in magnetization direction.

Trial wavefunction for SDW state

- A good starting point might be Overhauser's solution to the Hartree-Fock problem. Use spinors of the form

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}}(\cos\theta_k\alpha + \sin\theta_k e^{i\mathbf{q}\cdot\mathbf{r}}\beta),$$

where Overhauser found the functions θ_k by solving the self-consistent HF equations.

- When put inside a determinant, these orbitals give rise to a spiral spin density wave. The perpendicular component of the magnetization density obeys

$$\mathbf{P} = P(\cos(\mathbf{q}\cdot\mathbf{r})\hat{\mathbf{x}} + \sin(\mathbf{q}\cdot\mathbf{r})\hat{\mathbf{y}}),$$

with

$$P \propto \int d\mathbf{k} \sin(2\theta_k)$$

when \mathbf{q} points along the z-direction.

- We can therefore hope to fix both the amplitude and wavevector of the resulting spin density wave, and calculate the energy of such a state.

Conclusion

- In DFT, it takes a lot of effort to go beyond local approximations and deal with non-collinear spin in a manner that is suitable for describing non-local correlations.
- At the level of VMC at least, QMC provides a straightforward method for treating arbitrary spin configuration.
- Results of QMC calculations can potentially aid in the development of useful DFT functionals.
- QMC calculations of non-collinear spin configurations could by themselves yield interesting and useful results.
- The treatment of non-collinear spins in QMC is a whole new exciting area which is yet to be explored.