QMC study of electron-hole systems

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The quantum Monte Carlo method can determine the total energy of an assembly of quantum particles to a high degree of accuracy.

- In variational Monte Carlo (VMC), a trial wave function $\Psi_T(R)$ is used to evaluate an upper bound to the exact ground-state energy $E_0$.

$$E_{VMC} = \sum_{i=1}^{M} \frac{\hat{H}(R_i)\Psi_T(R_i)}{\Psi_T(R_i)} \simeq \int |\Psi_T(R)|^2 \frac{\hat{H}(R)\Psi_T(R)}{\Psi_T(R)} dR \geq E_0$$

- In diffusion Monte Carlo (DMC), imaginary-time propagation is used to project out the higher-energy components of $\Psi_T(R)$.

- For fermions, the fixed-node approximation is required. It is equivalent to constraining the nodal surface of the DMC wave function to equal that of $\Psi_T(R)$.
The following are typical fermionic trial wave functions:

- $\Psi_T(R) = \Psi_S(R)$  
  \((Slater or Hartree-Fock type)\)
  where $\Psi_S(R)$ is a Slater determinant (or a multi-determinant expansion) of suitable one-particle orbitals. With a single determinant, there are **no correlation effects**.

- $\Psi_T(R) = e^{J(R)} \Psi_S(R)$  
  \((Slater-Jastrow type)\)
  where $e^{J(R)}$ is a Jastrow correlation factor containing optimizable parameters.

- $\Psi_T(R) = e^{J(R)} \Psi_S[X(R)]$  
  \((Slater-Jastrow-backflow type)\)
  where $X(R)$ is a set of collective coordinates containing optimizable parameters.
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Key points:

- The quality of $\Psi_T(\mathbf{R})$, and in particular of its nodal surface, is paramount for the accuracy of the results.

- The Jastrow factor is the most important tool to improve upon $\Psi_S(\mathbf{R})$, but it does not change its nodes.

- There are ways to modify the nodal surface of $\Psi_S(\mathbf{R})$: orbital optimization, backflow transformations, multideterminant expansions, multi-Pfaffian wfn, etc. This is a very active area of research.
The electron-hole system is a model for excited semiconductors.

It is the simplest model system after the homogeneous electron gas, yet its phase diagram remains largely unknown.

Some electron-hole systems, such as the two-dimensional bilayer, can be recreated experimentally and display very interesting properties.

The aim of this work is to determine the phase diagram of electron-hole systems using QMC, to a greater degree of accuracy than previous studies.
Previous QMC studies have made use of the following scheme:

- Plane-wave orbitals
- Pairing orbitals
- Localized orbitals

QMC

Energy of fluid phase

Energy of excitonic phase

Energy of crystalline phase

Comparison gives relative stability

"Nodal argument": different orbitals give different nodes give different energies. Hence there is a correspondence between phase/orbitals (input) and energies (output).
However, in the limit of a perfect wave function:
An appropriate approach is:

Geometry → Wfn. capable of describing all 3 phases → QMC → Energy → Phase

And on the plus side, this requires fewer calculations.
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The wave functions are formed using products of Slater determinants:

\[ D[\phi] = \begin{vmatrix}
\phi_{11} & \phi_{12} & \ldots & \phi_{1N} \\
\phi_{21} & \phi_{22} & \ldots & \phi_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
\phi_{N1} & \phi_{N2} & \ldots & \phi_{NN}
\end{vmatrix} \]

with:

**Pairing:**
\[ \phi_{ij} = \phi_L(e_i - h_j) \]

**Fluid:**
\[ \phi_{ij} = e^{ik \cdot r_i} \]

**Crystal:**
\[ \phi_{ij} = \phi_C(r_i - R_j) \]

\[ \Psi_S = D_{e\uparrow h\downarrow} D_{e\downarrow h\uparrow} \]

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- **Fluid:**
  \[ \phi_{ij} = \sum_{l=0}^{N} c_l e^{i k_i (e_i - h_j)} \]
  \[ \Psi_S = D_{e\uparrow h\downarrow} D_{e\downarrow h\uparrow} \]

- **Crystal:**
  \[ \phi_{ij} = \phi_C(r_i - R_j) \]
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with:

Pairing:

\[ \phi_{ij} = \sum_{p=0}^{P} c_p e^{i k_p \cdot (r_i - r_j)} + \phi_L(e_i - h_j) \]

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Fluid, $E=-0.17879(3)$ a.u.

Exponential, $E=-0.18937(3)$ a.u.

Exponential+PWs, $E=-0.18979(3)$ a.u.
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Is the “nodal argument” reliable?

$r_s = 5, d = 1$
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VMC results [variance minimization]
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VMC results [energy minimization]
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BF-VMC results [energy minimization]
Improving the wave functions brings the energies closer together. Can the phase still be identified?

BF-VMC results [energy minimization]
The asymptotic behaviour of the two-body density matrix can be used to determine the phase:

\[
\rho^{(2)\text{TR}}_{\alpha\beta}(r)
\]

\[
\rho^{(1)\text{TR}}_{\alpha}(r)
\]

\[
\rho^{(1)\text{TR}}_{\beta}(r)
\]
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How about the crystalline phase?

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with:

Pairing:

$$\phi_{ij} = \sum_{p=0}^{P} c_p e^{i \mathbf{k}_p \cdot (\mathbf{r}_i - \mathbf{r}_j)} + \phi_L(\mathbf{e}_i - \mathbf{h}_j)$$

Fluid:

$$\phi_{ij} = \phi_C(\mathbf{r}_i - \mathbf{R}_j)$$

Crystal:

$$\Psi_S = D_{e\uparrow e\downarrow} D_{e\downarrow e\uparrow}$$

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  \[ \psi_{ij} = \sum_{q=0}^{Q} d_q e^{i k_q \cdot (r_i - R_j)} + \phi_C(r_i - R_j) \]

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  \]
- **Crystal:**
  \[
  \Gamma_{ij} = \phi(e_i, h_j) + \sum_{l=0}^{L} \psi(e_i - R_l) \psi(h_j - R_l)
  \]

\[
\Psi_S = D_{e \uparrow h \downarrow} D_{e \downarrow h \uparrow}
\]
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Conclusions and further work:

- Improvements over previous QMC calculations are possible. Need a different approach involving:
  - More general wave functions.
  - Expectation values of density-matrix related objects.
- Robust wave-function optimization is a key element to get results efficiently.
- Real test: compare against experiment.