Configuration interactionによるQMC全エネルギーの改善

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First-principles study

Difficulty of many body problem \( \leftarrow \) evaluation of correlation energy

\[
\frac{e^2}{|r - r'|}
\]

DFT

- Using *model XC potential*, solve as an one-body problem.
- Relatively fast
- Order(N) sometimes

Diffusion Monte Carlo

- Correlation energy, more than 90%
  \( \sim N^{3.5} \)
- Parallel, almost 100%
- *time: 1000 folds more than DFT*
- Little ambiguity, prediction without exp.
Correlated wavefunction, $\Psi$

$$\Psi = e^J \Phi$$

- $\Phi$: CISD, MC, CAS, Pfaffian (extension of Slater Determinant), ...
  usually carried out mechanically as a study of optimization algorithm.

- J: Jastrow factor (mainly electron electron repulsion)

- Few precedent. One must study how good/bad, and its accuracy
Nodes of correlated wavefunctions

3D harmonic well, unpolarized interacting Fermion

fill space with + and -

Too symmetric -> higher energy

O atom, nodes

Spin polarized

\( \Psi(r_1, r_2, \ldots, r_N) \)

Single Slater  Multi Pfaffian  CI

(Jastrow factor doesn’t change nodal structure.)

M. Bajdich, et al., PRL 96, 130201 (2006) and his thesis
Mn atom

• Mn: \((3d)^5(4s)^2\), ferromagnetic
• \(\text{Mn}_2\): \(r_e \approx 3.5\text{Å}\), a van der Waals molecule

Problems:
any good choice of configuration space?
convergence properties

– Li, Be: near degeneracy problem, \(E_{2s} \sim E_{2p}\)
~97% correlation energy for ~20 configuration

– Mn: \(E_{4s}, E_{4p}\) ? , f?
Calculations

$$\Psi = e^{-J \sum_{n_{\text{det}}} c_i \Phi_i}$$

$$\Phi_i = |\phi_i(r)|$$
Mn Cl/26(+s,p,d,f)

\[ \Psi = \Phi \]

\[ \Psi = e^J \Phi \]

\[ \Psi = \sum c_i \Phi_i \quad c_i: \text{CISD} \]