B13 Investigation of spin systems via *ab initio* Quantum Monte Carlo and perturbation theory

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Ab initio Quantum Monte Carlo

- General flow-chart of *ab initio* QMC

DFT → $D(\vec{R})$ Slater determinant (defines nodes) → VMC → $J(\vec{R})$ Jastrow factors → DMC → $\Phi_0(\vec{R})$ Ground state WF

- Trial WF [defines the nodal structure (zeros) of the target GS WF $\Phi_0(\vec{R})$]:

$$\Psi_T(\vec{R}) = e^{J(\vec{R})} D^{\uparrow}(\vec{r}_1,\ldots,\vec{r}_{N_\uparrow}) D^{\downarrow}(\vec{r}_{N_\uparrow+1},\ldots,\vec{r}_N), \quad \vec{R} = (\vec{r}_1,\ldots,\vec{r}_N)$$

All electrons' coordinates

- **Step 1**: Variational Monte Carlo (VMC)

$$E_0 \le E(J) = \int |\Psi_T(\vec{R},J)|^2 \frac{H\Psi_T(\vec{R},J)}{\Psi_T(\vec{R},J)} d\vec{R}$$

✓ Vary *J* to minimize *E*

✓ Since $|\Psi_T(\vec{R},J)|^2$ acts as a probability distribution function, evaluate the integral by using Markov chain Monte Carlo

- **Step 2**: Diffusion Monte Carlo (DMC)

$$-\partial_\tau \Phi(\vec{R},\tau) = (H - E_\Phi)\Phi(\vec{R},\tau)$$ Schrödinger equation in imaginary time τ

$$\Phi_0(\vec{R}) = \lim_{\tau\to\infty} \int G(\vec{R} \leftarrow \vec{R}_0,\tau)\Psi_T(\vec{R}_0) d\vec{R}_0$$ Integral form

Discretization in imaginary time

$$\Phi_0(\vec{R}) = \lim_{\substack{\Delta\tau\to 0 \\ n\to\infty}} \int G(\vec{R} \leftarrow \vec{R}_n,\Delta\tau)\ldots G(\vec{R}_1 \leftarrow \vec{R}_0,\Delta\tau)\Psi_T(\vec{R}_0) d\vec{R}_0 \ldots d\vec{R}_n$$

✓ Each application of *G* is interpreted as a stochastic process; propagation through *G* can be viewed as „diffusion" of Monte Carlo walkers (sequences of $\vec{R}$)

✓ The Green's function

$$G(\vec{R} \leftarrow \vec{R}',\Delta\tau) = \left\langle R \left| e^{-\Delta\tau(H-E_T)} \right| R' \right\rangle$$

can be easily evaluated in the limit $\Delta\tau \to 0$; E_T is some adjustable off-set energy

- **Fixed-node** approximation: To avoid the fermionic sign problem, the positive function

$$f(\vec{R},\tau) = \Phi(\vec{R},\tau)\Psi_T(\vec{R})$$

is being propagated instead:

✓ Walkers are not allowed to cross nodes

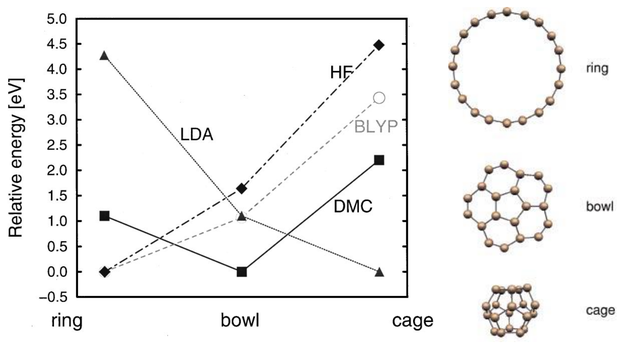
✓ The trial function serves as a *guiding function*

✓ The GS energy E_0 is then calculated as

$$E_0 = \lim_{\tau\to\infty} \frac{\int f(\vec{R},\tau)\Psi_T^{-1}(\vec{R})H\Psi_T(\vec{R})d\vec{R}}{\int f(\vec{R},\tau)d\vec{R}} = \lim_{\tau\to\infty} \frac{\int f(\vec{R},\tau)E_L(\vec{R})d\vec{R}}{\int f(\vec{R},\tau)d\vec{R}} \approx \frac{1}{M}\sum_m E_L(\vec{R}_m)$$

where $\{\vec{R}_m\}$ is the set of *M* samples of $f(\vec{R},\infty)$ resulting from the DMC run.

- Example from literature (C_{20} isomers)



Only DMC gives qualitative agreement with experiment on the most stable C_{20} isomer!

Grossman *et al.*, PRL **74**, 1323 (95)

Rayleigh-Schrödinger scheme

- Starting point: Hubbard Hamiltonian

$$H^{\text{Hub}} = \underbrace{\sum_{<i,l>\sigma} t_{pd} d^+_{i\sigma} p_{l\sigma} + \sum_{<l,n>\sigma} t_{pp} p^+_{l\sigma} p_{n\sigma}}_{H_1} + \underbrace{\sum_{i\sigma} \varepsilon_d d^+_{i\sigma} d_{i\sigma} + \sum_{l\sigma} (\varepsilon_d + \Delta) p^+_{l\sigma} p_{l\sigma} + U_d \sum_i d^+_{i\uparrow} d_{i\uparrow} d^+_{i\downarrow} d_{i\downarrow} + U_p \sum_l p^+_{l\uparrow} p_{l\uparrow} p^+_{l\downarrow} p_{l\downarrow}}_{H_0}$$

- Definitions:

TM	Transition metal
ε_d	TM on-site energy
Δ	Charge-transfer energy
$d^+_{i\sigma}, p^+_{l\sigma}$	Creation operators of a hole on a TM site and a ligand site
t_{pd}, t_{pp}	Electron hopping amplitudes
U_d	On-site repulsion on a TM site
U_p	On-site repulsion on a ligand site
H_0, H_1	Unperturbed part and perturbation
ϕ_0, E_0	Ground state WF and energy of H_0
P	Projector on ϕ_0
R	$= (1-P)/(E_0 - H_0)$

- Effective Hamiltonian:

$$H_{eff} = E_0 P + PH_1RH_1P + PH_1RH_1RH_1P + \underbrace{PH_1RH_1RH_1RH_1P}_{4^{\text{th}}\text{ order spin exchange}} + \underbrace{PH_1RH_1RH_1RH_1RH_1P}_{5^{\text{th}}\text{ order spin exchange}} + \cdots$$

- Advantages
  - ✓Efficient, expecially for evaluating interactions with phonons (avoids lengthy *ab initio* calculations)
  - ✓ Flexible (accuracy is controlled by the expansion order, number of parameters, *etc.*)
  - ✓ Model parameters are provided by *ab initio* calculations and Harrison's equations

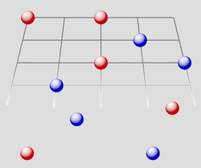
Techniques/Codes and Staffing

Techniques/Codes

Ab initio DFT	Codes: Wien2k, FPLO, FLEUR, VASP, Quantum Espresso Functionals: LDA, LDA+U, hybrid (B3LYP, HSE)
Ab initio QMC	QMCPACK (VMC, DMC, Hartree-Fock for atoms)
Pseudopotentials	OPIUM, VASP data base
Wannier functions	Wannier90 (maximally localized WF), projected symmetry-preserving WF, FLEUR (RPA)
Quantum chemistry	ORCA, TURBOMOLE

Staffing of the project from auxiliary support

N.N. (Ph.D. student)
- performance of perturbation theory calculations
- DFT calculations
- selected *ab initio* QMC calculations



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