Ab initio quantum Monte Carlo for strongly correlated systems

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Office of



Understanding & design of materials

Very accurate quantum simulations

Deriving effective low energy models

First principles quantum Monte Carlo Why we need accurate quantum simulations to understand quantum materials

A model of modeling

- f Effect in material
- x Calculated property

Our model:
$$f(x) = ax + c\chi$$

 χ Confounding factors/inaccuracies

Bayesian approach

 $p(a, c | \text{observations}) = p(\text{observations} | a, c) \frac{p(a, c)}{p(\text{observations})}$ $\prod_{i=1}^{n} \frac{1}{\sqrt{2\pi c}} \exp\left[\frac{(o_i - ax_i)^2}{2c^2}\right]$ Prior knowledge: 'physical values'

<u>Inferring values for theory</u>

<u>Adding an extra parameter</u>

 $f(x) = ax + b + c\chi$

More data —

(c=0.2)

Stability of prospective materials

False positive: P(not stable|DFT says stable)

False negative: *P*(stable|DFT says not stable)

Can be conservative and miss things **or** be thorough.

Narayan, Bhutani, Rubeck, Eckstein, Shoemaker, Wagner arXiv:1512.02214

Summary

To make inferences about descriptions of materials, we trade off:

- 1) Number of experiments
- 2) Number of plausible models
- 3) Parameters in models

Quantum/strongly correlated materials are often on the bad side of all these.

Higher accuracy calculations can reduce the number of parameters and plausible models.

First principles quantum Monte Carlo

First principles

Low energy eigenfunctions of

Variational Monte Carlo

$$\Psi(r_1, r_2, r_3, \ldots) = \exp(U) Det^{\uparrow} Det^{\downarrow}$$

$$U = \sum_{ij} f(r_i, r_j, \mathbf{r_i - r_j})$$

$$\langle E(\mathbf{P}) \rangle = \frac{\int \Psi^*(\mathbf{R}, \mathbf{P}) \hat{H} \Psi(\mathbf{R}, \mathbf{P}) d\mathbf{R}}{\int |\Psi(\mathbf{R}, \mathbf{P})|^2 d\mathbf{R}}$$

Use Monte Carlo to evaluate highdimensional integral

r_{ij}

Fumenal, Droghetti, Sanvito, Wagner (in preparation)

Diffusion Monte Carlo

Fixed node

Upper bound to ground state energy

$$\lim_{\tau \to \infty} e^{-H\tau} |\Psi_T\rangle$$

Isomorphism to stochastic process

Kinetic energy is diffusion, potential energy is birth/ death.

Realistic systems

Sample 1,000,000... get energy and other observables

Better wave functions: just need to calculate $\Psi(R), \nabla \Psi(R), \nabla^2 \Psi(R)$

Algorithms are very similar to Ceperley & Alder. PRL **45** 566 (1980)

Reynolds et al. JCP **77** 443766 (1983) Mitáš, et al. JCP 95 3467 (1991) Foulkes et al. RMP 73 33 (2001) Umrigar et al. PRL 98 110201 (2007)

Direct measurement of correlations

$$S(\mathbf{q}) = \frac{1}{N} \sum_{ij} \langle \exp\left[i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)\right] \rangle$$

Long-range density-density correlations in graphene

Huihuo Zheng, Yu Gan, P. Abbamonte, L.K.W. (in preparation)

Difference in Coulomb energy: ~1.5 eV/electron

Huihuo Zheng

Special for transition metal systems

PRB 92 235209 (2015)

Adjusts the amount of density on the TM versus oxygen atom.

Use hybrid functional to generate orbitals

Take lowest energy nodal surface

 $Ca_2CuO_2Cl_2$

Overall performance: gaps

 $e^{J}|\Psi_{T,\mathrm{ex}}\rangle = e^{J}c_{\mathrm{cbm}}^{\dagger}c_{\mathrm{vbm}}|\Psi_{T,\mathrm{gs}}\rangle$

Dependent on double occupancy cost ('U') and difference between p and d levels.

Wagner. PRB **92** 16116 (2015) Schiller, Wagner, Ertekin. arXiv:1509.08321 [cond-mat] (Phys. Rev. B in press) Yu, Wagner, Ertekin. arXiv:1509.04114 [cond-mat] (J. Chem. Phys. in press)

VO₂: metal-insulator transition

Metal-insulator transition Magnetic transition

First order

Huihuo Zheng

Kawakubo & Nakagawa J. Phys. Soc. Japan. **19** 517 (1964)

<u>Structure</u>

Cartoon explanations

Formation of dimers is major effect.

MIT is a function of structure

Peierls

Formation of dimers is secondary

MIT is a correlated 'traffic jam' effect

Mott

DFT: a zoo of functionals

LDA: no insulator!

Wentzcovitch, Schulz, Allen Phys. Rev. Lett. **72** 3389 Liebsch, Ishida, Bihlmayer Phys. Rev. B **71** 085109

LDA+U: depends sensitively on U (0.1 eV)

TABLE I. Band gaps obtained from HSE calculations of VO_2 phases in different magnetic configurations. Experimental values are from Refs. 19 and 21.

		E_g		
	NM	FM	AFM	Exp.
<i>M</i> 1	0.98	1.35	2.23	0.6-0.8
R	0	1.43	1.82	0

Hybrid: no metal!

Grau-Crespo, Wang & Schwingenschlögl. Phys. Rev. B 86, 081101 (2012).

<u>DFT+DMFT</u>

Dynamical Singlets and Correlation-Assisted Peierls Transition in VO₂

S. Biermann,^{1,2} A. Poteryaev,^{3,1} A. I. Lichtenstein,⁴ and A. Georges^{1,2}

Our results were obtained for a specific choice of the interaction parameters U = 4 eV and J = 0.68 eV. We have actually performed calculations for other choices and found that it is possible to stabilize an insulating state within C-DMFT for smaller values of U (e.g., U = 2 eV), but only if the Hund coupling J is taken to be small (in which case it is easier to redistribute the charge towards the

PRL 94, 026404 (2005)

Metal-insulator transition due to spin singlets

But

Magnetic susceptibility not explained

Need cluster DMFT

Parameters must be adjusted

Still an ongoing discussion: arXiv:1509.02968v2

<u>Setting up QMC</u>

Basic ground state properties:

- ·Local moments always exist
- Rutile is very weak AFM
- \cdot Monoclinic has tightly bound dimers.

Zheng & Wagner Phys. Rev. Lett. **114** 176401 (2015)

Optical excitation properties

Rutile: always zero gap

Monoclinic: gap when we allow for spins

Zheng & Wagner Phys. Rev. Lett. **114** 176401 (2015)

Magnetic properties

Zheng & Wagner Phys. Rev. Lett. **114** 176401 (2015)

Hopping or correlation?

Spin densitySpin densityCharge density3D[110][110]

Big change is in the intra-chain coupling

Zheng & Wagner Phys. Rev. Lett. **114** 176401 (2015)

Cartoon picture of VO₂

Charge delocalized Weak magnetic couplings

Large charge rearrangement Spin dimers: gap ~150 meV Charge dimers

Spin-Peierls like, explains both magnetic susceptibility and metal-insulator transition

Prediction

Spin flip transition:

k-independent excitation at 126(6) meV in inelastic neutrons

Some other applications

Water on boron nitride Wu, Aluru, Wagner J. Chem. Phys. **142**, 234702 (2015) & under review Al-Hamdani, Ma, Alfè, Lilienfeld & Michaelides J. Chem. Phys. **142**, 181101 (2015).

Pressure dependence of magnetic energies in FeSe Busemeyer, Dagrada, Sorella, Casula, Wagner arXiv:1602.02054 [cond-mat]

Magneto-phonon coupling Wagner, Abbamonte PRB **90** 125129 (2014)

Holes in high-Tc cuprates Wagner PRB **92** 161116(R) (2015)

Summary: towards higher accuracy

With one method, benchmark quality accuracy

Rigorous: understand causes of errors and how to fix them (in principle!)

Can simplify theory!

Deriving effective models: description of low-energy physics

Downfolding

Big Hilbert space

Small Hilbert space **Objective:** Hamiltonian in small Hilbert space

• Genomic fingerprint

- \cdot Larger scale simulations
- First step of renormalization analysis

$$\begin{split} |\Psi_{fp}\rangle \sim |\Psi_{m}\rangle \implies \\ \langle \Psi_{fp} | c_{i}^{\dagger} c_{j}^{\dagger} c_{k} c_{l} | \Psi_{fp}\rangle = \langle \Psi_{m} | c_{i}^{\dagger} c_{j}^{\dagger} c_{k} c_{l} | \Psi_{m}\rangle, \\ \forall i, j, k, l \\ \end{split}$$

Hitesh Changlani

Energy fitting algorithm

Require
$$\langle \Psi_{fp} | H_{fp} | \Psi_{fp} \rangle = \langle \Psi_m | H_m | \Psi_m \rangle$$

$$\langle \Psi_m | H_m | \Psi_m \rangle = \sum_{ij} t_{ij} \langle \Psi_m | c_i^{\dagger} c_j | \Psi_m \rangle + \sum_{ijkl} V_{ijkl} \langle \Psi_m | c_i^{\dagger} c_j^{\dagger} c_k c_l | \Psi_m \rangle$$

$$\langle \Psi_{fp} | c_i^{\dagger} c_j^{\dagger} c_k c_l | \Psi_{fp} \rangle = \langle \Psi_m | c_i^{\dagger} c_j^{\dagger} c_k c_l | \Psi_m \rangle$$

$$\langle \Psi_{fp} | H_{fp} | \Psi_{fp} \rangle = \sum_{ij} t_{ij} \langle \Psi_{fp} | c_i^{\dagger} c_j | \Psi_{fp} \rangle + \sum_{ijkl} V_{ijkl} \langle \Psi_{fp} | c_i^{\dagger} c_j^{\dagger} c_k c_l | \Psi_{fp} \rangle$$

The algorithm

$$\langle \Psi_{fp} | H_{fp} | \Psi_{fp} \rangle = \sum_{ij} t_{ij} \langle \Psi_{fp} | c_i^{\dagger} c_j | \Psi_{fp} \rangle + \sum_{ijkl} V_{ijkl} \langle \Psi_{fp} | c_i^{\dagger} c_j^{\dagger} c_k c_l | \Psi_{fp} \rangle$$

Compute using QMC techniques

Fit to QMC data

First principles wave functions must be in the low energy subspace

Does not matter if they are eigenfunctions

Similarity to fitting classical model

Can fit a potential even without finding the lowest energy

In QM, coordinates become density matrices

QMC gets us close to the ground state

Changlani, Zheng, Wagner. J. Chem. Phys. **143**, 102814 (2015)

Changlani, Zheng, Wagner. J. Chem. Phys. **143**, 102814 (2015)

More matrix elements

Subtracting electron

$$K_{ij}^{v} = \langle c_{i}^{\dagger}[c_{j}, H] \rangle$$

= $\sum_{n} \epsilon_{j,n} \langle c_{i}^{\dagger}c_{n} \rangle$ One body
+ $\sum_{nop} (V_{jnop} - V_{njop}) \langle c_{i}^{\dagger}c_{n}^{\dagger}c_{o}c_{p} \rangle$
Two body

N² linear equations per wave function

O(1) cost over regular QMC

All gets renormalized and screened by QMC process

Adding electron

$$K_{ij}^{c} = \langle c_{i}[H, c_{j}^{\dagger}] \rangle$$

= $\epsilon_{ij} - \sum_{m} \epsilon_{mj} \langle c_{m}^{\dagger} c_{i} \rangle$ One body
+ $\sum_{mo} 2(V_{imoj} - V_{mioj}) \langle c_{m}^{\dagger} c_{o} \rangle$ 'Hartree' interaction
+ $\sum_{mno} (V_{mnoj} - V_{mnjo}) \langle c_{m}^{\dagger} c_{n}^{\dagger} c_{i} c_{o} \rangle$
Two body

Simple example: H₂ molecule

Questions: what are *t* and *U* as a function of r?

				C	C.	$C \tau \tau$	$K^{v/c}$
channel	spin	i	j	c_ϵ	c_t	c_U	i i j
valence	up	0	0	0.476544	0.472914	0.113752	-0.336855
valence	down	0	0	0.477404	0.472732	0.113752	-0.337076
conduction	up	0	0	0.523456	-0.472914	0.363652	0.374592
conduction	down	0	0	0.522596	-0.472732	0.362792	0.374550
valence	up	0	1	0.472914	0.476544	0.112334	-0.329039
valence	down	0	1	0.472732	0.477404	0.112475	-0.328964
conduction	up	0	1	-0.472914	0.523456	-0.112475	-0.316596
conduction	down	0	1	-0.472732	0.522596	-0.112334	-0.316811
valence	up	1	0	0.472914	0.475849	0.112886	-0.329039
valence	down	1	0	0.472732	0.475073	0.112639	-0.328964
conduction	up	1	0	-0.472914	0.524151	-0.112639	-0.317746
conduction	down	1	0	-0.472732	0.524927	-0.112886	-0.317898
valence	up	1	1	0.475849	0.472914	0.113032	-0.336167
valence	down	1	1	0.475073	0.472732	0.113032	-0.335719
conduction	up	1	1	0.524151	-0.472914	0.362041	0.373517
conduction	down	1	1	0.524927	-0.472732	0.362818	0.374043

 $K_{ij}^{v/c} = c_{\epsilon}\epsilon + c_t t + c_U U$

RMS deviations

distance in Bohr (0.5 angstroms) U/t in Hartree

Better fits for larger r

 $\epsilon = -13.6 \text{ eV}$

Proof of concept: 3-band model of Ca₂CuO₂Cl₂

56 atom unit cell Optimized minimal basis Slater-Jastrow wave function

1 QMC calculation: 2304 data points

Minimal preliminary model:

ed	-15.2(3)
ep	-6.25(7)
Ud	7.6(1)
Up	1.71(3)
t _{pd}	-2.64(5)
t _{pp}	-1.79(3)

RMS errors ~0.7 eV

Summary

Clean model derivation: one- and two-body terms on same footing.

r=2

r =

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Backup slides

Energetics of different magnetic orderings

PRB **92** 161116(R) (2015)

Emery and Reiter. PRB 4547 (1988) Nagaev. J. Exp. Theor. Phys. Lett. 74 431 (2001)

Reference state for 3-band downfolding

No doping, AFM order

1/8 doping, spin polaron (ground state in QMC)

Spin

<u>3-band basis</u>

Basis:

- $\cdot Lowdin \ orthogonalize \ AO \ basis$
- Compute 1-RDM in e.g. O px basis
- ·Diagonalize 1-RDM in subspace

FeSe Selenium height

<u>FeSe P(V)</u>

Checkerboard would be insulating

<u>Comparison of S(q) for different methods</u> (graphene)

