Numerical Methods for Correlated Electron Systems

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and
The Simons Foundation

Support: DOE ER-046169 and NSF DMR 13086282
The Flatiron Institute of the Simons Foundation

Mission: computationally oriented research in the physical and life sciences

When fully established:
- 250 staff members
- 4 scientific units + computational core
- Now open for business
  - CCA (Astronomy) 2016
  - CCB (Life Sciences) 2015
  - and...

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Center for Computational Quantum Physics (CCQ)

Director: Antoine Georges

Antoine Georges to Lead New Center for Computational Quantum Physics
January 8, 2017

The Simons Foundation is delighted to announce the formation of the Center for Computational Quantum Physics (CCQ), in the foundation’s new Flatiron Institute, and the appointment of Antoine Georges as its director.

A new era is dawning in our ability to understand and control the behavior of materials and molecules. The CCQ will develop the concepts, algorithms and computational tools needed to handle many-body quantum systems and capture the quantum dynamics of electrons and ions in chemically realistic environments and make them available to the scientific community. The center will also host a lively array of meetings, workshops and conferences, serving as a focal point for computational materials science internationally. At full strength, the center is expected to comprise up to 60 scientific and support personnel, including both junior and senior positions, as well as sabbatical and summer visitors.

Antoine Georges holds the chair in condensed matter physics at the Collège de France and is also professor of physics at the École Polytechnique and at the University of Geneva. His work has been recognized by numerous fellowships and awards, including the André and Suzanne Abragam Prize of the French Academy of Sciences, the 2004 Prix Dragales, the 2006 Condensed Matter Europhysics Prize, the 2007 Médaille d’Argent of the CNRS, a 2012 Synergy award from the European Research Council and the 2014 Hamburg Prize for Theoretical Physics. He is a member of the French Academy of Sciences.

Andrew Mills, professor of physics at Columbia University, will serve as co-director of the CCQ.

Mission: concepts, theory, algorithms, codes and comparison to experiment for chemistry, condensed matter physics, materials science….

Official Start: 9/1/2017

co-Director: AJM

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CCQ is now recruiting postdocs

Look for Flatiron Research Fellow CCQ on

https://simonsfoundation.wd1.myworkdayjobs.com/simonsfoundationcareers

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Define "strong correlations":

electron propagation

Electron Spectral function $A(k,\omega)$

Fig. 3, Damascelli, Hussain and Shen RMP 75 473 (2003)
Alternative definition: wave function

\[ \mathbf{A}(k, \omega) = \text{Im} \left[ G^R(k, \omega) \right] = \sum_m < GS | \psi_k | \Psi^m_{N+1} > < \Psi^m_{N+1} | \psi_k^\dagger | GS > \delta(\omega - E^m_{N+1}) \]

\[ + \sum_m < GS | \psi_k^\dagger | \Psi^m_{N-1} > < \Psi^m_{N-1} | \psi_k | GS > \delta(\omega - E^m_{N-1}) \]

If ground state is close to single Slater Determinant

\[ |GS\rangle = \text{Det} \begin{bmatrix}
\phi_{k_1}(x_1) & \phi_{k_2}(x_1) & \phi_{k_3}(x_1) & \cdots \\
\phi_{k_1}(x_2) & \phi_{k_2}(x_2) & \phi_{k_3}(x_2) & \cdots \\
\phi_{k_1}(x_3) & \phi_{k_2}(x_3) & \phi_{k_3}(x_3) & \cdots \\
\phi_{k_1}(x_4) & \phi_{k_2}(x_4) & \phi_{k_3}(x_4) & \cdots \\
\vdots & \vdots & \vdots & \ddots 
\end{bmatrix} \]

Spectral function is close to delta-function
``Strong correlation”

\[ \Rightarrow \]

Multireference

\[ |\text{GS}\rangle = a_1 \text{Det1} + a_2 \text{Det2} + \ldots \]

If ``very many” “very different” determinants are involved, correlations are ``strong”

Notice: 2 related but conceptually different issues

• Ground state
• Excitation

some methods optimized for ground states, others aimed at excitations
Approximately free electrons:  
— Coulomb interaction (long range)

\[ H[Ry] = -\frac{1}{r_s^2} \sum_i \nabla u_i^2 + \frac{1}{r_s} \sum_{i \neq j} \frac{1}{|\vec{u}_i - \vec{u}_j|} \]

\( r_s \sim \) inter-electron spacing in units of bohr radius.

Small \( r_s \) (high density) \( \iff \) weak correlations because Coulomb interaction is well screened

Graphene (and cousins): important special case
Coulomb physics

- Perturbation theory (RPA): $r_S \sim 1$
- Typical wide-band metals: $r_S \sim 2-6$
- Wigner crystal $r_S \sim 30-80$ (dimension)

Hartree term fixes charge distribution.
Exchange terms control fluctuations about this.
Taxonomy of correlation: II

Partially filled, relatively localized (tight-binding-like) orbitals
* transition metals and their oxides (and sulfides and calcogenides): transition metal d shell
* rare earth and actinide materials (f shell)
* organics (effective orbital)


*Key role of intra-orbital interactions
* Certain atomic configurations suppressed
Taxonomy of correlation: IIa

Mott-Hubbard.

— ‘Coulomb blockade’ (some charge configurations suppressed)
— importance of ‘new’ degree of freedom (here, spin)
— near commensurability of electron and lattice densities=> ‘jamming”

Model ‘Hubbard’ Hamiltonian:

\[ H = - \sum_{ij} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]
Charge Transfer Insulators

$2d^n \rightarrow d^{n-1}d^{n+1}$ not the only process. Ligands also important.

Fragment of CuO$_2$ plane

Cuprates:

$$2d^9 \rightarrow d^8d^{10} \quad 8\text{eV}$$

$$2d^9 \rightarrow d^9Op^5d^{10} \quad 2\text{eV}$$

ZSA Phase Diagram

many 3d TMO (cuprates, ferrites, manganites…)

Nickelates

4d, 5d TMO (ruthenate, irridates…) also organics
Open questions:

- how much of the correlation physics of the ligand ions do we need to know
- does an effective low energy model suffice?

Open question: in this physics, ligand to transition metal charge fluctuations are important. Do we need to include dynamics of intersite Coulomb physics
Taxonomy of correlation: IIb

‘Hunds Physics’.

—free space: 10-fold degenerate d-level.
—$M$ electrons $\Rightarrow 10!/(\{(10-M)!M!\}$ states
—Ligand field and intra-orbital Coulomb interaction
$\Rightarrow$ some states disfavored.
—Hund’s rule: High spin states preferred $\Rightarrow$ new physics

Rondinelli and Spaldin, Adv. Mater. 23

Werner, Gull, Troyer, Millis PRL 2008
Haule and Kotliar NJP 2009
Georges, deMedici and Mravlje, Ann Rev CMP 2012
Correlated subspace: transition metal d orbitals

\[ H_{\text{one-electron}} = \sum_a E_a c_a^\dagger c_a \]

Interaction: Full multiplet structure of d-shell  
(here written for O(3) symmetry \( t_{2g} \) or \( e_g \))

\[
H = U \sum_a n_a^\uparrow n_a^\downarrow + (U - 2J) \sum_{a>b, \sigma=\uparrow,\downarrow} n_a^\sigma n_b^\sigma \\
+ (U - 3J) \sum_{a\neq b} n_a^\sigma n_b^{\bar{\sigma}} - J \sum_{a\neq b} c_a^\uparrow c_a^\downarrow c_b^\uparrow c_b^\downarrow + c_a^\uparrow c_b^\downarrow c_b^\uparrow c_a^\downarrow
\]

\( U \): screened in solid—
\( J \): close to atomic limit value
Spin Freezing

Georges, deMedici and Mravlje, Ann Rev CMP 2012

H. Dang and AJM, unpub 2014

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Taxonomy of correlation: III

Heavy Fermions

key physics—weakly correlated band coupled to slowly fluctuating local degree of freedom
Taxonomy of correlation: IV

Special cases
— one dimensional systems
— quantized hall states
— impurity models: quantum dots and molecular conductors

....
Impurity model: finite set of correlated orbitals coupled to bath

\[ H_{\text{QI}} = \sum_{ab} d_{a}^{\dagger} E_{\text{QI}}^{ab} d_{b} + \text{Interactions} \]

\[ + \sum_{p,ab} \left( V_{pab}^{p} d_{a}^{\dagger} c_{pb} + H.c \right) + H_{\text{bath}} \left\{ c_{pa}^{\dagger} c_{pa} \right\} \]

Important part of bath: ‘hybridization function’

\[ \Delta_{ab}^{ab}(z) = \sum_{p} V_{ac}^{p} \left( \frac{1}{z - \varepsilon_{p}^{\text{bath}}} \right) V_{cb}^{p,\dagger} \]
Solving impurity models

Typically need $G$ at ‘all’ interesting frequencies computed with uniform accuracy over whole relevant frequency range.

This is challenging.

Challenge is much more severe if

\[ \left[ \hat{\Delta}, \hat{E} \right] \neq 0 \]

i.e. if electron can go off impurity and come back to a different state
What’s the problem?


“The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are known…”

“The difficulty lies only in the fact that these laws lead to equations too complex to be solved.”

“It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed.”
Computational cost

- $M$ atoms per unit cell
- Energy cutoff $\Rightarrow L$ orbitals/atom
- Retain $N$ unit cells

Hilbert Space Dimension

$$= 2^{M \times L \times N}$$

Interaction terms

(4 center integrals)

$$\sim (M \times L)^4 \times N^3$$

$\Rightarrow$ exponential times large power-law prefactor
Fermion sign

*electrons are fermions: wave function is antisymmetric

$$\psi(r_1, \sigma_1; r_2, \sigma_2; \ldots) = -\psi(r_2, \sigma_2; r_1, \sigma_1; \ldots)$$

Quantum mechanics entangles electron coordinates over large distances

=> severe numerical complications
What do you do

Hilbert Space Dimension

\[ = 2^{M \times L \times N} \]

Interactions

\[ \sim (M \times L)^4 \times N^3 \]
What do you do

Hilbert Space Dimension

\[ = 2^{M \times L \times N} \]

Interactions

\[ \sim (M \times L)^4 \times N^3 \]

Avoid the problem: density functional band theory
(numerical task—essentially, invert a large matrix)
OR

Hilbert Space Dimension

\[ = 2^{M \times L \times N} \]

Interactions

\[ \sim (M \times L)^4 \times N^3 \]

- Embedding (analyse only subset of matrix elements)
  - DMFT (or DFT+U)
  - DMET
  - SEET

- Model system (e.g. Hubbard model) =>
  - minimize number of interaction parameters

- Find correct corner of Hilbert Space
  - CI and generalizations
  - DMRG/MPS

- Explore Hilbert space stochastically

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Density functional theory

Two aspects:

• algorithm for ground state energy and density
• statement about (approximation to) ground state wave function and excitations => base for more sophisticated theory
From a formal point of view


DFT as functional of density and conjugate potential

\[
\Phi[\{V^{H-\text{xc}}, \rho\}] = \text{Tr} \left[ \ln \left( \partial_{\tau} - \frac{1}{2} \nabla^2 - V^{\text{ext}}(r) - V^{H-\text{xc}}(r) \right) \right]^{-1}
\]

\[+ \Phi_{\text{HK}}[\{\rho\}] - \int d^3r V^{H-\text{xc}}(r) \rho(r)\]

stationarity:

\[
\frac{\delta \Phi}{\delta V^{H-\text{xc}}} = 0 \Rightarrow \rho(r) = \text{Tr} \left[ \left( \partial_{\tau} - \frac{1}{2} \nabla^2 - V^{\text{ext}} - V^{H-\text{xc}} \right)^{-1} \right]
\]

\[
\frac{\delta \Phi}{\delta \rho} = 0 \Rightarrow V^{H-\text{xc}} = \frac{\delta \Phi_{\text{HK}}}{\delta \rho}
\]
Stationarity with respect to variations of density and $V^{H-\text{xc}}$ yields EXACT ground state energy and electron density if EXACT exchange-correlation potential is known

$$\frac{\delta \Phi_{\text{HK}}(\{\rho\})}{\delta \rho(r)} = V^{H-\text{xc}}(\{\rho\}, r)$$

In practice, exact $V$ not known; approximation is needed

Question: how good is the approximation
Kohn-Sham bands

\[ \frac{\delta \Phi}{\delta V_{H-\text{xc}}} = 0 \Rightarrow \rho(r) = \text{Tr} \left[ \left( \partial_\tau - \frac{1}{2} \nabla^2 - V^{\text{ext}} - V^{H-\text{xc}} \right)^{-1} \right] \]

Evaluating the trace <=> solving a single-particle Schroedinger equation (the "Kohn-Sham equation")

LaTiO\textsubscript{3}

http://dmft.rutgers.edu/LDA/lmto/lmto\_run.htm

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Kohn-Sham bands

\[
\frac{\delta \Phi}{\delta V_{H-\text{xc}}} = 0 \Rightarrow \rho(r) = \text{Tr} \left[ \left( \partial_\tau - \frac{1}{2} \nabla^2 - V^{\text{ext}} - V^{H-\text{xc}} \right)^{-1} \right]
\]

Questions:
— is the single slater-determinant of occupied Kohn-Sham states a good approximation to the ground state wave function
— are the eigenvalues of the Kohn-Sham Hamiltonian good approximations to transition energies
Limitations of DFT

Spin Crossover Molecule

Fe(phen)$_2$(NCS)$_2$

DFT: overestimates energy diff

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Limitations of DFT

Rare earth nickelates: $\text{RNI}_3$

For all R except La: materials are insulating and bond-disproportionated

DFT: does not predict structural distortion for any R
predicts metallic behavior for all R
In experimental structure
DFT predicts metal

H. Park, AJM, and C. Marianetti,
Metallic LaNiO$_3$:
DFT makes quantitative errors in bands


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=> Need beyond DFT method
OR

Hilbert Space
Dimension

\[ = 2^{M \times L \times N} \]

Interactions

\[ \sim (M \times L)^4 \times N^3 \]

• Embedding (analyse only subset of matrix elements)
  – DMFT (or DFT+U)
  – DMET
  – SEET

• Model system (e.g. Hubbard model) =>
  – minimize number of interaction parameters

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+DMFT

See also DMET (self-consistently embedded density matrix)


and SEET (self-energy embedding theory—conceptually DFT +DMFT but (a) NOT built on DFT and (b) not necessarily built on local orbitals
DFT+DMFT now ~20 years old

Proposal: Lichtenstein/Katsnelson late 1990s

Key papers:

• Georges 2004 Windsor notes
• Kotliar et al RMP 2006
• Held and Vollhardt 2006
DFT+DMFT: quad variable functional theory-
DFT plus many-body theory of correlated subspace

\[
\Phi\left[\{V^{H-\text{xc}}, \rho; \Sigma_{\text{corr}}, G_{\text{corr}}\}\right] = \\
\text{Tr} \left[ \ln \left( \partial_\tau - \frac{1}{2} \nabla^2 - V^{\text{ext}}(r) - V^{H-\text{xc}}(r) - P_{\text{corr}} \Sigma_{\text{corr}} P_{\text{corr}} \right)^{-1} \right] \\
+ \Phi_{\text{DFT+DMFT}}[\{G_{\text{corr}}, \rho\}] - \text{Tr} [\Sigma_{\text{corr}} G_{\text{corr}}] - \int d^3r V^{H-\text{xc}}(r) \rho(r)
\]

Stationarity:

\[
\frac{\delta \Phi_{\text{DFT+DMFT}}}{\delta \rho(r)} = V^{H-\text{xc}}(r) \\
\frac{\delta \Phi_{\text{DFT+DMFT}}}{\delta G_{\text{corr}}} = \Sigma_{\text{corr}} \\
\frac{\delta \text{Tr}[\ln]}{\delta V^{H-\text{xc}}(r)} \equiv G(r, r; \tau \to 0^-) = \rho(r) \\
\frac{\delta \text{Tr}[\ln]}{\delta \Sigma_{\text{corr}}} \equiv P_{\text{corr}} G P_{\text{corr}} = G_{\text{corr}}
\]
formally exact
Approximations needed in two places

$$\frac{\delta \Phi_{\text{DFT+DMFT}}}{\delta \rho(r)} = V^{H-\text{xc}}(r) \quad \text{(getting } V^{H-\text{xc}} \text{ from charge)}$$

$$\frac{\delta \Phi_{\text{DFT+DMFT}}}{\delta G_{\text{corr}}} = \Sigma_{\text{corr}} \quad \text{(formulating and solving many body problem)}$$

Note: formulating the correlation problem includes defining orbitals and specifying interactions
Self Energy

\[ P_{\text{corr}} \Sigma_{\text{corr}} P_{\text{corr}} \]

is a matrix acting on a pre-identified subspace of correlated orbitals.

\[ V^{H-\text{xc}}(r) \text{ also has matrix elements in correlated space} \]

\[ \implies \text{``double counting''} \]

\[ \frac{\delta \Phi_{\text{DFT+DMFT}}}{\delta G_{\text{corr}}} = \Sigma_{\text{corr}} \]

\[ \frac{\delta \text{Tr}[\ln]}{\delta \Sigma_{\text{corr}}} \equiv P_{\text{corr}} G P_{\text{corr}} = G_{\text{corr}} \]
What is done in practice

$$\Phi_{\text{DFT+DMFT}}[\rho, G_{\text{corr}}] =$$

$$\Phi_{\text{HK}}[\rho] + \Phi_{\text{DMFT}}[G_{\text{corr}}] - \Phi_{\text{DC}}[G_{\text{corr}}]$$

- $V^{H-\text{xc}}$ from DFT using density from full many body solution
- Correlated subspace: defined via Wannier or projector
- $G_{\text{corr}}$ from DFMT procedure (single-site+’Slater-Kanamori’ U/J interactions (c-RPA))
- Double counting term

Note: DFT+U is DFT+DMFT with impurity model solved in Hartree approximation
What is done in practice

\[ \Phi_{DFT+DMFT}[\rho, G_{corr}] = \]

\[ \Phi_{HK}[\rho] + \Phi_{DMFT}[G_{corr}] - \Phi_{DC}[G_{corr}] \]

- \( V^H_{xc} \) from DFT using density from full many body solution
- Correlated subspace: defined via Wannier or projector
- \( G_{corr} \) from single-site DFMT procedure (single-site+’Slater-Kanamori’ U/J interactions (c-RPA))
- Double counting term

\[ \Rightarrow \text{energy as function of atomic position now available} \]
\[ \Rightarrow \text{forces and relaxation (Leonov, Haule, Park)} \]
Beyond DFT: the spin crossover molecule


DFT+U: gets energy of high spin state right but gets energy of low spin state wrong (for reasonable U ~5eV)
Application to Spin Crossover Molecules


DFT+DMFT ``works’’!

DFT+U: gets energy of high spin state right but gets energy of low spin state wrong

DMFT: fixes problem with energy of low spin state.
Occupation Histograms

Low Spin: \( N_d = 6.7 \)
\( t_{2g} \) fully occupied.
Correlation physics affects charge fluctuations into \( e_g \)
\( \Rightarrow \) "multireference"

High Spin: \( N_d = 5.3 \)
Majority spin orbitals occupied.
Minority spin orbitals empty.
\( \Rightarrow \) "single reference".
DFT+U is OK

DMFT: captures energetics of valence fluctuation in correlated environment
Role of charge self-consistency

$N_d$ in starting DFT is $\sim 6.8$. d-occupancy in HS state is $N_d \sim 5.3$, much less than DFT value. Full charge self-consistency allows charge on ligand to relax to screen E-field from change in d occupancy; does not change $N_d$ much.
Sensitivity to interaction strength

DMFT: correct energy difference for reasonable U,J
Right choice of double counting crucial
Method not yet at chemical accuracy
DFT+DMFT for rare earth nickelates
DFT+DMFT: technicalities

DFT: VASP GGA; PAW, 6x6x6 (exc 8x8x8 for LaNiO$_3$) k-point mesh; 600 eV energy cutoff

DMFT: Atomic d-orbital (MLFW from d-p complex) Slater-Kanamori interaction, $U=5\text{eV}$, $U'=4.8\text{eV}$ $J=0.67\text{eV}$, single-site, CT-QMC

Compute energy along 1d path interpolating from experimental high-T to experimental low-T structure
Onsite interaction and double counting determined phenomenologically
Energy vs lattice distortion at different unit cell volumes

(Note colors mean different things on different plots)
Method gets correct ground state structural/metal-insulator phase diagram


Does the DFT Functional you use make a difference?

DFT+U: small diff

spin-polarised DFT +U: much larger differences
spin-dependent functionals have a large intrinsic Hund's coupling

SrMnO$_3$  Fe

H, Chen and AJM, Phys. Rev. B93, 045133 (2016)
Intrinsic ``J'' interacts badly with +U/+J methods

SrMnO$_3$  
U=6eV, J=1eV
In practice: double counting is a hartree term in self energy

$$\Sigma_{\text{corr}} \rightarrow \Sigma_{\text{DMFT}}(\omega) - V_{\text{DC}}$$

fixes mean d-level energy relative to other levels; in particular, to $O_{2p}$

Standard approach: `Fully Localized Limit’ form

$$V_{\text{DC}} = U' \langle N_d \rangle - \frac{5}{2} J \langle N_d \rangle$$

Traditional choice: $U' = U$. Essentially removes Hartree term in DMFT self energy—fixes p-d energy difference at band theory value. **No reason to choose $U' = U$**

LaTiO$_3$: Full charge sc +FLL double counting produces metal even for large U

U=9eV

Experimental structure
At Fixed Double Counting:
Charge transfer energy is indep of U

(c) LaTiO$_3$

$U=5eV$

$U=7eV$

$U=9eV$

Expt Structure
FLL Double Counting
Standard double counting puts O2p at DFT position

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to get correct physics: adjust p-d energy splitting

\[ V_{DC} = U' \langle N_d \rangle - \frac{5}{2} J \langle N_d \rangle \]

U=5eV, J=0.65eV

expt structures
Summary: DFT+DMFT

• Many-body treatment crucial for energetics of hybridization in correlated environment
• Charge self-consistency: crucial for ‘embedding’ (allowing background degrees of freedom to adjust to configuration of correlated site)
• Numerically exact solutions restricted to cases where correlated ion has not too low point symmetry
• Uncertainties:
  – formulation of many-body problem (what are the correlated orbitals and interactions)
  – the double-counting correction
  – values of beyond DFT interactions (‘U,J’)
  – adequacy of solution of many body problem (is single-site DMFT good enough)
  – DONT build a theory on spin-dependent functionals