"Nano-DMFT": the electronic structure of small, strongly correlated, systems

Recommended with a Commentary by A. J. Millis
Department of Physics, Columbia University

All chemistry is local, as erstwhile Speaker of the US House of Representatives Thomas P. ("Tip") O'Neill did not quite say (he was referring to politics), while condensed matter physics is largely concerned with long wavelength properties. Nevertheless chemistry and condensed matter physics share a need to calculate the ground state energies and electronic excitation spectra of systems with strong electronic correlations. Direct approaches, including the configuration-interaction and coupled-cluster methods of quantum chemistry as well as straightforward quantum Monte Carlo, have not solved the strong correlation problems of physics and chemistry. In this situation, one may turn to indirect approaches, in which the solution of a simpler auxiliary problem is used to obtain information about a restricted set of properties of the full system.

The best known of the indirect approaches is density functional theory, for which Wal-

ter Kohn was awarded part of the 1998 Nobel Prize for Chemistry. The restricted set of properties are the electron density and ground state energy and the auxiliary problem is a one-electron Schroedinger equation with a potential self-consistently determined from the electron density. Density functional theory (while exact in principle) alsoencounters difficulties in the strong correlation situation and indeed a good working definition of the strong correlations problem is 'the behavior of materials for which current implementations of density functional theory fail to provide a good description of the ground state and low-lying excitations'.

"Dynamical mean field theory" is a different indirect approach developed over the last two decades in the condensed matter community.[1–3] Here, the restricted properties are suitable averages over the spatial dependence of the electron Greens function (or self energy) and the auxiliary problem is a "quantum impurity model": a finite system coupled to a noninteracting reservoir of states with the system-reservoir coupling is self-consistently determined from the (approximation to the) electron Greens function. Different flavors of dynamical mean field theory exist, including the original single-site version [1], 'cluster' extensions [2] which provide more accurate accounts of energetics and physical properties at the expense of solving a more complicated impurity model, and "dual fermion" [4] and "$D - \Gamma$" [5] methods which incorporate spatial dependence by use of vertices constructed from solution of single-site dynamical mean field equations. "LDA+DMFT" approaches use band theoretic methods to obtain more realistic approximations to the many-body models which are actually solved[3, 6]. The methods can capture prototypical strong correlation phenomena such as local moment creation and its interplay with band formation and are proving useful in understanding the electronic structure and physics of materials with "strong correlations".

Dynamical mean field theory should be as applicable to nanosystems as to bulk materials. In Phys. Rev. Lett. **99** 046402 (2007), S. Florens took a first step in this direction, introducing the idea of using dynamical mean field theory to study both isolated finite systems and nanocontacts (small systems more or less weakly coupled to noninteracting leads). He defined a general procedure and outlined a range of systems to which it might be applied and presented results obtained using a single-site approximation to the Hubbard model defined on a finite sized Bethe lattice. Florens' main scientific focus was on the metal-insulator transition. He found oscillations in the quasiparticle weight related to the

Friedel oscillations coming from the cluster boundary, and (in contrast to what is found in the single-site dynamical mean field approximation to the the bulk system) a first order jump as the insulating phase is approached by increasing interaction strength.

Three recent publications have implemented, extended and applied Florens' ideas. In Phys. Rev. Lett. **104** 246402 (2010), Valli et al. applied the dynamical mean field approximation to investigate the conductance of nanocontacts, modeled as finite Hubbard clusters coupled to leads. (Note: the authors refer to the "nano-$D - \Gamma$" method, but it appears what is actually used is the single-site dynamical mean field approximation: the extra steps involved in constructing the vertex needed for the full $D-\Gamma$ method seem not yet to have been undertaken). Their work took a step beyond Florens' by using geometries more realistic than the Bethe lattice and by comparing the dynamical mean field results to those obtained by simply solving the entire problem using a quantum Monte Carlo method. An example of the rather encouraging comparisons between the dynamical mean field and full quantum Monte Carlo results is shown in Fig. 1.
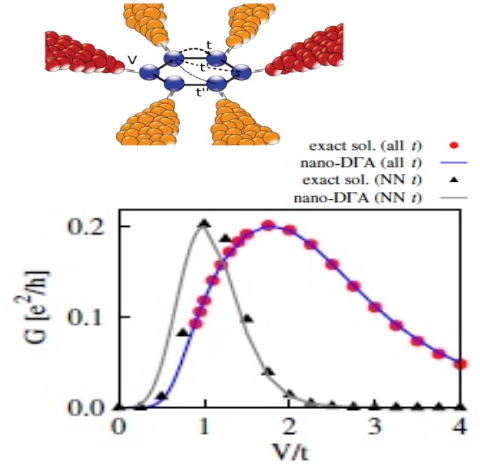

FIG. 1: *Upper panel: sketch of model system studied by Valli et. al. Lower panel; linear response conductance across ring computed from dynamical mean field approximation and from an exact quantum Monte Carlo calculation, for two cases: all sites coupled and only nearest neighbor sites coupled.*

In Phys. Rev. **B82**, 195115 (2010), Jacobs, Kotliar and Haule take the same set of ideas in a "real materials" direction, using the "LDA+DMFT" methodology to calculate various properties of 2 and 10 atom Ni clusters arranged as nanocontacts between (001)-orientd Cu nanowires. The single-site DMFT approximation was again used, but all of the Ni d-orbitals were treated and realistic on-site interactions were incorporated. Among other things a temperature-dependent Fano resonance (not present in the standard LSDA band theory method) was found in the transmission amplitude (see Fig. 2).

Finally, in J. Phys.: Condens. Matter **22** 462202 (2010), Turkowski et al. use dynamical mean field ideas to compute the properties of Fe_n molecules with $2 \leq n \leq 5$.
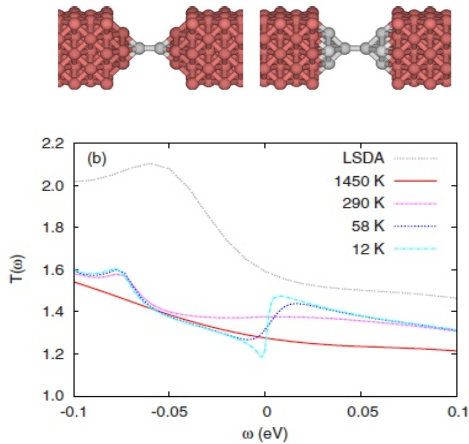
FIG. 2: *Sketch of model systems and energy-dependent electron transmission amplitude of Ni-dimer nanojunction (left sketch) computed from dynamical mean field approximation and compared to results of local spin density approximation (LSDA). Structure around $\omega = 0$ is interpreted as a Fano resonance arising from quasiparticles which become coherent only at low T.*

The authors apparently (the presentation is somewhat terse) use "GGA+U" band theory methods to obtain structures (dimer, equiliateral triangle, single-sided and bi-pyramid for $n = 2, 3, 4, 5$ respectively). A tight-binding model is then constructed for the Fe s and d electrons using the standard Harrison rules (with due attention to the relative orientation of the Fe atoms) but with hopping amplitudes renormalized by an apparently arbitrarily chosen factor of 0.367. The difference in on-site energies between the s and d orbitals is not stated. A phenomenologically adjustable interaction U (but no J) is then applied (presumably to the d orbitals), and the resulting model is solved using the single-site dynamical mean field approximation.

Results (see Fig. 3) for the magnetization (red squares) do not seem to be a qualitative improvement on those obtained by other methods such as the local spin density approximation. While the "GGA+U" method yields a magnetization which is too high, the single-site dynamical mean field approximation seems rather to over-correct these, possibly because of the neglect of the 'J' interaction or because the single-site dynamical mean field method is a quantitatively poor approximation in many cases.

The phenomenological manner in which the interaction and hopping parameters seem to have been chosen is somewhat at variance with the ethos of quantum chemistry, which emphasizes first principles computation and quantitative accuracy. Also, what was studied was not quite an isolated molecule: the molecules were placed on a lattice and a (presumably weak, but unspecified) inter-molecular coupling was included so an existing infinite-system DMFT code could be used. But these are quibbles, easily remedied. They should not distract one from the real achievement of this paper, which is the demonstration that dynamical mean field ideas can be used in a quantum chemical context and can produce nontrivial results.

The works of Florens, of Valli et. al., of Jacob et. al. and of Turkowski et. al.

establish that something potentially interesting can be done in both the nanoscience and the quantum chemistry context. (My opinions are not entirely unbiassed: my collaborators and I have applied dynamical mean field techniques to molecules (arXiv:1010.3180)). The important questions now are: how do you best do it, and how good are the answers. While I have presented the story in terms of the application of dynamical mean field theory to new areas, the most interesting consequence may be the effect of the other areas on the dynamical mean field method. The focus on quantitative accuracy and computational efficiency characteristic of quantum chemistry poses a severe challenge to the dynamical mean field community. Meeting this challenge will, among other things, improve our ability to calculate properties of the bulk correlated electron materials whose behavior was the original motivation for the development of dynamical mean field theory.
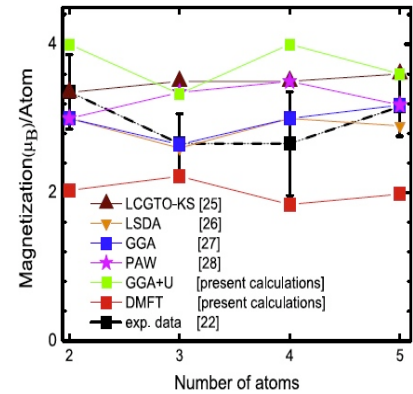

FIG. 3: *Magnetization per atom for Fe_n clusters computed by Turkowski et. al. using dynamical mean field method (red boxes) and compared to results obtained from band theory methods and experimental data.*

[1] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).

[2] T. Maier, M. Jarrell, T. Pruschke, and M. H. Hettler, Rev. Mod. Phys. **77**, 1027 (2005).

[3] G. Kotliar, S. Y. Savrasov, K. Haule, et al., Rev. Mod. Phys. **78**, 865 (2006).

[4] A. N. Rubtsov, M. I. Katsnelson, and A. I. Lichtenstein, Phys. Rev. B **77**, 033101 (pages 4) (2008).

[5] A. Toschi, A. A. Katanin, and K. Held, Phys. Rev. B **75**, 045118 (pages 8) (2007).

[6] K. Held, I. A. Nekrasov, G. Keller, V. Eyert, N. Bluemer, A. K. McMahan, R. T. Scalettar, T. Pruschke, V. I. Anisimov, and D. Vollhardt, Phys. Status Solidi **243**, 2599 (2006).