Bridging the gap between weak and strong correlation: A new way forward?

Kieron Burke and Peter Elliott UC Irvine Physics and Chemistry Adam Wasserman Chemistry, Purdue University Morrel H Cohen Physics, Rutgers and Princeton



http://dft.uci.edu

Summary

- I'll discuss a new formalism which makes explicit connections between band theory and atomistic limit.
- Only model calculations done so far, but I expect that to change.
- Many opportunities for making connections between two camps.
- Apologies: Written in DFT language

Outline

- Brief review of modern DFT
- Partition theory
- Fragment calculations
- Implications

Kohn-Sham equations (1965)

$$\left[-\frac{1}{2}\nabla^2 + \mathbf{v}_s[\boldsymbol{\rho}](\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

 $\rho(\mathbf{r}) = \sum_{i=1}^{N} \left| \phi_i(\mathbf{r}) \right|^2 =$

ground-state density of interacting system

$$\mathbf{v}_{s}(\mathbf{r}) = \mathbf{v}_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mathbf{v}_{xc}[\rho](\mathbf{r})$$

$$E_0 = T_S + V + U + E_{XC}[\rho]$$

$$v_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}$$

He atom in Kohn-Sham DFT



Everything has (at most) one KS potential

Dashed-line:

EXACT KS potential

Problems with standard DFT

- Band gaps are bad
- Symmetry dilemma for stretched H₂
- Self-interaction error (now called delocalization error)
- Too many functionals (but see our semiclassical work: Explains why DFT works at all).





Things users despise about DFT

- No simple rule for reliability
- No systematic route to improvement
- If your property turns out to be inaccurate, must wait several decades for solution
- Complete disconnect from other methods
- Full of arcane insider jargon
- Too many functionals to choose from
- Can only be learned from another DFT guru

Things developers love about DFT

- No simple rule for reliability
- No systematic route to improvement
- If a property turns out to be inaccurate, can take several decades for solution
- Wonderful disconnect from other methods
- Lots of lovely arcane insider jargon
- So many functionals to choose from
- Must be learned from another DFT guru

Distinctions

- Calculations
 - Is my bond length right? Is the magnetic state correct?
- Approximations
 - LDA is an approximation used in DFT
 - Single-site DMFT is an approximation to DMFT
- Formalisms
 - Schrodinger equation and wavefunctions
 - Green's functions
 - Path integrals

DFT

Important distinction

- Suppose I give you the **EXACT** XC functional
- You don't get
 - Excitations, response properties, in general
 - A KS band-gap equal to the correct one
- You can get
 - all ground-state energies and densities right, including Pu and fractional quantum hall states.
 - The fundamental gap I-A

Errors in standard functionals



1: A.J. Cohen, P. Mori-Sánchez, W. Yang, Science 321, 792 (2008).

Key difference between DFT and strongly-correlated treatments

- DFT is always in real-space, basis-set independent results.
- Strongly-correlated treatments usually begin from model Hamiltonian on a lattice, e.g. Hubbard model.
- Prototype example: Stretched H₂, with relative spin states.

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Partition Theory

Precursor

 Cortona's crystal potential (PRB, 1991) J. Phys. Chem. A 2007, 111, 2229-2242

On the Foundations of Chemical Reactivity Theory

Morrel H. Cohen

Department of Physics and Astronomy, Rutgers University, 126 Frelinghuysen Road, Piscataway, New Jersey 08854

Adam Wasserman*

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

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In formulating chemical-reactivity theory (CRT) so as to give it a deep foundation in density-functional theory (DFT), Pair, his collaborators, and subsequent workers have introduced reactivity indices as properties of isolated reactants, some of which are in apparent conflict with the underlying DFT. Indices which are first derivatives with respect to electron number are staircase functions of number, making electronegativity equalization problematic. Second derivative indices such as hardness vanish, putting hardness-based principles out of reach. By reformulating CRT within our partition theory, which provides an exact decomposition of a system into its component species, we resolve the conflict. We show that the reactivity of a species depends on its chemical context and define that context. We establish when electronegativity equalization holds and when it fails. We define a generalization of hardness, a hardness matrix containing the self-hardness of the individual species and the mutual hardnesses of the pairs of species of the system, and identify the physical origin of hardness. We introduce a corresponding generalization of the Fukui function as well as of the local and global softnesses and the softness kernel of the earlier formulation. We augment our previous formulation of the partition theory by introducing a model energy function and express the difference between the exact and the model forces on the nuclei in terms of the new reactivity indices. For simplicity, our presentation is limited to time-reversal invariant systems with vanishing spin density; it is straightforward to generalize the theory to finite spin density.

Simplified atoms

We use a simple
Eckhardt potential in
1d, non-interacting
electrons, and one
electron per site in all
illustrations.



Simplified moleule

• Here's our 1d H₂



Basic partition theory

 Consider atoms as isolated and minimize the sum of their energies, but requiring sum of densities equal molecular density:

$$E_f = \min_{\substack{\{n_\alpha\},\\\sum_{\alpha=1}^{N_f} n_\alpha(\mathbf{r}) = n(\mathbf{r})}} \sum_{\alpha=1}^{N_f} \left(F[n_\alpha] + \int d^3 r \, n_\alpha(\mathbf{r}) \, v_\alpha(\mathbf{r}) \right)$$

Basic partition theory

• How to find minimum? Use Lagrange multipliers:

$$\mathcal{G} = E_f + \int d^3 r \ v_p(\mathbf{r}) \left(n(\mathbf{r}) - \sum_{\alpha=1}^{N_f} n_\alpha(\mathbf{r}) \right)$$

• Lagrange multiplier is called partition potential, $v_p(\mathbf{r})$, a global property of the molecule

Partition potential



Relations in KS-DFT

- Total energy $E[n] = F[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r})$
- 'KS energy'

$$E_{\rm s}[n] = \langle \Phi_{\rm s}[n] | \hat{T} + \hat{V} | \Phi_{\rm s}[n] \rangle = T_{\rm s}[n] + \int d^3 r \, n(\mathbf{r}) \, v(\mathbf{r})$$

- Difference: $E_{\text{HXC}}[n] = E[n] E_{\text{s}}[n]$
- Change in v(r) $v_{\text{HXC}}(\mathbf{r}) = \delta E_{\text{HXC}}[n]/\delta n(\mathbf{r})$

Relations in Partition Theory

- Total energy $E[n] = F[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r})$
- 'Fragment energy'

$$E_f = \min_{\substack{\{n_\alpha\},\\\sum_{\alpha=1}^{N_f} n_\alpha(\mathbf{r})=n(\mathbf{r})}} \sum_{\alpha=1}^{N_f} \left(F[n_\alpha] + \int d^3 r \, n_\alpha(\mathbf{r}) \, v_\alpha(\mathbf{r}) \right)$$

- Partition energy: $E_p[\{n_\alpha\}] = E[n] E_f[\{n_\alpha\}]$
- Change in $v(\mathbf{r})$: $v_p(\mathbf{r}) = \delta E_p[\{n_\alpha\}]/\delta n_\alpha(\mathbf{r}).$

Fragment calculations

- Can you do a calculation on a set of isolated fragments?
- Need to calculate partition potential 'on the fly'
- Can you ensure it recovers the 'exact' molecular density?

Advantages of partitioning

- Can calculate $E_p[\{n_{\alpha}\}] = E[n] E_f[\{n_{\alpha}\}]$ molecular energy by correcting atomic energies $E_{dis} = E - E^{(0)}$
- E_p much smaller than E

$$E_{rel} = E_f^{(0)} - E_f$$

Partition potential from energy

- Thus $v_p(r) = \frac{\delta E_p[\{n_\alpha\}]}{\delta n_\alpha(r)}$
- Once E_p[{n_a}] is known or approximated, one can perform self-consistent calculation:
 - Guess fragment densities, {nº(r)}
 - Calculate partition potential, $v_p(r)$
 - Use vp to find new fragment densities
 - and so on until self-consistency

Self-consistent fragment equations

 $v_{\mathrm{S},f,\alpha}[n_{\alpha},\bar{n}_{\alpha}](\mathbf{r}) = v_{\mathrm{S}}[n_{\alpha}](\mathbf{r}) + (v(\mathbf{r}) + v_{\mathrm{HXC}}[n](\mathbf{r}) - v_{\mathrm{S}}[n](\mathbf{r}))$

 $v_{\rm s}[n](\mathbf{r}) = -\delta T_{\rm s}[n]/\delta n(\mathbf{r})$

- The second term is the kicker, because you need KS potential for entire molecule.
- But easy for 2-particles, since it's just von Weisacker.

Convergence for H₂



Fractional occupations

 For system in contact with reservoir, the total energy between integers is given by straightline segments (PPLB, PRL 1982)

$$n_{\alpha}(\mathbf{r}) = (1 - \nu_{\alpha})n_{p_{\alpha}}(\mathbf{r}) + \nu_{\alpha}n_{p_{\alpha}+1}(\mathbf{r})$$

$$F[n_{\alpha}] = (1 - \nu_{\alpha})F[n_{p_{\alpha}}] + \nu_{\alpha}F[n_{p_{\alpha}+1}]$$









The Road to Partition

 Use PPLB for energy and density for fragments with a non-integer N:

$$\epsilon_{\alpha} = (1 - \nu_{\alpha}) E_{\alpha}[n_{p_{\alpha}}] + \nu_{\alpha} E_{\alpha}[n_{p_{\alpha}+1}]$$

$$N_{\alpha} = p_{\alpha} + v_{\alpha}$$

$$n_{\alpha} = (1 - \nu_{\alpha}) n_{p_{\alpha}} + \nu_{\alpha} n_{p_{\alpha}+1}$$

Total fragment energy

$$\epsilon = \sum_{\alpha} \epsilon_{\alpha}$$

• Minimize ϵ with the constraints that nM(r) is the sum of the fragment densities and N is sum of the fragment N_{_{\!\alpha}}

1d H-He+

- Exact partitioning of molecular density
- Fractional occupations 0.7 and 1.3
- MC,AW, Roberto Car, and Kieron, J.
 Phys. Chem. A 2009, 113, 2183





KITP: Materials by design

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Iterative scheme for N-particle KS potential

$$v_{\mathrm{s},f,\alpha}[n_{\alpha},\bar{n}_{\alpha}](\mathbf{r}) = v_{\mathrm{s}}[n_{\alpha}](\mathbf{r}) + (v(\mathbf{r}) + v_{\mathrm{HXC}}[n](\mathbf{r}) - v_{\mathrm{s}}[n](\mathbf{r}))$$
$$v_{\mathrm{s}}[n](\mathbf{r}) = -\delta T_{\mathrm{s}}[n]/\delta n(\mathbf{r})$$

- Can use any of many algorithms to find a KS potential for a given density: Make inner loop $v_{s}^{(m+1)}(\mathbf{r}) = v_{s}^{(m)}(\mathbf{r}) + \gamma \left[n^{(m)}(\mathbf{r}) n^{(k)}(\mathbf{r}) \right]$
- In outer loop, minimize chemical potential difference:

$$N_{\alpha}^{(k+1)} = N_{\alpha}^{(k)} - \Gamma\left(\mu_{\alpha}^{(k)} - \bar{\mu}^{(k)}\right)$$



- Construct chain of Eckhardt potentials
- Peter Elliott solved 12 single-atom fragment problems.

Partition potential in chain



FIG. 2: The exact partition potential (solid line) for the atomized chain and the fragment potential for the last atom (dashed line). The ground state with an occupation of 0.77 in this potential can be seen as the end fragment density in Fig 1.

Occupation numbers in chain

 $N_{\alpha} =$ 1.20.77,1.13, 0.98,1.06, zď 1.02,1.04 0.8

0.6 40 80 Iteration cycle

FIG. 3: The convergence of the fragment occupation values, N_{α} , during an exact PDFT calculation.

Relative sizes of energies

- Traditional calculation:
 - One 'atom' is -27.2 eV
 - Entire molecule is -418.54 eV

$$-E_{dis} = -418.54 + 12x27.2 = -92 \text{ eV}$$

• Partition theory:

- At end of calculation, E_f =-320.43 eV, E_p =-98.1 eV

$$-$$
 So $E_{dis} = E_p - E_{rel} = -98.1 + 6.1 = -92.0 eV$

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Atomic limit

$$E = \sum_{\alpha=1}^{N_f} \mathcal{E}_{f,\alpha} + E_P$$

- If XC contribution to $E_P=0$, automatically gets atomic limit right.
- So both H₂⁺ and H₂ behave correctly.
- Thus, can handle both self-interaction and strong correlation automatically.
- Sadly, then lousy back at equilibrium.

New many-body approximations $E_p = \Delta T_s[n_\alpha] + \Delta E_{HXC}[n_\alpha] + \sum_{\alpha,\beta\neq\alpha}^{N_f} \int d^3r \, n_\alpha(\mathbf{r}) v_\beta(\mathbf{r})$

- If you set XC contribution to zero, automatically dissociate correctly.
- Hartree partition energy contains long-range polarizing Coulomb effects.
- Partition theory bridges gap between lattices and real-space approaches.

Orbital-free DFT/ O(N)

- If we knew T_s[n] sufficiently accurately, we would not need to solve for KS orbitals.
- Codes would be much faster.

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Ab Initio Approach for Many-Electron Systems without Invoking Orbitals: An Integral Formulation of Density-Functional Theory

Weitao Yang

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PHYSICAL REVIEW LETTERS

18 MARCH 1991

Direct Calculation of Electron Density in Density-Functional Theory

Weitao Yang

Department of Chemistry, Duke University, Durham, North Carolina 27706 (Received 5 September 1990)

QM/MM



Figure 2

Illustration of the pseudobond method. The side chain of the Gln residue is described with quantum mechanics (*yellow region*) and the C_{α} atom has a designed effective core potential, one free valence, and a special basis set. The C_{α} - C_{β} bond becomes a pseudobond with similar bond length, bond strength, and charge distributions as in a normal C(*sp3*)–C(*sp3*) single bond.

Annu. Rev. Phys. Chem. 2008. 59:573-601

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The Annual Review of Physical Chemistry is online at http://physchem.annualreviews.org Free Energies of Chemical Reactions in Solution and in Enzymes with Ab Initio Quantum Mechanics/Molecular Mechanics Methods

Hao Hu and Weitao Yang

Department of Chemistry, Duke University, Durham, North Carolina 27708; email: hao.hu@duke.edu, weitao.yang@duke.edu

Atoms in molecules

 Many attempts to define atoms in molecules, e.g. Bader, Parr, ...

Information theory, atoms in molecules, and molecular similarity

Roman F. Nalewajski*† and Robert G. Parr†‡

*K. Guminski, Department of Theoretical Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland; and [†]Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290

Contributed by Robert G. Parr, May 15, 2000

Using information theory, it is argued that from among possible definitions of what an atom is when it is in a molecule, a particular one merits special attention. Namely, it is the atom defined by the "stockholders partitioning" of a molecule invented by Hirshfeld [(1977) *Theor. Chim. Acta* 44, 129]. The theoretical tool used is the minim

to the effective atomic number of the nucleus (16). AIM densities should be related to both promolecule and molecular densities, as representing the atomic fragments in a particular molecular system. One would want some degree of overlap between the densities of these chemical atoms to reflect the



Atomic 'charges'

• Mulliken,...

- Boys localization (50's)
- Maximally localized Wannier functions (Vanderbilt, etc.)

Conclusions

- Partition theory provides an exact decomposition of molecule into fragments.
- In KS-DFT, a simple algorithm allows fragment calculations.
- Allows many new ways to approximate the energy, including ways that include strongly correlated systems.
- How does DMFT look in this scheme?
- Thanks to NSF.

$$\begin{aligned} v_{\rm s}^{(m+1)}(\mathbf{r}) &= v_{\rm s}^{(m)}(\mathbf{r}) + \gamma \left[n^{(m)}(\mathbf{r}) - n^{(k)}(\mathbf{r}) \right] \\ &= E_{\rm Hxc}[n] = E[n] - E_{\rm s}[n] \\ \mathcal{G} &= E_f + \int d^3 r \ v_p(\mathbf{r}) \left(n(\mathbf{r}) - \sum_{\alpha=1}^{N_f} n_\alpha(\mathbf{r}) \right)^{-\mathbf{r}} = \delta E_{\rm Hxc}[n] / \delta n(\mathbf{r}) \\ \stackrel{^{\prime}E_{rel}}{E_{rel}} v_{\rm s} \ E_p &= \Delta T_{\rm s}[n_\alpha] + \Delta E_{\rm Hxc}[n_\alpha] + \sum_{\alpha,\beta\neq\alpha}^{N_f} \int d^3 r \ n_\alpha(\mathbf{r}) v_\beta(\mathbf{r}) \mathbf{r})) \\ E_f &= \min_{\substack{\{n_\alpha\},\\ \sum_{\alpha=1}^{N_f}, n_\alpha(\mathbf{r}) = n(\mathbf{r})}} \sum_{\alpha=1}^{r} \left(F[n_\alpha] + \int d^3 r \ n_\alpha(\mathbf{r}) \ v_\alpha(\mathbf{r}) \right) \\ v_{\rm s}[n](\mathbf{r}) &= -\delta T_{\rm s}[n] / \delta n(\mathbf{r}) \\ E_p &= \Delta T_{\rm s}[n_\alpha] + \Delta E_{\rm Hxc}[n_\alpha] + \sum_{\alpha,\beta\neq\alpha}^{N_f} \int d^3 r \ n_\alpha(\mathbf{r}) v_\beta(\mathbf{r}) \\ E_p &= E_{dis} + E_{rel}^{r(\mathbf{r})} = \delta E_p[\{n_\alpha\}] / \delta n_\alpha(\mathbf{r}). \\ E_{dis} &= E - E_{dis}^{(0)} \end{aligned}$$





















FIG. 1: Solid line: The exact spin-unpolarized ground state of 12 electrons in the potential of Eq. (17). Dashed lines: The fractionally occupied fragment densities. By symmetry, the other half of the density is simply the mirror image of that shown.