Session I: Recent progress in DFT?

9:10 – 10:00 **John Perdew** (Temple University, Philadelphia)

How far can we go with semilocal density functionals, and how can we go beyond them?

10:00 – 10:50 **Weitao Yang** (Duke University, Durham)

Going Beyond Conventional Functionals with Local Scaling Corrections and Pairing Fluctuations in DFT

10:50 – 11:10 Coffee break

11:10 – 12:00 **Xin Xu** (Fudan University, Shanghai)

Recent advances on the XYG3-type of doubly hybrid density functionals

Walter Kohn (1923-2016)

KS equations (1965)

Define *fictitious* non-interacting electrons satisfying:

$$\left\{-\frac{1}{2}\nabla^2 + v_{\rm S}(\mathbf{r})\right\}\phi_j(\mathbf{r}) = \epsilon_j\phi_j(\mathbf{r}), \qquad \sum_{j=1}^{N}|\phi_j(\mathbf{r})|^2 = n(\mathbf{r}).$$

where $v_{\rm S}(\mathbf{r})$ is *defined* to yield $n(\mathbf{r})$.

Define $T_{\rm S}$ as the kinetic energy of the KS electrons, U as their Hartree energy and

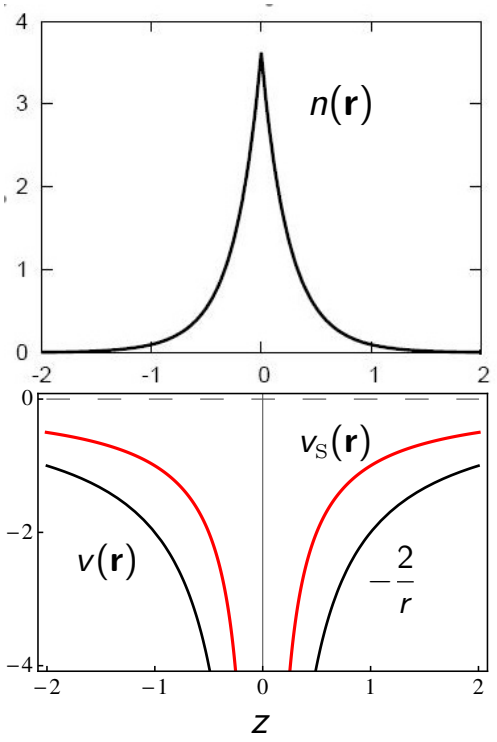
$$T + V_{\rm ee} = T_{\rm S} + U + E_{\rm XC}$$

the remainder is the exchange-correlation energy.

Most important result of exact DFT:

$$v_{\rm S}(\mathbf{r}) = v(\mathbf{r}) + \int d^3r\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\rm XC}[n](\mathbf{r}), \qquad v_{\rm XC}(\mathbf{r}) = \frac{\delta E_{\rm XC}}{\delta n(\mathbf{r})}$$

Knowing $E_{\rm XC}[n]$ gives closed set of self-consistent equations.



Today's commonly-used functionals

- Local density approximation (LDA)
  - Uses only n(**r**) at a point.

$$E_{\mathrm{X}}^{\mathrm{LDA}}[n] = A_{\mathrm{X}} \int d^3r \; n^{4/3}(\mathbf{r})$$

$$A_{\mathrm{X}} = -(3/4)(3/\pi)^{1/3} = -0.738.$$

- Generalized gradient approx (GGA)
  - Uses both n(**r**) and |∇n(**r**)|
  - Should be more accurate, corrects overbinding of LDA
  - Examples are PBE and BLYP

$$E_{\mathrm{XC}}^{\mathrm{GGA}} = \int d^3r \, e_{\mathrm{XC}}^{\mathrm{GGA}}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$$

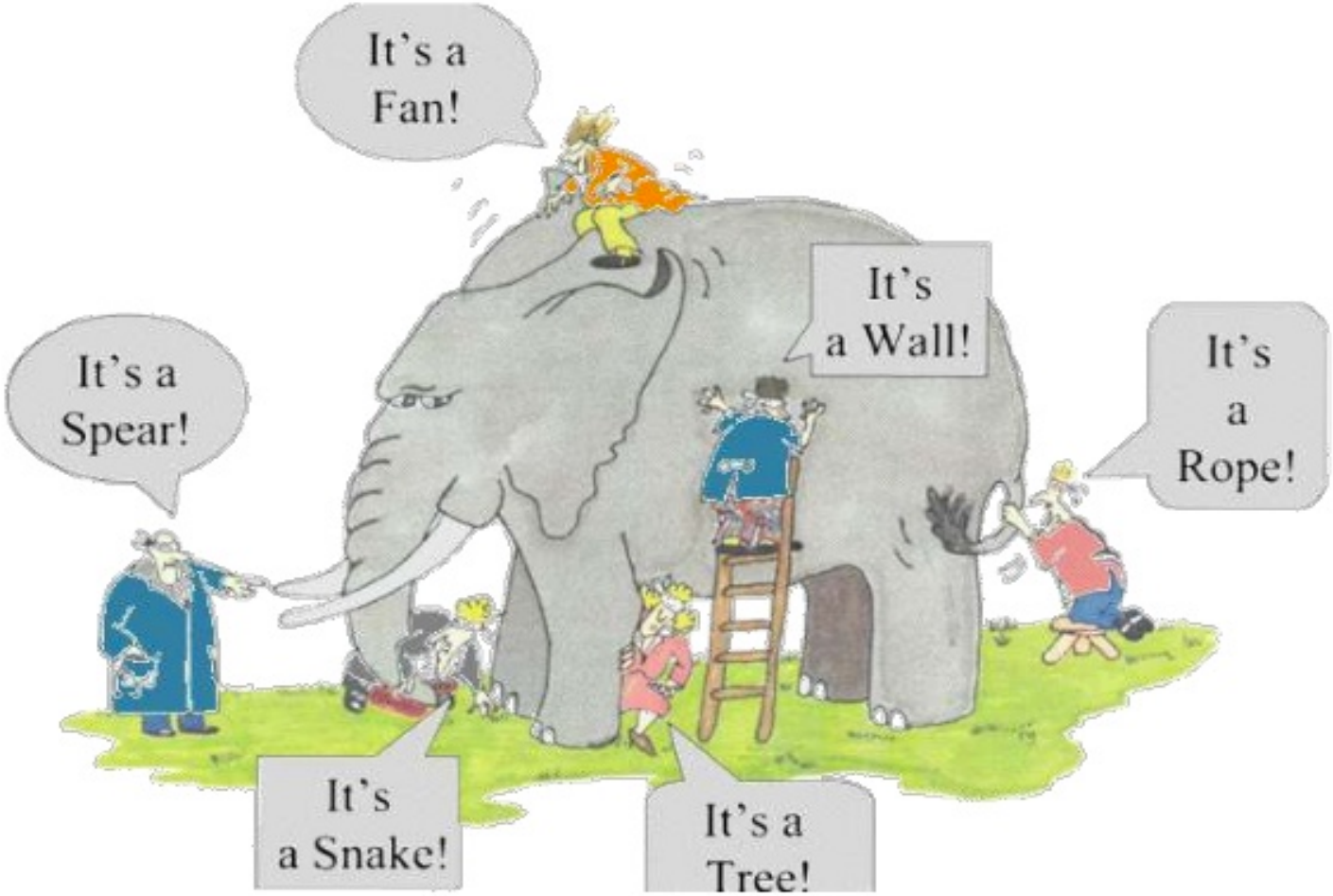
- Hybrid:
  - Mixes some fraction of HF with GGA
  - Examples are B3LYP and PBE0

$$E_{\mathrm{XC}}^{\mathrm{hyb}} = a\,(E_{\mathrm{X}} - E_{\mathrm{X}}^{\mathrm{GGA}}) + E_{\mathrm{XC}}^{\mathrm{GGA}}$$

Some crucial elements

- KS-DFT is not many-body theory!
- Knowledge of $E_{XC}[n]$ does not yield excitations, etc. in general
- The KS gap is not equal to the true gap (I-A).
- Orbital-dependent functionals give better gaps within the generalized KS scheme.
- Standard approximations begin locally (or semilocally).
- Standard approximations have poor potentials
- Procrustean dilemma:
  - Want small a for energies, but large a for potentials

My view of modern DFT research



Global Action Plan International

Challenges

- Incomplete understanding of approximations
- Rise of empiricism and direct models of E_{XC}
- Very demanding to do everything our present functionals do, but do it better
- If it does not begin with semilocal approximation, hard to beat existing approxs everywhere
- If it does begin locally, hard to build in static correlation, etc.

Discussion

- Please send me (kieron@uci.edu) email with your question.
- Please include your name.
- Please say if directed to any speaker or more general.
- Please indicate if you want ME to ask the question, or to call on YOU to ask.
- If you wish, you can remain anonymous.

Session II: Advanced? Electronic structure methods beyond LDA and GGA

14:40 – 15:30 **Xinguo Ren** (USTC, Hefei)

Random-Phase approximation and beyond for materials: concepts, practice, and future perspectives

15:30 – 16:20 **Adrienn Ruzsinszky** (Temple University, Philadelphia)

A Non-Local, Energy-Optimized Kernel for Structural Properties

16:20 – 16:40 Coffee break

16:40 – 17:30 **Gustavo E. Scuseria** (Rice University, Houston)

New Vistas on the Strong Correlation Problem

Molecules versus materials

- Quantum chemistry more more developed than materials science
- Much better reproducibility of calculations
- Much more reliable benchmark data
- Source of much DFT development
- Materials much harder to calculate
- All states are continuous in thermodynamic limit
- QC methods designed for discrete levels

RESEARCH ARTICLE SUMMARY

DFT METHODS

Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere,* Gustav Bihlmayer, Torbjörn Björkman, Peter Blaha, Stefan Blügel, Volker Blum, Damien Caliste, Ivano E. Castelli, Stewart J. Clark, Andrea Dal Corso, Stefano de Gironcoli, Thierry Deutsch, John Kay Dewhurst, Igor Di Marco, Claudia Draxl, Marcin Dułak, Olle Eriksson, José A. Flores-Livas, Kevin F. Garrity, Luigi Genovese, Paolo Giannozzi, Matteo Giantomassi, Stefan Goedecker, Xavier Gonze, Oscar Grånäs, E. K. U. Gross, Andris Gulans, François Gygi, D. R. Hamann, Phil J. Hasnip, N. A. W. Holzwarth, Diana Iuşan, Dominik B. Jochym, François Jollet, Daniel Jones, Georg Kresse, Klaus Koepernik, Emine Küçükbenli, Yaroslav O. Kvashnin, Inka L. M. Locht, Sven Lubeck, Martijn Marsman, Nicola Marzari, Ulrike Nitzsche, Lars Nordström, Taisuke Ozaki, Lorenzo Paulatto, Chris J. Pickard, Ward Poelmans, Matt I. J. Probert, Keith Refson, Manuel Richter, Gian-Marco Rignanese, Santanu Saha, Matthias Scheffler, Martin Schlipf, Karlheinz Schwarz, Sangeeta Sharma, Francesca Tavazza, Patrik Thunström, Alexandre Tkatchenko, Marc Torrent, David Vanderbilt, Michiel J. van Setten, Veronique Van Speybroeck, John M. Wills, Jonathan R. Yates, Guo-Xu Zhang, Stefaan Cottenier*

INTRODUCTION: The reproducibility of results is one of the underlying principles of science. An observation can only be accepted by the scientific community when it can be confirmed by independent studies. However, reproducibility does not come easily. Recent works have painfully exposed cases where previous conclusions were not upheld. The scrutiny of the scientific community has also turned to research involving computer programs, finding that reproducibility depends more strongly on implementation than commonly thought. These problems are especially relevant for property predictions of crystals and molecules, which hinge on precise computer implementations of the governing equation of quantum physics.

RATIONALE: This work focuses on density functional theory (DFT), a particularly popular quantum method for both academic and industrial applications. More than 15,000 DFT papers are published each year, and DFT is now increasingly used in an automated fashion to build large databases or apply multiscale techniques with limited human supervision. Therefore, the reproducibility of DFT results underlies the scientific credibility of a substantial fraction of current work in the natural and engineering sciences. A plethora of DFT computer codes are available, many of them differing considerably in their details of implementation, and each yielding a certain "precision" relative to other codes. How is one to decide for more than a few simple cases which code predicts the correct result, and which does not? We devised a procedure to assess the precision of DFT methods and used this to demonstrate reproducibility among many of the most widely used DFT codes. The essential part of this assessment is a pairwise comparison of a wide range of methods with respect to their predictions of the equations of state of the elemental crystals. This effort required the combined expertise of a large group of code developers and expert users.

RESULTS: We calculated equation-of-state data for four classes of DFT implementations, totaling 40 methods. Most codes agree very well, with pairwise differences that are comparable to those between different high-precision experiments. Even in the case of pseudization approaches, which largely depend on the atomic potentials used, a similar precision can be obtained as when using the full potential. The remaining deviations are due to subtle effects, such as specific numerical implementations or the treatment of relativistic terms.

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Read the full article at http://dx.doi.org/10.1126/science.aad3000

CONCLUSION: Our work demonstrates that the precision of DFT implementations can be determined, even in the absence of one absolute reference code. Although this was not the case 5 to 10 years ago, most of the commonly used codes and methods are now found to predict essentially identical results. The established precision of DFT codes not only ensures the reproducibility of DFT predictions but also puts several past and future developments on a firmer footing. Any newly developed methodology can now be tested against the benchmark to verify whether it reaches the same level of precision. New DFT applications can be shown to have used a sufficiently precise method. Moreover, high-precision DFT calculations are essential for developing improvements to DFT methodology, such as new density functionals, which may further increase the predictive power of the simulations. ■

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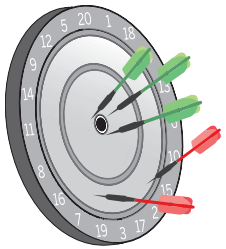
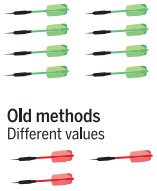
Recent DFT methods yield reproducible results. Whereas older DFT implementations predict different values (red darts), codes have now evolved to mutual agreement (green darts). The scoreboard illustrates the good pairwise agreement of four classes of DFT implementations (horizontal direction) with all-electron results (vertical direction). Each number reflects the average difference between the equations of state for a given pair of methods, with the green-to-red color scheme showing the range from the best to the poorest agreement.





Scorecard

	0.3	0.3	0.6	1.0	0.9	0.3	1.5	0.6	0.9	0.4	1.0	0.4	0.4	6.3	13.5	1.1	2.1	0.7	1.4
0.3		0.1	0.5	0.9	0.8	0.2	1.5	0.6	0.8	0.4	1.0	0.5	0.3	6.3	13.4	1.1	2.1	0.7	1.4
0.3	0.1		0.5	0.9	0.8	0.2	1.5	0.6	0.8	0.4	0.9	0.5	0.3	6.3	13.4	1.1	2.1	0.7	1.4
0.6	0.5	0.5		0.8	0.6	0.4	1.5	0.6	0.8	0.6	1.0	0.7	0.5	6.3	13.2	1.0	1.9	0.6	1.3
1.0	0.9	0.9	0.8		0.9	0.9	1.8	0.9	1.3	1.0	1.4	1.0	0.9	6.4	13.0	1.2	1.8	1.0	1.6
0.9	0.8	0.8	0.6	0.9		0.8	1.7	0.7	1.1	0.8	1.3	1.0	0.8	6.5	13.2	1.1	1.8	0.8	1.5
0.3	0.2	0.2	0.4	0.9	0.8		1.5	0.5	0.8	0.3	1.0	0.5	0.3	6.2	13.4	1.0	2.0	0.6	1.4

THEORETICAL CHEMISTRY

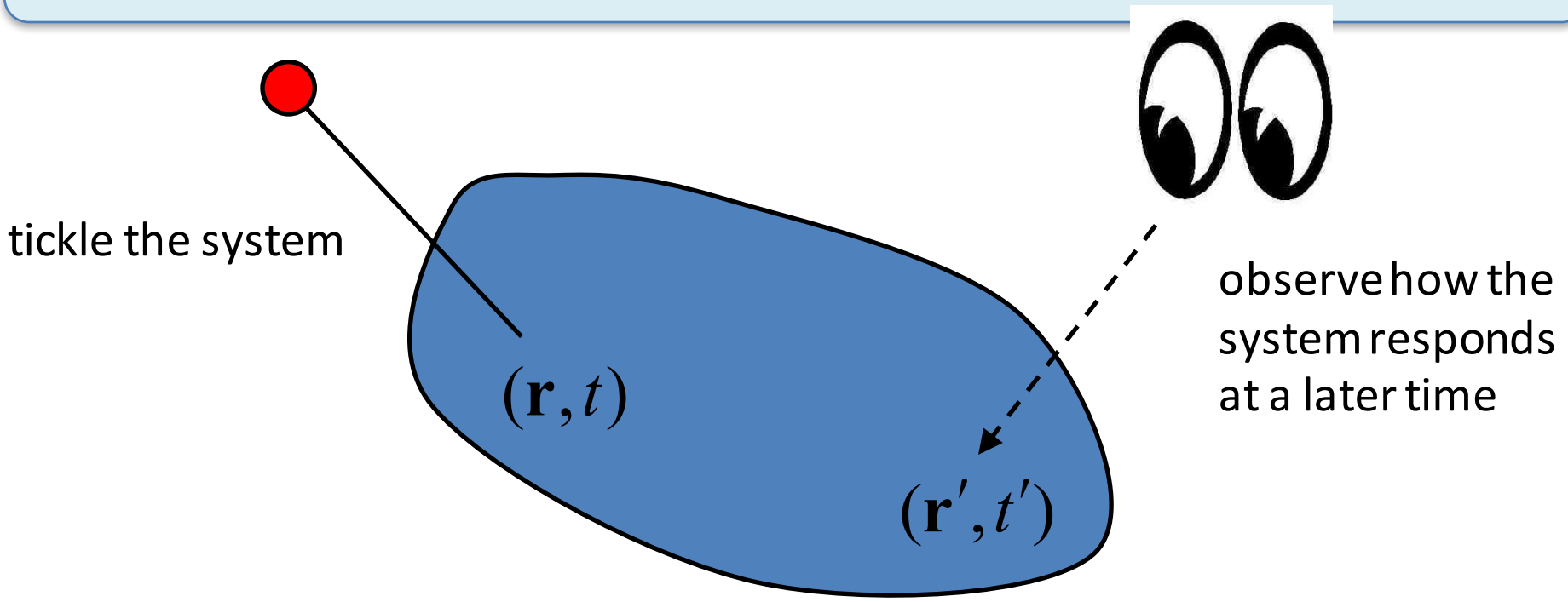
Ab initio determination of the crystalline benzene lattice energy to sub-kilojoule/mole accuracy

Jun Yang,[1] Weifeng Hu,[1] Denis Usvyat,[2] Devin Matthews,[3] Martin Schütz,[2] Garnet Kin-Lic Chan[1]*

Computation of lattice energies to an accuracy sufficient to distinguish polymorphs is a fundamental bottleneck in crystal structure prediction. For the lattice energy of the prototypical benzene crystal, we combined the quantum chemical advances of the last decade to attain sub-kilojoule per mole accuracy, an order-of-magnitude improvement in certainty over prior calculations that necessitates revision of the experimental extrapolation to 0 kelvin. Our computations reveal the nature of binding by improving on previously inaccessible or inaccurate multibody and many-electron contributions and provide revised estimates of the effects of temperature, vibrations, and relaxation. Our demonstration raises prospects for definitive first-principles resolution of competing polymorphs in molecular crystal structure prediction.

Crystal structure prediction is a scientific challenge affecting diverse fields ranging from pharmaceuticals to energy research. Two decades ago, Maddox argued that failures in a priori prediction amounted to "one of the continuing scandals in the physical sciences" (*1*). The crystal structure prediction (CSP) competitions held by the Cambridge Crystallographic Data Centre serve as convenient snapshots of progress (*2*). The twin tasks

Density-density response



$$n_1(\mathbf{r},t) = \int d\mathbf{r}' \int dt' \, \chi(\mathbf{r},t,\mathbf{r}',t') V_1(\mathbf{r}',t')$$

density response

density-density response function

perturbation

KS susceptibility

- Response of non-interacting KS electrons

$$\chi_{\mathrm{KS}}(\boldsymbol{r},\boldsymbol{r}',\omega) = 2 \lim_{\eta\to 0^+} \sum_q \left\{ \frac{\xi_q(\boldsymbol{r})\ \xi_q^*(\boldsymbol{r}')}{\omega-\omega_q+\mathrm{i}\eta} - \frac{\xi_q^*(\boldsymbol{r})\ \xi_q(\boldsymbol{r}')}{\omega+\omega_q-\mathrm{i}\eta} \right\}$$

$$\omega_q = \varepsilon_a - \varepsilon_i$$

$$\xi_q(\boldsymbol{r}) = \varphi_i^*(\boldsymbol{r})\varphi_a(\boldsymbol{r})$$

- Constructed from KS orbitals (occ + unocc)

Extracting Exc

- Fluctuation-dissipation theorem:
  - Extract E_{XC} by integral over response function.
- RPA: or time-dependent Hartree
  - Start from KS response function
  - Include only Coulomb (direct) interaction
  - Yields RPA response function
- Pure RPA: Insert RPA response function.
- Yields RPA $E_{XC}[n]$

Pro's and con's

- Yields useful approximation to van der Waals, including $1/R^6$
- Many bond rearrangement processes highly accurate, but not atomization energies
- Used with E_x, no mysterious cancellation of errors
- …

- Does not reduce to LDA/GGA
- Computational cost (but getting cheaper all the time)
- Self-consistency?
- Still have self-interaction for correlation.

Strong correlation

- Largely interested in localization of electrons when bonds are stretched.
- Local/semilocal functionals do not dissociate to correct limit.
- Paradigm example: Stretched H_2
- Symmetry dilemma with local approximations:
  - Break spin symmetry, but get right energetics
  - Restrict spin, but get bad energies.

Strong correlation II

- Molecular importance:
  - A small but important effect for molecules at equilibrium
  - Bigger for double and triple bonds and huge for Cr_2
  - Explanation of a=0.25 for hybrids
  - Bigger effects for transition state barriers
- Solid-state:
  - Dynamical mean field theory (DMFT) is popular for cases where standard DFT fails
  - Even GW or RPA fail for these systems
  - Many energy-related materials have some aspect