Ensemble TDDFT for excitations

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http://dft.uci.edu

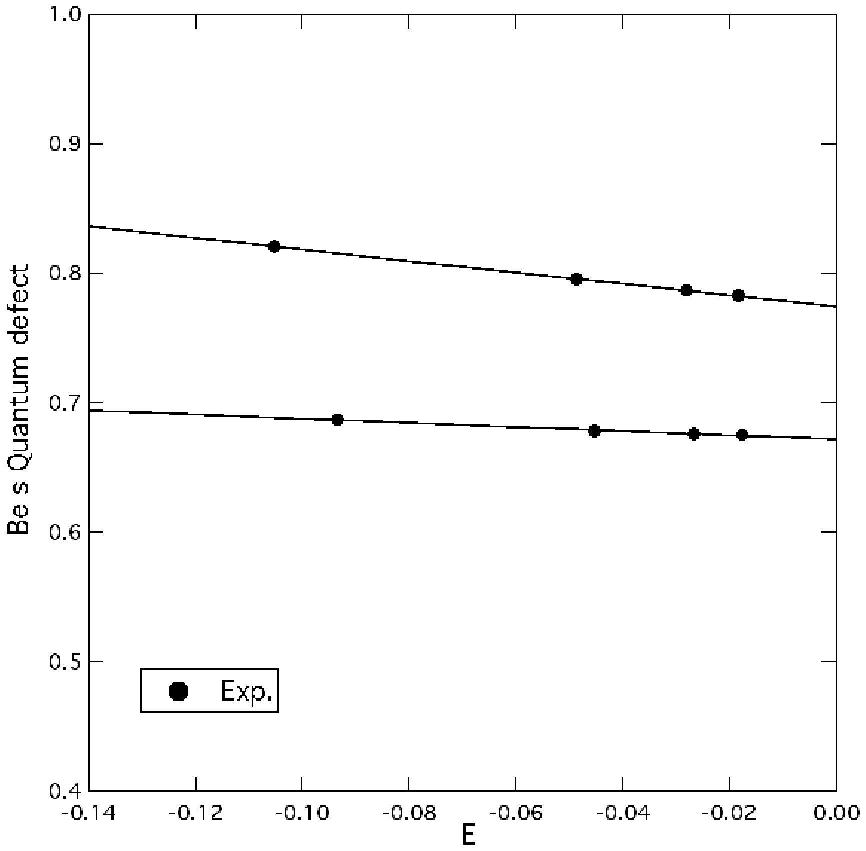
Does TDDFT really work?

Quantum defect of Rydberg series

$$\omega_{nl} = I - \frac{1}{2(n-\mu_{nl})^2}$$

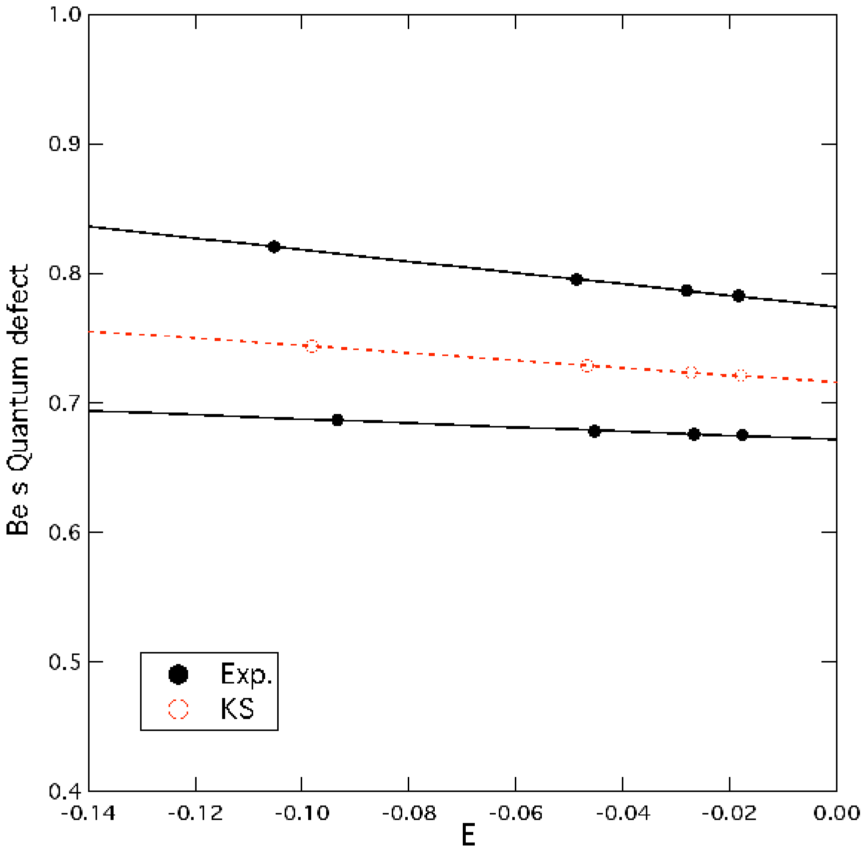
- I=ionization potential, n=principal, l=angular quantum no.s
- Due to long-ranged Coulomb potential
- Effective one-electron potential decays as -1/r.
- Absurdly precise test of excitation theory, and very difficult to get right.

Be s quantum defect: expt

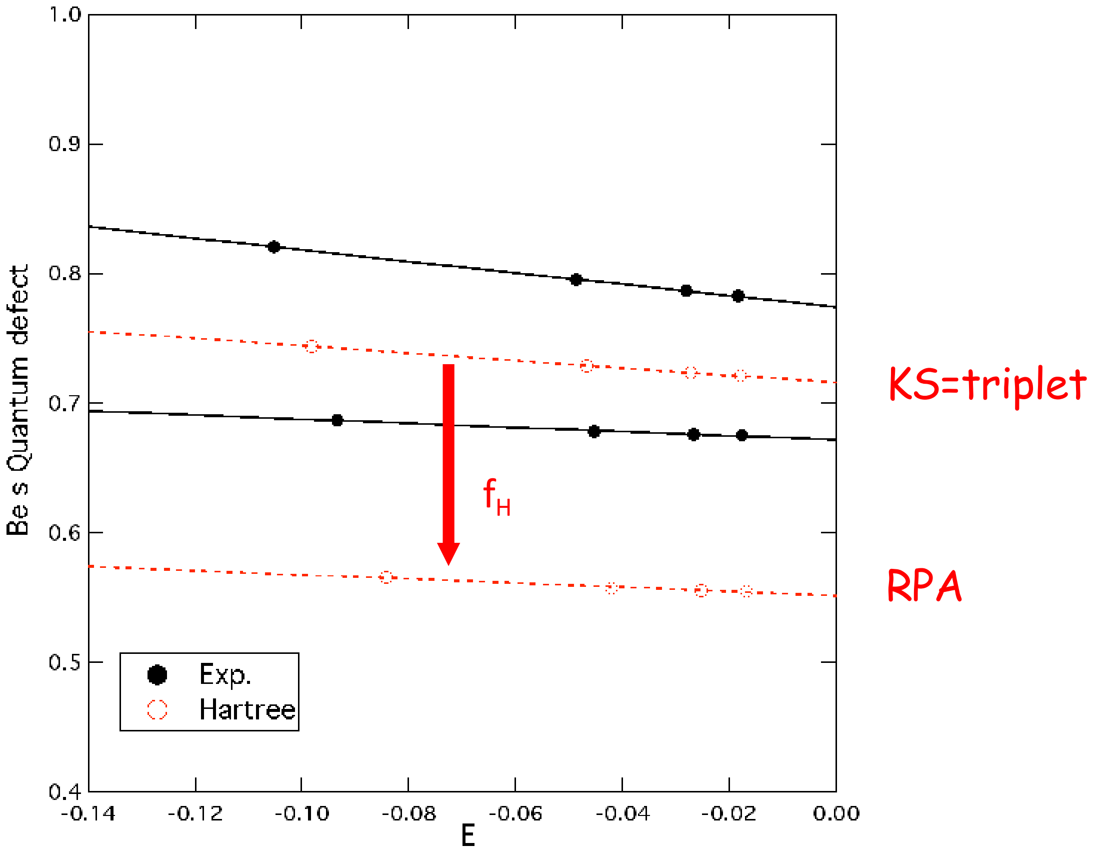


Top: triplet, bottom: singlet

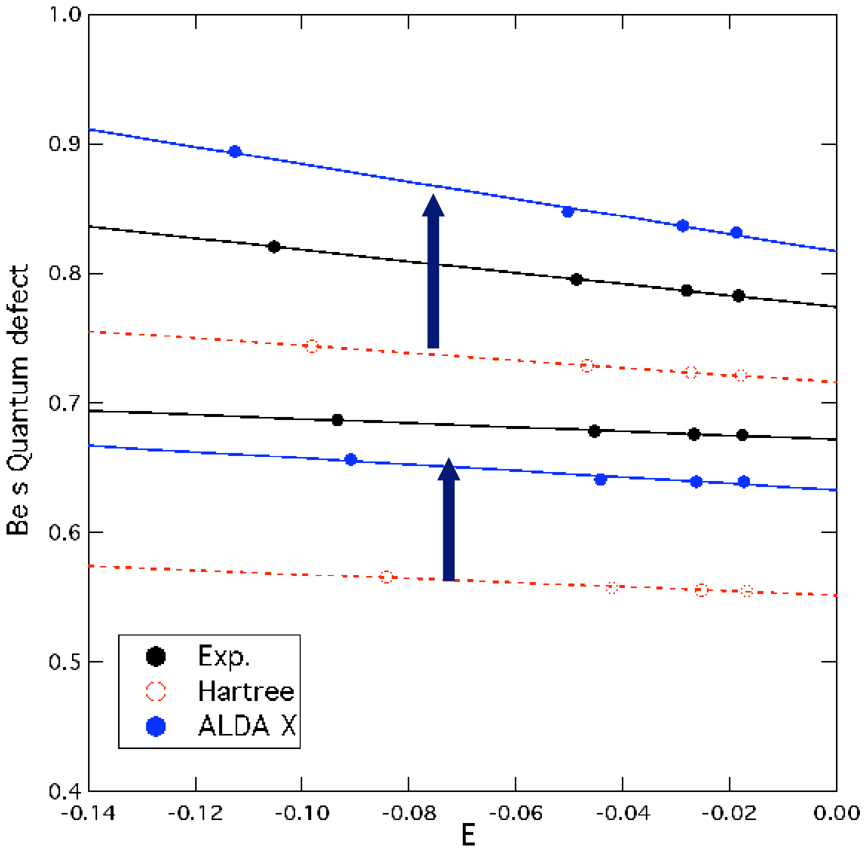
Be s quantum defect: KS



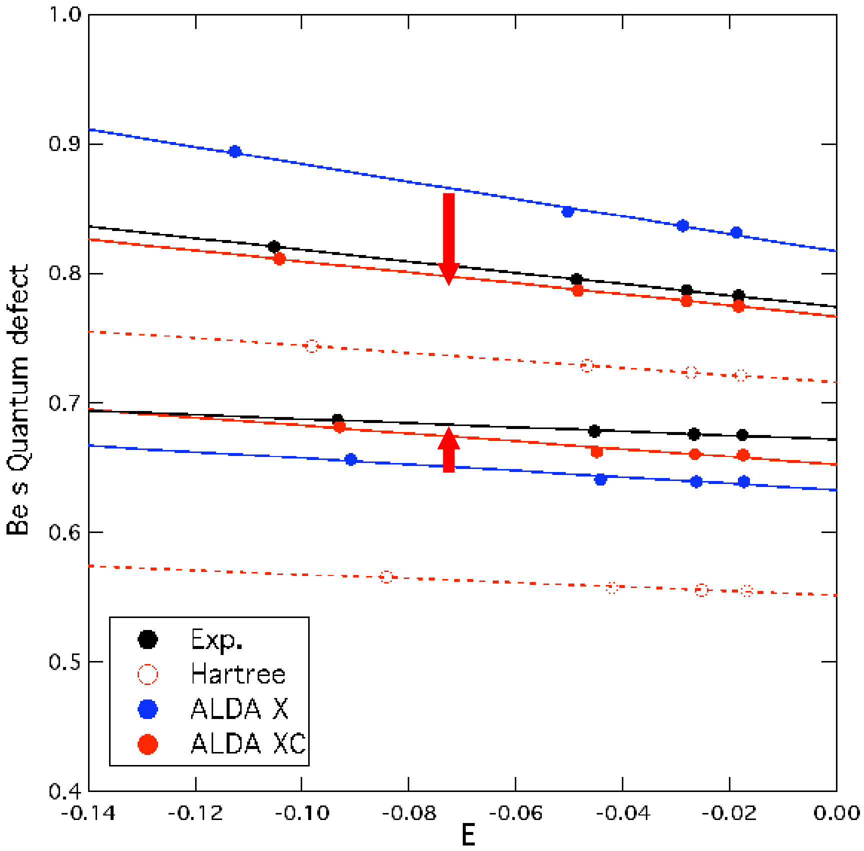
Be s quantum defect: RPA



Be s quantum defect: ALDAX



Be s quantum defect: ALDA

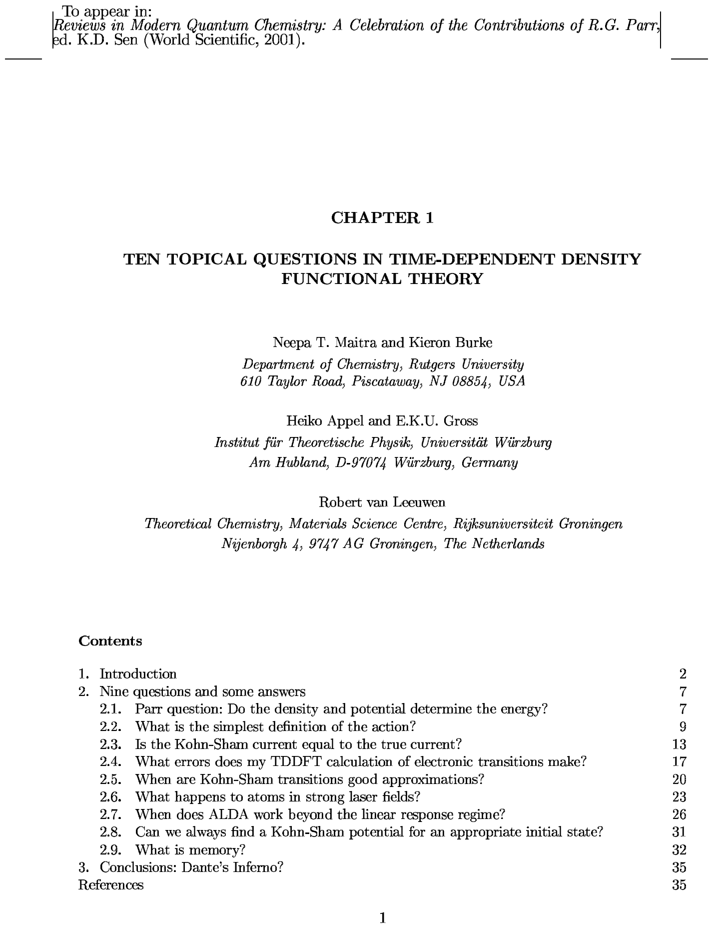


Accurate atomic quantum defects from particle–particle random phase approximation Yang Yang, Kieron Burke and Weitao Yang, *Molecular Physics* **114**, 1189-1198 (2016).

Old friends and new

Franco Bonafe (MPSD Hamburg)	Stefan Kurth (CSIC - UPV/EHU, San Sebastian)	Gianluca Stefanucci (University of Rome Tor Vergata)
Dominik Sidler (Paul Scherrer Institute, Villingen)	Eric Suraud (Paul Sabatier University, Toulouse)	Sangeeta Sharma (Max Born Institute, Berlin)
I-Te Lu (MPSD Hamburg)	Simone Latini (Technical University of Denmark)	Carsten Ullrich (University of Missouri)
Raffaele Resta (IOM-CNR Democriitos, Trieste)	Ivano Tavernelli (IBM Zurich)	Kazuhiro Yabana (University of Tsukuba, Japan)
Stephan Kuemmel (University of Bayreuth)	Robert van Leeuwen (University of Jyväskylä)	Steven G. Louie (University of California, Berkeley)
Kieron Burke (UC Irvine)	Giovanni Vignale (University of Missouri)	Andreas Goerling (University of Erlangen-Nürnberg)
Lucia Reining (LSI, Ecole Polytechnique Palaiseau, CNRS)	Leeor Kronik (Weizmann Institute of Science)	Shane Parker (Case Western Reserve University, Cleaveland, Ohio)
David Strubbe (University of California, Merced)		

From BEFORE Benasque



To appear in:
Reviews in Modern Quantum Chemistry: A Celebration of the Contributions of R.G. Parr,
ed. K.D. Sen (World Scientific, 2001).

CHAPTER 1

TEN TOPICAL QUESTIONS IN TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

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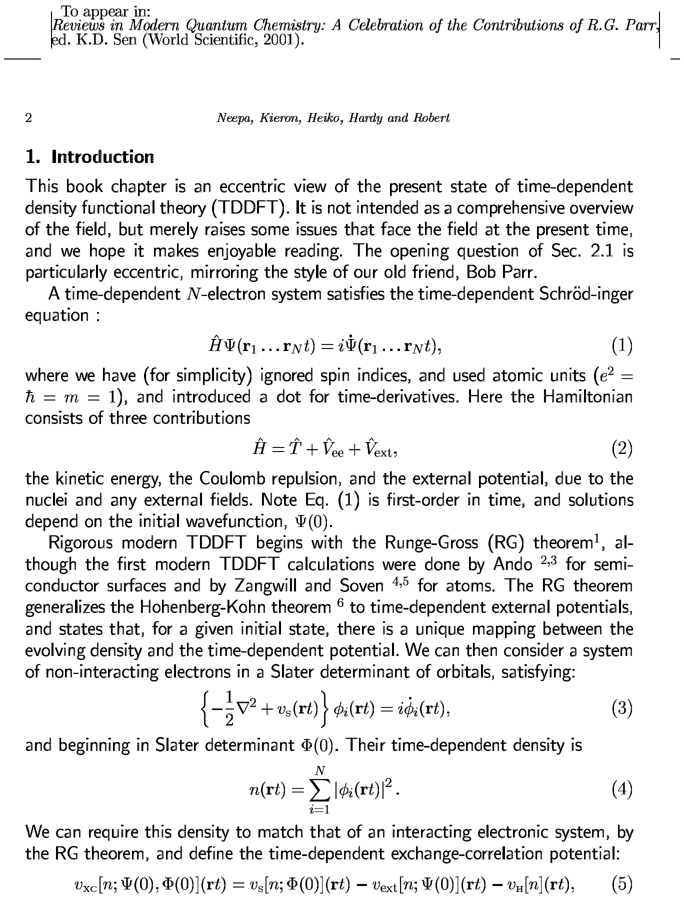
Contents



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Reviews in Modern Quantum Chemistry: A Celebration of the Contributions of R.G. Parr,
ed. K.D. Sen (World Scientific, 2001).

1. Introduction

This book chapter is an eccentric view of the present state of time-dependent density functional theory (TDDFT). It is not intended as a comprehensive overview of the field, but merely raises some issues that face the field at the present time, and we hope it makes enjoyable reading. The opening question of Sec. 2.1 is particularly eccentric, mirroring the style of our old friend, Bob Parr.

A time-dependent N-electron system satisfies the time-dependent Schröd-inger equation :

$$\hat{H}\Psi(\mathbf{r}_1 \ldots \mathbf{r}_N t) = i\dot{\Psi}(\mathbf{r}_1 \ldots \mathbf{r}_N t), \tag{1}$$

where we have (for simplicity) ignored spin indices, and used atomic units ($e^2 = \hbar = m = 1$), and introduced a dot for time-derivatives. Here the Hamiltonian consists of three contributions

$$\hat{H} = \hat{T} + \hat{V}_{\rm ee} + \hat{V}_{\rm ext}, \tag{2}$$

the kinetic energy, the Coulomb repulsion, and the external potential, due to the nuclei and any external fields. Note Eq. (1) is first-order in time, and solutions depend on the initial wavefunction, $\Psi(0)$.

Rigorous modern TDDFT begins with the Runge-Gross (RG) theorem[1], although the first modern TDDFT calculations were done by Ando [2,3] for semiconductor surfaces and by Zangwill and Soven [4,5] for atoms. The RG theorem generalizes the Hohenberg-Kohn theorem [6] to time-dependent external potentials, and states that, for a given initial state, there is a unique mapping between the evolving density and the time-dependent potential. We can then consider a system of non-interacting electrons in a Slater determinant of orbitals, satisfying:

$$\left\{-\frac{1}{2}\nabla^2 + v_{\rm s}(\mathbf{r}t)\right\}\phi_i(\mathbf{r}t) = i\dot{\phi}_i(\mathbf{r}t), \tag{3}$$

and beginning in Slater determinant $\Phi(0)$. Their time-dependent density is

$$n(\mathbf{r}t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r}t)|^2 . \tag{4}$$

We can require this density to match that of an interacting electronic system, by the RG theorem, and define the time-dependent exchange-correlation potential:

$$v_{\rm xc}[n;\Psi(0),\Phi(0)](\mathbf{r}t) = v_{\rm s}[n;\Phi(0)](\mathbf{r}t) - v_{\rm ext}[n;\Psi(0)](\mathbf{r}t) - v_{\rm H}[n](\mathbf{r}t), \tag{5}$$

20 years of Benasque TDDFT

- Initiated by Angel Rubio and Miguel Marques
- Very fond memories of many late nights, discussing twisted logic of TDDFT
- Led to edited volume, TDDFT, 1st and 2nd editions (now also have Carsten's textbook).
- Molecular electronics was a very hot topic for a while.
- Carsten Ullrich and I initiated analog in US (St John's school, GRC, Telluride meetings…)

outline

- Ensemble DFT
- Recent activity
- New work with Kim Daas

Two old theorems

- Runge-Gross theorem (1984) puts TDDFT on firm footing.

- But Gross-Olivera-Kohn (1988) also establish EDFT, a variational approach giving access to excited state energies (and related properties)

Many uses of ensembles in DFT

- Most famous: Ensemble of fractional particle numbers, used to see ground-state derivative discontinuity (PPLB)
- Thermal ensembles, used for simulating WDM with thDFT
- Ensembles of fixed N, differing occupations, used for excited states (eDFT)✓
- All originate from Levy-Lieb density matrix formulation for F[n].

Use of Hubbard model in DFT

- Key reviews:

The Hubbard dimer: a density functional case study of a many-body problem D J Carrascal D.J., Ferrer, J., Smith, J. *and KB* 2015 *J. Phys.: Condens. Matter* **27** 393001

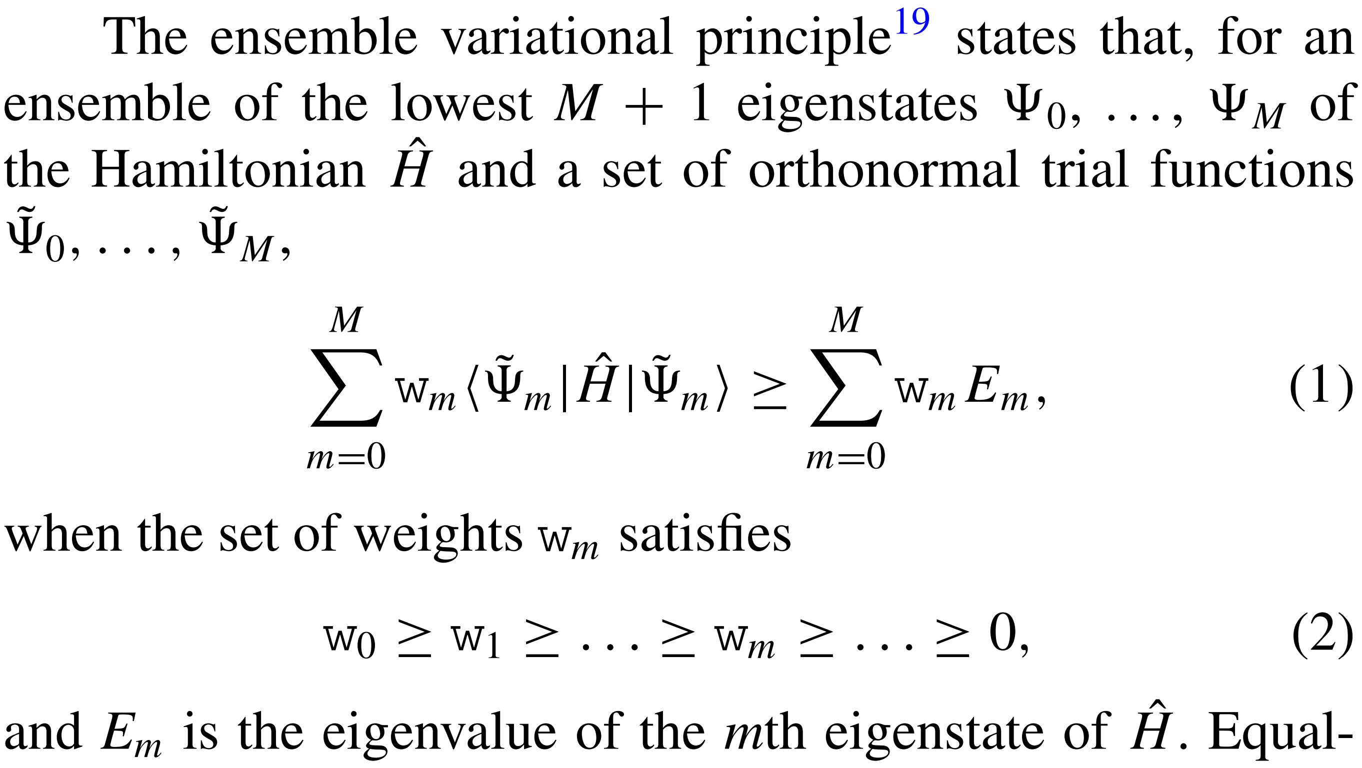
Linear response time-dependent density functional theory of the Hubbard dimer Carrascal, D.J., Ferrer, J., Maitra, N. *and KB.* Linear response time-dependent density functional theory of the Hubbard dimer. *Eur. Phys. J. B* **91,** 142 (2018).

- Extremely limited Hilbert space
- Mostly analytic results-questions of principle
- Can study strong correlation
- But learn NOTHING about approximate functionals in 'real' world

eDFT history

- 1979: Theophilou formulates theorem
- 1988: GOK papers
  - Good theorem, poor approximation
- 2002: GPG Gidapoulus and Gross
  - Identify ghosts in Ex and how to remove them
- 2017: Yang, Pribram-Jones, Ullrich, KB
  - Exact w-dependent potentials
  - DEC: Special ensemble, w->0
- Since then: Much recent activity
  - Fromager
  - Gould and Pittalis

Variational theorem



The ensemble variational principle[19] states that, for an ensemble of the lowest $M + 1$ eigenstates $\Psi_0, \ldots, \Psi_M$ of the Hamiltonian $\hat{H}$ and a set of orthonormal trial functions $\tilde{\Psi}_0, \ldots, \tilde{\Psi}_M$,

$$\sum_{m=0}^{M} \mathrm{w}_m \langle \tilde{\Psi}_m | \hat{H} | \tilde{\Psi}_m \rangle \geq \sum_{m=0}^{M} \mathrm{w}_m E_m , \qquad (1)$$

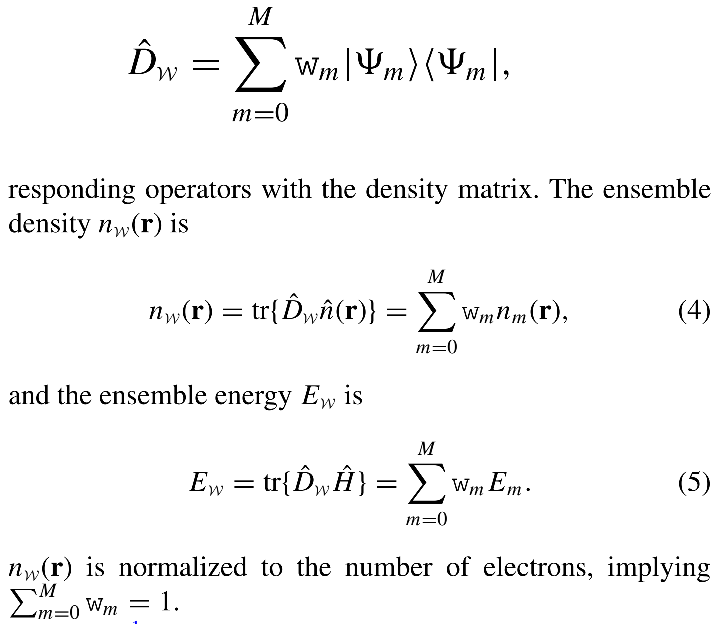
when the set of weights w_m satisfies

$$\mathrm{w}_0 \geq \mathrm{w}_1 \geq \ldots \geq \mathrm{w}_m \geq \ldots \geq 0, \qquad (2)$$

and E_m is the eigenvalue of the mth eigenstate of $\hat{H}$. Equal-

A.Theophilou, J. Phys. C **12**, 5419 (1979)

DFT version



$$\hat{D}_{\mathrm{w}} = \sum_{m=0}^{M} \mathrm{w}_m |\Psi_m\rangle\langle\Psi_m|,$$

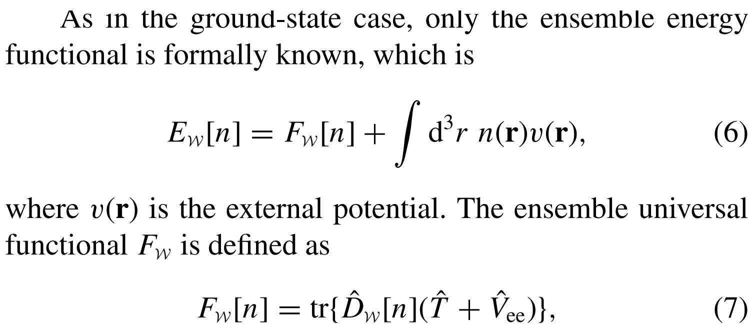
responding operators with the density matrix. The ensemble density $n_{\mathrm{w}}(\mathbf{r})$ is

$$n_{\mathrm{w}}(\mathbf{r}) = \mathrm{tr}\{\hat{D}_{\mathrm{w}}\hat{n}(\mathbf{r})\} = \sum_{m=0}^{M} \mathrm{w}_m n_m(\mathbf{r}), \tag{4}$$

and the ensemble energy E_{w} is

$$E_{\mathrm{w}} = \mathrm{tr}\{\hat{D}_{\mathrm{w}}\hat{H}\} = \sum_{m=0}^{M} \mathrm{w}_m E_m. \tag{5}$$

$n_{\mathrm{w}}(\mathbf{r})$ is normalized to the number of electrons, implying $\sum_{m=0}^{M} \mathrm{w}_m = 1$.



As in the ground-state case, only the ensemble energy functional is formally known, which is

$$E_{\mathrm{w}}[n] = F_{\mathrm{w}}[n] + \int \mathrm{d}^3r\; n(\mathbf{r})v(\mathbf{r}), \tag{6}$$

where $v(\mathbf{r})$ is the external potential. The ensemble universal functional F_{w} is defined as

$$F_{\mathrm{w}}[n] = \mathrm{tr}\{\hat{D}_{\mathrm{w}}[n](\hat{T} + \hat{V}_{\mathrm{ee}})\}, \tag{7}$$

Ensemble KS equations

$$\left\{-\frac{1}{2}\nabla^2 + v_{\mathrm{S},w}[n_w](\mathbf{r})\right\}\phi_{j,w}(\mathbf{r}) = \epsilon_{j,w}\phi_{j,w}(\mathbf{r}).$$

$$n_w(\mathbf{r}) = \sum_{m=0}^{M} \mathrm{w}_m n_m(\mathbf{r}) = \sum_{m=0}^{M} \mathrm{w}_m n_{\mathrm{S,m}}(\mathbf{r}),$$

$$\begin{aligned} E_w[n] &= T_{\mathrm{S},w}[n] + V[n] + E_{\mathrm{H}}[n] + E_{\mathrm{XC},w}[n] \\ &= \mathrm{tr}\{\hat{D}_{\mathrm{S},w}\hat{T}\} + \int \mathrm{d}^3r\ n(\mathbf{r})v(\mathbf{r}) \\ &\quad + E_{\mathrm{H}}[n] + E_{\mathrm{XC},w}[n], \end{aligned}$$

Two 2014 papers on exact eDFT

[Y14] Exact and approximate Kohn-Sham potentials in ensemble density-functional theory, Zeng-hui Yang, John R. Trail, Aurora Pribram-Jones, Kieron Burke, Richard J. Needs, Carsten A. Ullrich, *Phys. Rev. A* **90**, 042501 (2014).

Exact eDFT XC potentials and energies in 3D real space

[P14] Excitations and benchmark ensemble density functional theory for two electrons Aurora Pribram-Jones, Zeng-hui Yang, John R. Trail, Kieron Burke, Richard J. Needs, Carsten A. Ullrich *The Journal of Chemical Physics* **140**, (2014)

Exact eDFT XC potentials in 1d real-space and careful definition of SEHX approximation

Warning

[151] Excitations and benchmark ensemble density functional theory for two electrons A. Pribram-Jones, Z. Yang, J. Trail, K. Burke, R. Needs, and C. Ullrich, *J. Chem. Phys.* **140**, (2014). DOI: 10.1063/1.4872255

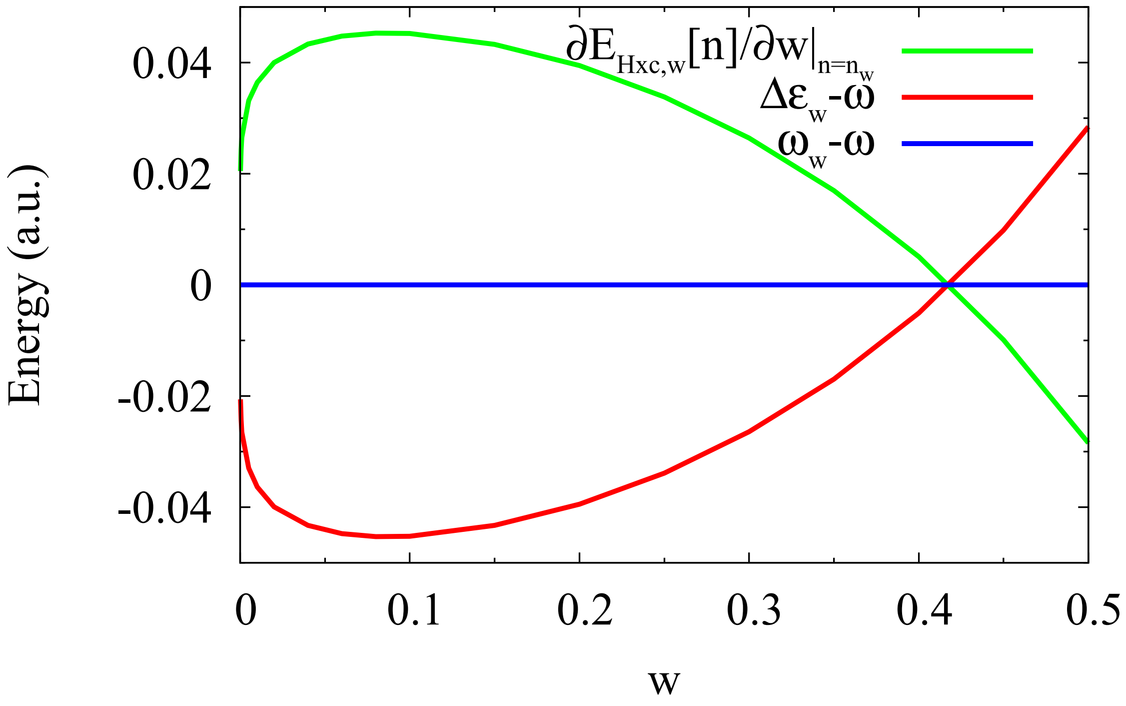


FIG. 7. (Color online) Equation (10) applied to the exact helium singlet ensemble, demonstrating the exact cancellation of all w dependence in KS gaps (red bottom line for small w) and corrections to the KS gap (green top line for small w), leading to no w dependence

Zenghui's insight

- Uses a different ensemble
- Takes w->0, so produces a correction on ground-state calculation (no longer need find w-dependent density).
- We call it Direct Excitation Correction (DEC)
- Insert SEHX
- Find all intermediate levels cancel, so can get e.g.,12th excitation as simple correction to KS transition.

[179] Direct Extraction of Excitation Energies from Ensemble Density-Functional Theory Z. Yang, A. Pribram-Jones, K. Burke, and C. Ullrich, *Phys. Rev. Lett.* **119**, 033003 (2017). DOI: 10.1103/PhysRevLett.119.033003

[188] Accurate double excitations from ensemble density functional calculations F. Sagredo and K. Burke, *J. Chem. Phys.* **149**, 134103 (2018). DOI: 10.1063/1.5043411

Does eDFT really work?

PRL **119,** 243001 (2017) PHYSICAL REVIEW LETTERS week ending 15 DECEMBER 2017

Hartree and Exchange in Ensemble Density Functional Theory:

PHYSICAL REVIEW LETTERS **123,** 016401 (2019)

PHYSICAL REVIEW LETTERS **130,** 106401 (2023)

Editors' Suggestion Featured in Physics

Electronic Excited States in Extreme Limits via Ensemble Density Functionals

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ierarchical

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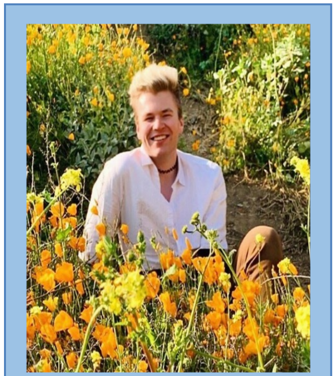
(Received 10 January 2021; revised 26 March 2021; accepted 2 June 2021; published 7 July 2021)

Last year

Thais Scott



John Kozlowski

Steven Crisostomo

Aurora Pribram-Jones

[228] Exact Conditions for Ensemble Density Functional Theory T. Scott, J. Kozlowski, S. Crisostomo, A. Pribram-Jones, and K. Burke, *Phys. Rev. B* **109**, 195120 (2024)

Results in that paper

- New exact conditions for eDFT functionals
- Illustration on Hubbard dimer
- New derivative discontinuity
- Comprehensive Supp Info of many figures for Hubbard dimer

Introducing ETDDFT

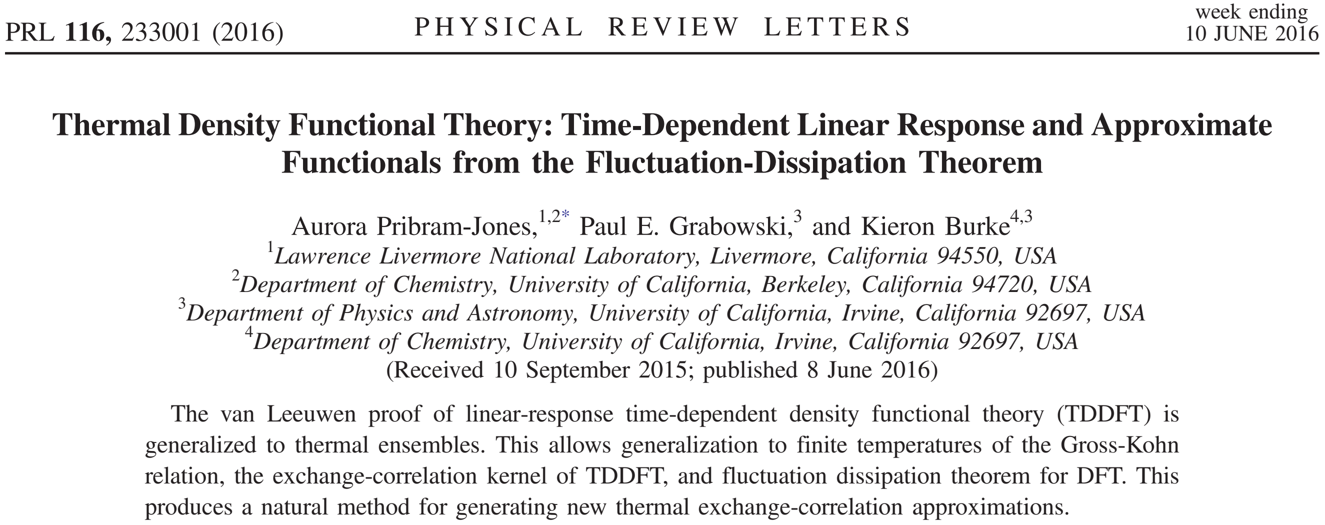
- Create an ensemble of fixed weights
- Time-evolve a Hamiltonian with those fixed weights
- Consider linear response with those weights
- Weights are static, chosen by the user, and same in both systems
- The usual theorems go through

Double Gross

Ensemble-weighted response function

$$\chi^w(\mathbf{r},\mathbf{r}',\omega) = \sum_{m=0}^{M}\sum_{J\neq m}^{W} w_m \frac{\langle m|\,\hat{n}(\mathbf{r})\,|J\rangle\,\langle J|\,\hat{n}(\mathbf{r}')\,|m\rangle}{\omega-(E_J-E_m)+i\eta} + cc..,$$

Van Leeuwen proof in linear response



PRL **116,** 233001 (2016) PHYSICAL REVIEW LETTERS week ending 10 JUNE 2016

Thermal Density Functional Theory: Time-Dependent Linear Response and Approximate Functionals from the Fluctuation-Dissipation Theorem

Aurora Pribram-Jones,[1,2*] Paul E. Grabowski,[3] and Kieron Burke[4,3]
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(Received 10 September 2015; published 8 June 2016)

The van Leeuwen proof of linear-response time-dependent density functional theory (TDDFT) is generalized to thermal ensembles. This allows generalization to finite temperatures of the Gross-Kohn relation, the exchange-correlation kernel of TDDFT, and fluctuation dissipation theorem for DFT. This produces a natural method for generating new thermal exchange-correlation approximations.

$$m^{\tau}(s) = \int d^3r\,\delta n^{\tau}(\mathbf{r},s)\,\delta v(\mathbf{r},s).$$

$$m^{\tau}(s) = -2\sum_{i=0}^{\infty}\sum_{j=i+1}^{\infty}\frac{(w_i - w_j)\omega_{ji}}{s^2+\omega_{ji}^2}|\Delta V_{ij}^{\tau}(s)|^2.$$

Ensemble Gross-Kohn equation

$$\chi_w(\mathbf{r},\mathbf{r}',\omega) = \chi_{s,w}(\mathbf{r},\mathbf{r}',\omega) + \int d^3r_1 \int d^3r_2 \;\; \chi_{s,w}(\mathbf{r},\mathbf{r}_1,\omega) f_{\mathrm{HXC,w}}(\mathbf{r}_1\mathbf{r}_2,\omega)\chi_w(\mathbf{r}_2,\mathbf{r}',\omega)$$

Ensemble HXC kernel

- Linguistics:
  - Adiabatic and dynamic just like in TDDFT
  - Pure- and ensemble- mean w=0 or non-zero

	$w \to 0$	$w \neq 0$
$\omega \to 0$	Pure Adiabatic	Ensemble Adiabatic
$\omega \neq 0$	Pure Dynamic	Ensemble Dynamic

- 5 approximations of RPA type:
  - Hartree, i.e., RPA
  - Hartee-exchange (w-dependent)
  - Exact pure adiabatic approx.
  - Exact pure dynamic approx.
  - Exact ensemble adiabatic

Ensemble relation between coupling constant and scaling

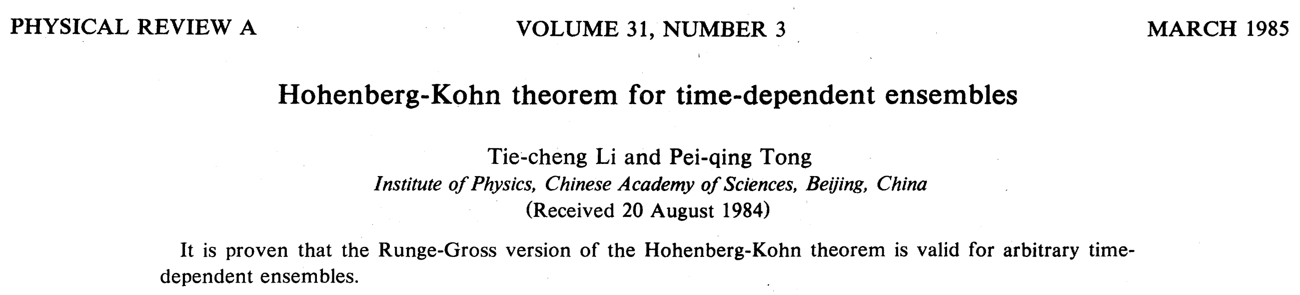
$$v^{\lambda}_{xc,w}[n](\mathbf{r},\omega) = \lambda^2 v_{xc,w}[n_{1/\lambda}](\lambda\mathbf{r},\lambda^2\omega).$$

Ensemble ACFDT

$$E_{xc,w}[n] = -\int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \left\{ \frac{n_w(\mathbf{r})}{2} \delta(\mathbf{r}-\mathbf{r}') + \int_0^\infty \frac{d\omega}{2\pi} \, \mathrm{Im}\, \chi_w^\lambda(\mathbf{r},\mathbf{r}',\omega) \right\},$$

Relation between kernel and potential

- General case



PHYSICAL REVIEW A VOLUME 31, NUMBER 3 MARCH 1985

Hohenberg-Kohn theorem for time-dependent ensembles

Tie-cheng Li and Pei-qing Tong
Institute of Physics, Chinese Academy of Sciences, Beijing, China

(Received 20 August 1984)

It is proven that the Runge-Gross version of the Hohenberg-Kohn theorem is valid for arbitrary time-dependent ensembles.

$$f_{\mathsf{Hxc}}[n_{GS}](\mathbf{r},\mathbf{r}',t-t') = \left.\frac{\delta v_{\mathsf{Hxc}}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}\right|_{n=n_{\rm GS}}$$

Connection to general time-dependence

- In fact, full RG proof generalized to initial ensemble density matrix
- In general case, this leads to dependence on initial density-matrix (both interacting and KS) as well as time-dependent density
- But, for an initial non-degenerate ground-state, this initial dependence is eliminated via HK theorems
- Real content: For a (monotonically decreasing) initial ensemble, initial density matrix dependence is absorbed via GOK

5 topical questions in TDDFT

1. How to go beyond the adiabatic approximation?
2. Why not report adiabatic LDA and PBE results to show spread whenever calculations done?
3. Is there an analog of the RG theorem for the one-body Green’s function?
4. What is the semiclassical limit of TDDFT, analogous to the Lieb-Simon limit of ground-state DFT?
5. Can one derive iDFT for molecular electronics from TDDFT?
6. How to use ML in TDDFT?

What does ETDDFT buy us?

- Access to transitions between excited states
- Possibility of feedback:
  - Approximate kernel, extract approximate transitions from resulting static ensemble functional
  - Construct approximate kernel using approx. transitions
  - EDFT does give double excitations
- Maybe best of both worlds?
- Hope to have answers shortly on Hubbard dimer…

Summary

- EDFT is a growing competitor to TDDFT for low-lying excitations
- ETDDFT is a new alternative that combines the best(?) of both
- Will illustrate on the Hubbard dimer
- All work of Kim Daas, Chancellor's Postdoctoral Fellow, UCI
- Also support of NSF.