Basics of DFT

Kieron Burke and Lucas Wagner

Departments of Physics and of Chemistry, University of California, Irvine, CA 92697, USA

March 13, 2012

Outline

1. General background

2. DFT
   - background
   - Kohn-Sham

3. Common functionals
   - LDA
   - GGA
   - Hybrids

Outline

1. General background
2. DFT
   - background
   - Kohn-Sham
3. Common functionals
   - LDA
   - GGA
   - Hybrids

Electronic structure problem

- What atoms, molecules, and solids can exist, and with what properties?

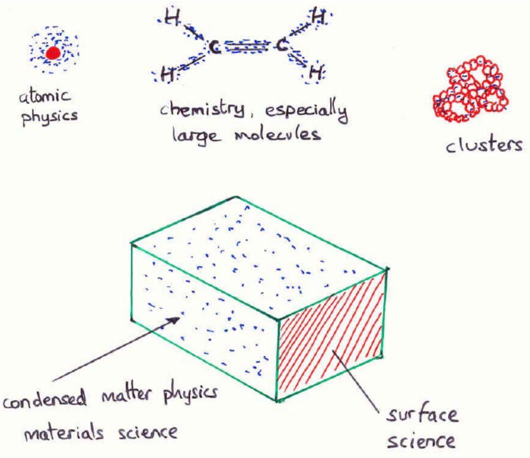


Figure: My first ever DFT transparency

Atomic units

- In atomic units, all energies are in Hartree (1H$=$ 27.2 eV) and all distances in Bohr ($1a_0 = 0.529$ Å)
- To write formulas in atomic units, set $e^2 = \hbar = m_e = 1$
- In regular units,
    - 1 H $=$ 27.2eV
    - 1 eV $=$ 23.06 kcal/mol
    - 1 kcal $=$ 4.184 kJ/mol $=$ 503K.

Born-Oppenheimer approximation

- Because of difference between proton and electron mass, can separate wavefunction into product to an excellent approximation.
- Because electronic energies are in eV and much greater than 300K, electrons always in ground state.
- Yields

$$E_{total} = E_{nuc}(\{\mathbf{R}_\alpha\}) + E_{elec}(\{\mathbf{R}_\alpha\})$$

  where electons are in ground state.

- Knowing $E_{total}(\{\mathbf{R}_\alpha\})$ yields structures from minima, vibrations from curvature, all reaction energies from well-depths, all transition states from saddle points, etc.

Hamiltonian

- Hamiltonian for N electrons in the presence of external potential $v(\mathbf{r})$:

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

  where the kinetic and elec-elec repulsion energies are

  $$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2, \qquad \hat{V}_{\rm ee} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

  and difference between systems is N and the one-body potential

  $$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i)$$

- Often $v(\mathbf{r})$ is electron-nucleus attraction

  $$v(\mathbf{r}) = -\sum_{\alpha}\frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|}$$

  where α runs over all nuclei, plus weak applied **E** and **B** fields.

Schrödinger equation

- $6N$-dimensional Schrödinger equation for stationary states

$$\{\hat{T} + \hat{V}_{\rm ee} + \hat{V}\}\,\Psi = E\,\Psi, \qquad \Psi \text{ antisym}$$

- The one-particle density is much simpler than Ψ:

$$n(\mathbf{r}) = N \sum_{\sigma_1} \ldots \sum_{\sigma_N} \int d^3r_2 \ldots d^3r_N |\Psi(\mathbf{r}\sigma_1, \mathbf{r}_2\sigma_2, \ldots, \mathbf{r}_N\sigma_N)|^2$$

  and $n(\mathbf{r})\,d^3r$ gives probability of finding any electron in d^3r around $\mathbf{r}$.
- Wavefunction variational principle:
  - $E[\Psi] \equiv \langle\Psi|\hat{H}|\Psi\rangle$ is a *functional*
  - Extrema of $E[\Psi]$ are stationary states, and ground-state energy is

$$E = \min_{\Psi} \langle\Psi|\,\hat{T} + \hat{V}_{\rm ee} + \hat{V}|\Psi\rangle$$

  where Ψ is normalized and antisym.

First principles

- A *model chemistry* is given by specifying:
  - Level of treatment
  - Basis sets: plane-wave or localized
  - Pseudopotential
- Surfaces:
- Different methods:
  - Physics: Green's functions , QMC, DMRG, DMFT, ...
  - Quantum chemistry: CI, CC, MCSCF, CASSCF, MP2, MP4, ...
- *Ab initio* versus DFT

Outline

1. General background

2. DFT
   - background
   - Kohn-Sham

3. Common functionals
   - LDA
   - GGA
   - Hybrids

References for ground-state DFT

- *ABC of DFT*, by KB and Rudy Magyar, http://dft.uci.edu/
- *A Primer in Density Functional Theory*, edited by C. Fiolhais et al. (Springer-Verlag, NY, 2003)
- *Density Functional Theory*, Dreizler and Gross, (Springer-Verlag, Berlin, 1990)
- *Density Functional Theory of Atoms and Molecules*, Parr and Yang, (Oxford, New York, 1989)
- *A Chemist's Guide to Density Functional Theory*, Koch and Holthausen (Wiley-VCH, Weinheim, 2000)
- *Which functional should I choose?* Rappoport, Crawford, Furche, and Burke. http://dft.uci.edu/

Brief history of DFT

- 1926: Old DFT was Thomas-Fermi theory and extensions.
- 50's and 60's: Slater and co-workers develop Xα as crude KS-LDA.
- 1965: Modern DFT begins with Kohn-Sham equations. By introducing orbitals, get 99% of the kinetic energy right, get accurate $n(\mathbf{r})$, and only need to approximate a small contribution, $E_{\rm XC}[n]$.
- 1965: KS also suggested local density approximation (LDA) and gradient expansion approximation.
- 1993: More modern functionals (GGA's and hybrids) shown to be usefully accurate for thermochemistry
- 1998: Kohn and Pople win Nobel prize in chemistry
- 2010: DFT in materials science, geology, soil science, astrophysics, protein folding,...

Hohenberg-Kohn theorem (1964)

1. Rewrite variational principle (Levy 79):

$$
\begin{aligned}
E &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{\rm ee} + \hat{V} | \Psi \rangle \\
&= \min_{n} \left\{ F[n] + \int d^3r \; v(\mathbf{r}) n(\mathbf{r}) \right\}
\end{aligned}
$$

where

$$
F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{\rm ee} | \Psi \rangle
$$

- The minimum is taken over all positive $n(\mathbf{r})$ such that $\int d^3r \; n(\mathbf{r}) = N$

2. The external potential $v(\mathbf{r})$ and the hamiltonian $\hat{H}$ are determined to within an additive constant by $n(\mathbf{r})$

- P. Hohenberg and W. Kohn, Phys. Rev. **136**, B 864 (1964).
- M. Levy, Proc. Natl. Acad. Sci. (U.S.A.) **76**, 6062 (1979).

Kohn-Sham 1965

- Define *fictitious* non-interacting electrons satisfying:

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

  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

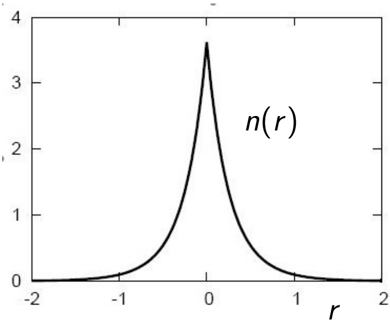
$$T + V_{\rm ee} = T_{\rm S} + U + E_{\rm XC}$$

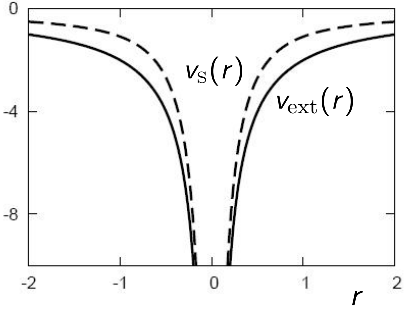
  the remainder is the exchange-correlation energy.
- Most important result of exact DFT:

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

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

KS potential of He atom





Every density has (at most) one KS potential.[1]
Dashed line: $v_{\mathrm{S}}(r)$ is the *exact* KS potential.

---

[1] *Accurate exchange-correlation potentials and total-energy components for the helium isoelectronic series*, C. J. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994).

Kohn-Sham energy components

- The KS kinetic energy is the kinetic energy of the KS orbitals

$$T_{\rm S}[n] = \frac{1}{2}\sum_{i=1}^{N}\int d^3r\ |\nabla\phi_i(\mathbf{r})|^2 \quad > 0$$

- The Hartree (aka Coulomb aka electrostatic) repulsive self-energy of a charge density is

$$U[n] = \frac{1}{2}\int d^3r \int d^3r'\, \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad > 0$$

- The exchange energy is

$$-\frac{1}{2}\sum_{\sigma}\sum_{\substack{i,j\\ occ}}\int d^3r\int d^3r'\ \frac{\phi^*_{i\sigma}(\mathbf{r})\phi^*_{j\sigma}(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}')\phi_{j\sigma}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

- $E_{\rm C}$ is everything else.

Kohn-Sham elementary facts

- T and $V_{\rm ee}$ are both positive, trying to rip system apart, but overcome by more negative V.
- Kinetic energies are positive, and $T > T_{\rm S}$ by definition.
- U is positive and dominates the electron-electron repulsion.
- $E_{\rm X}$ only has contributions from same-spin electrons and is negative. This part is given exactly by a HF calculation.
- The electron-electron repulsion of the KS wavefunction is just

$$\langle \Phi[n] | \hat{V}_{\rm ee} | \Phi[n] \rangle = U[n] + E_{\rm X}[n]$$

- $E_{\rm C}$ contains both kinetic and potential contributions:

$$\begin{aligned} E_{\rm C} &= \langle \Psi[n] | \hat{T} + \hat{V}_{\rm ee} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{V}_{\rm ee} | \Phi[n] \rangle \\ &= (T - T_{\rm S}) + (V_{\rm ee} - U - E_{\rm X}) = T_{\rm C} + U_{\rm C} \end{aligned}$$

Energy components of small spherical atoms

	T	$V_{\rm ext}$	$V_{\rm ee}$	$T_{\rm S}$	U	$E_{\rm X}$	$T_{\rm C}$	$U_{\rm C}$	$E_{\rm C}$
He	2.904	-6.753	0.946	2.867	2.049	-1.025	.037	-.079	-.042
Be	14.67	-33.71	4.375	14.59	7.218	-2.674	.073	-.169	-.096
Ne	128.9	-311.1	53.24	128.6	66.05	-12.09	.33	-.72	-.39

Table: Energy components found from the exact densities.

- Huang and Umrigar, Phys. Rev. A **56**, 290, (1997)
- Thanks to Cyrus Umrigar, Xavier Gonze, and Claudia Filippi.

Important points about KS calculations

- The total energy is *not* the sum of the orbital energies:

$$E \neq \sum_{i=1}^{N} \epsilon_i$$

- If some approximation is used for $E_{\rm XC}$, then energy can go *below* the exact ground-state energy.
- Any given formula for $E_{\rm XC}$, no matter where it came from, produces a *non-empirical* scheme for *all* electronic systems.
- The KS scheme, even with the exact functional, yields only E and $n(\mathbf{r})$ (and anything that can be deduced from them).
- In principle, from HK, *all* properties are determined by $n(\mathbf{r})$, but in reality, we only know one really well.

The KS HOMO-LUMO gap is not the fundamental gap

- The fundamental gap of any system
    - $\Delta = I - A \qquad (= 24.6\,\text{eV for He})$
- The exact Kohn-Sham gap:
    - $\Delta_{\rm S} = \epsilon_{\rm HOMO} - \epsilon_{\rm LUMO} \qquad (= \epsilon_{1s} - \epsilon_{2s} = 21.16\,\text{eV for He})$
- These gaps are *not* the same!
- KS gap is typically smaller than Δ
- Most notorious case: bulk Si
- The *exact* ground-state $E_{\rm XC}[n]$ produces a KS gap different from the fundamental gap.

Spin DFT

- In modern reality, everyone uses *spin*-density functional theory
  - U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
- Can easily generalize theorems and equations to spin densities, $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, with two different KS potentials.
- No difference for spin-unpolarized systems, but much more accurate otherwise (odd electron number, radicals, etc.)
- Spin-scaling trivial for $E_{\rm X}$, not so for correlation.
- Can handle collinear **B** fields

Lessons about basic DFT

- DFT is
    - different from all other methods of directly solving the Schrödinger equation.
    - in principle exact for E and $n(\mathbf{r})$, knowing only $E_{\rm XC}[n]$.
    - approximate in practice.

- Exact DFT tells us what we can and cannot expect our functionals to be able to do.

- $v_{\rm S}(\mathbf{r})$ and $\phi_j(\mathbf{r})$ are *not* real, just logical constructions. The $\phi_j(\mathbf{r})$ can be very useful interpretative tools and follow intuition, but $v_{\rm S}(\mathbf{r})$ is dangerous.

Outline

1. General background

2. DFT
   - background
   - Kohn-Sham

3. Common functionals
   - LDA
   - GGA
   - Hybrids

Functionals in common use

- Local density approximation (LDA)
  - Uses only $n(\mathbf{r})$ at a point,

$$E_{\rm XC}^{\rm LDA}[n] = \int d^3r\ e_{\rm XC}^{\rm unif}(n(\mathbf{r}))$$

- Generalized gradient approx (GGA)
  - Uses both $n(\mathbf{r})$ and $|\nabla n(\mathbf{r})|$

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

  - Examples are PBE and BLYP
- Hybrid:

$$E_{\rm XC}^{\rm hyb}[n] = a(E_{\rm X} - E_{\rm X}^{\rm GGA}) + E_{\rm XC}^{\rm GGA}[n]$$

  - Mixes some fraction of HF, a usually about 25%
  - Examples are B3LYP and PBE0

Functional Soup

- Good: choose one functional of each kind and stick with it (e.g., LDA, PBE, or PBE0).

- Bad: Run several functionals, and pick 'best' answer.

- Ugly: Design your own functional with 2300 parameters.

- Empirical
  - GGA: BLYP
  - Hybrid: B3LYP
- Names:
  - B=B88 exchange
  - LYP = Lee-Yang-Parr correlation

- Non-empirical
  - GGA:PBE
  - Meta-GGA: TPSS
  - Hybrid: PBE0

Functional Soup

- Good: choose one functional of each kind and stick with it (e.g., LDA, PBE, or PBE0).
- Bad: Run several functionals, and pick 'best' answer.
- Ugly: Design your own functional with 2300 parameters.

- Empirical
  - GGA: BLYP
  - Hybrid: B3LYP
- Names:
  - B=B88 exchange
  - LYP = Lee-Yang-Parr correlation

- Non-empirical
  - GGA:PBE
  - Meta-GGA: TPSS
  - Hybrid: PBE0

Functional Soup

- Good: choose one functional of each kind and stick with it (e.g., LDA, PBE, or PBE0).
- Bad: Run several functionals, and pick 'best' answer.
- Ugly: Design your own functional with 2300 parameters.

- Empirical
  - GGA: BLYP
  - Hybrid: B3LYP
- Names:
  - B=B88 exchange
  - LYP = Lee-Yang-Parr correlation

- Non-empirical
  - GGA:PBE
  - Meta-GGA: TPSS
  - Hybrid: PBE0

Local density approximation (LDA)

- Exchange is trivial (Dirac, 1931)

$$e_{\rm X}^{\rm unif}(n) = A_{\rm X}\, n^{4/3}, \qquad A_{\rm X} = -0.738$$

- Correlation energy known:
  $e_{\rm C}^{\rm unif}(n)$ was accurately calculated by QMC
  - D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- Several different accurate parametrizations in use:
  - PW92 – Perdew and Wang, Phys. Rev. B **45**, 13244 (1992)
  - PZ81 – Perdew and Zunger, Phys. Rev. B **23**, 5048 (1981)
  - VWN80, aka S-VWN-5
    S. H. Vosco, L. Wilk, and M. Nusair, Can. J. Phys. **58**(8): 1200 (1980)

LDA (or LSDA) general performance

- For total energies, E_{X} is underestimated by about 10%, E_{C} is overestimated by about 200%, so E_{XC} is good to about 7% (mysterious cancellation of errors).
- For bond dissociation energies, LDA overbinds by about 1 eV /bond (30 kcal/mol), so no good for thermochemistry.
- Typical bond lengths are underestimated by 1% (unless involving an H atom), so excellent geometries and vibrations. So still used for structure.
- Bulk Fe is non-magnetic, because wrong structure has lowest energy.
- Transitions to unoccupied orbitals in bulk insulators a rough guide to quasiparticle excitations, except for too small gap.

Densities

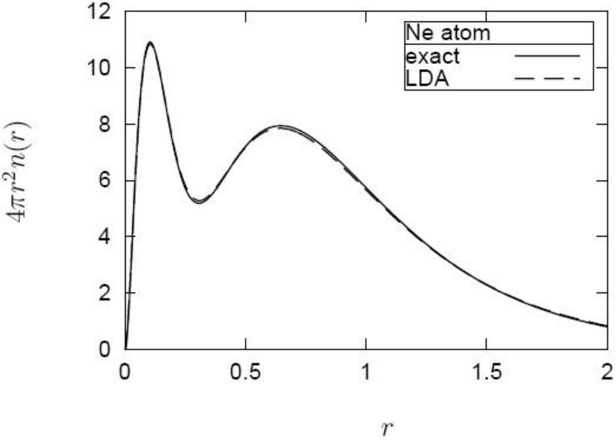


Figure: Exact and LDA radial densities of the Ne atom.

Easy conditions

- Size-consistency:

$$E_{\mathrm{XC}}[n_A + n_B] = E_{\mathrm{XC}}[n_A] + E_{\mathrm{XC}}[n_B],$$

  where $n_A(\mathbf{r})$ and $n_B(\mathbf{r})$ do not overlap.

- Uniform limit: Recover exact XC bulk jellium energy if n is constant.
- Linear response of uniform gas: LDA is almost exact for linear response to perturbation $\cos(\mathbf{q}\cdot\mathbf{r})$ for $q \leq 2k_{\mathrm{F}}$.
- Lieb-Oxford bound: Magnitude of E_{XC} cannot be greater than 2.3 $E_{\mathrm{X}}^{\mathrm{LDA}}$.

Uniform coordinate scaling

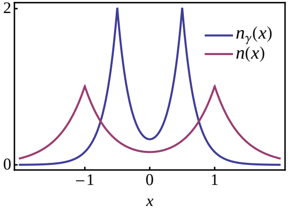


Figure: A one-dimensional density (red) being squeezed by $\gamma = 2$ (blue)

- A very handy way to study density functionals, especially in limits:

$$n_\gamma(\mathbf{r}) = \gamma^3\, n(\gamma \mathbf{r}), \qquad 0 \le \gamma \le \infty$$

  - For $\gamma > 1$, squeezes up the density, preserving norm; for $\gamma < 1$, stretches it out.
- Exchange: Require $E_{\rm X}[n_\gamma] = \gamma\, E_{\rm X}[n]$
- Correlation: $E_{\rm C}[n_\gamma] = B[n] + C[n]/\gamma + ...$ for high density limit of *finite* systems. (Violated by LDA!)

History of GGA

- Gradient expansion approximation (GEA): Expansion in density gradients that is valid for slowly-varying gas, discussed in KS65.
- Langreth-Mehl 81: First modern GGA, but cut-off in wavevector space.
- PW86: Early version of Perdew strategy, cutting off gradient-expanded hole in real space. (Phys. Rev. B, **33**)
- B88: Axel Becke $E_{\mathrm{X}}^{\mathrm{GGA}}$, based on energy density of atoms, one parameter (Phys. Rev. A. **38**)
- LYP, 88: Lee-Yang-Parr turn Colle-Salvetti orbital functional for atoms into an $E_{\mathrm{C}}[n]$ (Phys. Rev. B. **37**)
- PW91: Parametrization of real-space cut-off procedure
- PBE, 96: A re-parametrization and simplification of PW91
- RPBE, 99: Danish version, improves surface energetics
- PBEsol, 08: Revised PBE for solids

Philosophy of GGA

- If LDA is very reliable using only $n(\mathbf{r})$, surely can be more accurate if use $\nabla n(\mathbf{r})$ too.
- Use exact conditions to constrain construction.
- Non-empirical (Perdew):
  - Use known QM limits to fix all parameters.
  - Retains systematic error
  - Controlled extrapolation away from known limits
- Empirical (Becke):
  - Fit parameters to atoms and molecules.
  - Minimizes error on fitted and similar systems
  - Fails badly when applied elsewhere
- Pragmatic (Kieron):
  - Judge a Perdew functional by its derivation, not its numbers
  - Judge a Becke functional by the numbers, not its derivation.

PBE, 1996

- Correlation:
  - In slowly varying limit, $E_{\rm C} \to E_{\rm C}^{\rm GEA}$.
  - In rapidly varying limit, $E_{\rm C} \to E_{\rm C}^{\rm LDA}$.
  - In high-density limit, $E_{\rm C} \to -{\rm const.}$
- Exchange:
  - Under uniform scaling, $E_{\rm X}[n_\gamma] = \gamma E_{\rm X}[n]$.
  - Under spin-scaling, $E_{\rm X}[n_\uparrow, n_\downarrow] = (E_{\rm X}[2n_\uparrow] + E_{\rm X}[2n_\downarrow])/2$.
  - Linear response same as LDA.
  - Lieb-Oxford bound: $E_{\rm XC} \geq 2.3\, E_{\rm X}^{\rm LDA}$.

  Leads to enhancement factor:

$$F_{\rm X}(s) = 1 + \kappa - \kappa/(1 + \mu s^2/\kappa), \qquad \kappa \leq 0.804.$$

- Performance
  - Reduces LDA overbinding by 2-3.
  - Overcorrects bond lengths to about $+1\%$.

GGA general performance

- GGA reduces LSDA error in total energies by a factor of 3 or so, retaining cancellation of errors.
- For bond dissociation energies, PBE cures LDA overbinding by about a factor of 3 (typical error 0.3 eV/bond), so greatly improves thermochemistry. But still overbinds.
- BLYP is about 2 times better on G2 data set, but less systematic in errors.
- PBE *overcorrects* the LSDA error in bond lengths, from about -1% to about $+$ 1%.
- Bulk Fe is magnetic in PBE, because right structure has lowest energy.
- Transitions to unoccupied orbitals in bulk insulators a rough guide to quasiparticle excitations, except for too small gap, just as in LSDA.

Hybrids

- A hybrid functional replaces some fixed fraction of GGA exchange with exact exchange.
- First proposed by Becke
  - A.D. Becke, J. Chem. Phys. 98, 5648 (1993).
- Morphed into the infamous B3LYP, now most used functional in DFT.
- The 3 in B3LYP is 3 fitted parameters, but other 2 just modify GGA.
- PBE0 is the derived version, with 1/4 mixing rationalized.
  - Burke, Ernzerhof, and Perdew. Chem. Phys. Lett. **265**, 1996

Typical results with functionals

G2 Data Set of small molecules

m.a.e.	HF	LDA	PBE	BLYP	Hybrid
kcal/mol	100	30	10	6	3

BLYP for uniform gas

r_s	0.1	1	2	5	10
error	-50%	-30%	-40%	-50%	-60%

- Successive improvement (in energetics) at increasing computational cost.

Hybrid general performance

- PBE0 reduces PBE error in *bond energies* by a factor of 3 or so, retaining cancellation of errors.
- Typical chemical transition-state barriers are too low (even 0) in LSDA, better but too low in PBE, and best in hybrids such as PBE0.
- For G2 data set, B3LYP thermochemistry is better by factor of 2 than PBE0.
- Hybrids do not improve over GGA for ionization potentials or transition metal complexes.
- Myserteriously, hybrids calculated with HF exchange give better gaps for semiconductors.

Lessons about standard functionals

- No approximation is exact or even highly accurate.

- Use only standard functionals, preferably L(S)DA, PBE, PBE0
- Report results with LDA *and* PBE, making sure they're consistent.
- LSDA gives highly accurate densities and bond lengths, and moderately accurate energetics (but not good enough for thermochemistry).
- LSDA is very *reliable* because it satisfies many exact conditions because it uses energetics of uniform gas.
- Non-empirical GGA, such as PBE, tries to keep all good features of LSDA but improve energetics.
- Good empirical functionals are more accurate on the systems they're designed for, but less reliable away from those.

TDDFT

Kieron Burke and Lucas Wagner

Departments of Physics and of Chemistry, University of California, Irvine, CA 92697, USA

March 13, 2012

Outline

1. Time-dependent quantum mechanics
2. TDDFT: formalism
3. Linear response theory
4. Performance
5. Back to the ground state

Outline

1. Time-dependent quantum mechanics
2. TDDFT: formalism
3. Linear response theory
4. Performance
5. Back to the ground state

Time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r}_1, ..., \mathbf{r}_N; t) = (\hat{T} + \hat{V}(t) + \hat{V}_{\rm ee})\Psi(\mathbf{r}_1, ..., \mathbf{r}_N; t)$$

with kinetic energy operator:

$$\hat{T} = -\frac{1}{2}\sum_{j=1}^{N}\nabla_j^2$$

electron interaction:

$$\hat{V}_{\rm ee} = \frac{1}{2}\sum_{j\neq k}\frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}$$

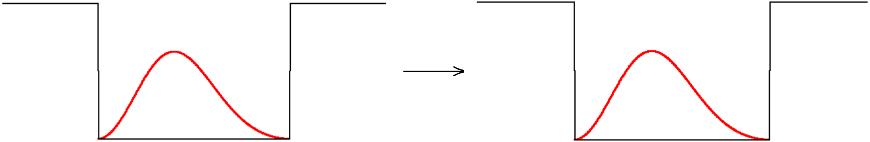
The TDSE describes the time evolution of a many-body state $\Psi(t)$ starting from an initial state $\Psi_0 = \Psi(t_0)$, under the influence of an external time-dependent potential:

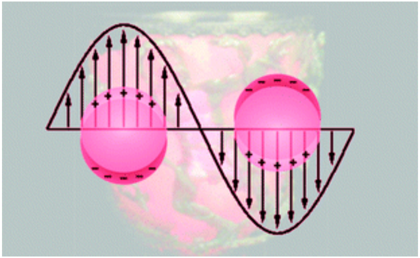
$$\hat{V}(t) = \sum_j v(\mathbf{r}_j, t).$$

Two types of time-dependence: 1. Due to initial state

Initial wavefunction is not an eigenstate: e.g.

$$\psi(x, t=0) = \frac{1}{\sqrt{5}}\{2\phi_1(x) + \phi_2(x)\}.$$





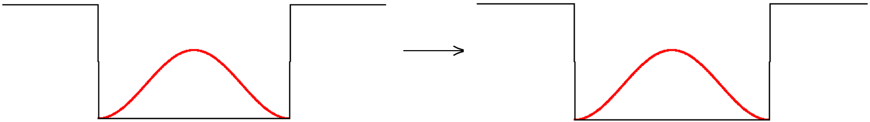
Plasmonics: oscillations of nanoparticles

- New J. Chem. **30**, 1121 (2006)
- Nature Mat. Vol. **2** No. 4 (2003)

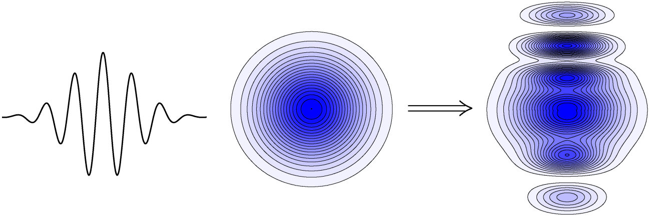
- Ullrich and Maitra's March 2010 APS TDDFT presentation

2nd type: Potential starts changing

Start in ground state, evolve in time-dependent potential $v(x,t)$:



Nonlinear response of molecules in strong laser fields:



- Ullrich and Maitra's March 2010 APS TDDFT presentation

Conservation of density in time-dependent problems

- Current operator:

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2}\sum_j (\hat{\mathbf{p}}_j \delta(\mathbf{r}-\mathbf{r}_j) + \delta(\mathbf{r}-\mathbf{r}_j)\hat{\mathbf{p}}_j)$$

- Acting on wavefunction:

$$\mathbf{j}(\mathbf{r},t) = N\int d^3r_2 \cdots \int d^3r_N \; \Im\{\Psi(\mathbf{r},\mathbf{r}_2,...,\mathbf{r}_N;t)\nabla\Psi^*(\mathbf{r},\mathbf{r}_2,...,\mathbf{r}_N;t)\}$$

- Continuity:

$$\frac{\partial n(\mathbf{r},t)}{\partial t} = -\nabla\cdot\mathbf{j}(\mathbf{r},t)$$

Outline

1. Time-dependent quantum mechanics
2. TDDFT: formalism
3. Linear response theory
4. Performance
5. Back to the ground state

Recent reviews on TDDFT

- *Excited states from time-dependent density functional theory*, P. Elliott, F. Furche, and K. Burke, in Reviews in Computational Chemistry, eds. K. B. Lipkowitz and T. R. Cundari, (Wiley, Hoboken, NJ, 2009), pp 91-165. Also arXiv:cond-mat/0703590
- *Time-dependent density functional theory*, edited by M. Marques, C.A. Ullrich, F. Noguiera, A. Rubio, K. Burke, and E.K.U. Gross (Springer, Heidelberg, 2006).
- *Time-dependent density functional theory: Past, present, and future* K. Burke, Jan Werschnik, and E.K.U. Gross, J. Chem. Phys. 123, 062206 (2005)
- Time-dependent density-functional theory Phys. Chem. Chem. Phys., 2009 DOI: 10.1039/b908105b, eds. Miguel Marques and Angel Rubio.

Basic proof: Runge–Gross theorem (1984)

- Any given current density, $\mathbf{j}(\mathbf{r}, t)$, initial wavefunction, statistics, and interaction, there's only one external potential, $v(\mathbf{r}, t)$, that can produce it.
- Imposing a boundary condition and using continuity, find also true for $n(\mathbf{r}, t)$.
- Action in RG paper is WRONG.
- van Leeuwen gave a constructive proof (PRL98).

Basic points

TDDFT:

- is an addition to DFT, using a different theorem
- allows you to convert your KS orbitals into optical excitations of the system
- for excitations usually uses ground-state approximations that usually work OK
- has not been very useful for strong laser fields
- is in its expansion phase: Being extended to whole new areas, not much known about functionals
- with present approximations has problems for solids
- with currents is more powerful, but harder to follow
- yields a new expensive way to get ground-state E_{XC}.

TD Kohn–Sham equations

- Time-dependent KS equations:

$$i\frac{\partial}{\partial t}\phi_j(\mathbf{r},t) = \left\{-\frac{1}{2}\nabla^2 + v_{\rm S}(\mathbf{r},t)\right\}\phi_j(\mathbf{r},t)$$

- Density:

$$n(\mathbf{r},t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r},t)|^2$$

- The KS potential is

$$v_{\rm S}(\mathbf{r},t) = v(\mathbf{r},t) + \int d^3r' \ \frac{n(\mathbf{r},t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\rm XC}[n;\Psi_0,\Phi_0](\mathbf{r},t),$$

  where $v_{\rm XC}$ depends on memory:
  - entire history of $n(\mathbf{r},t)$
  - initial state Ψ_0 and Φ_0.

Adiabatic approximation

- Almost all calculations use adiabatic approximation
- No standard improvement over this
- Use ground state functional $v_{\mathrm{XC}}^{\mathsf{GS}}$ on time-dependent $n(\mathbf{r}, t)$:

$$v_{\mathrm{XC}}^{\mathsf{adia}}[n](\mathbf{r}, t) = v_{\mathrm{XC}}^{\mathsf{GS}}[n(t)](\mathbf{r}).$$

Overview of *ALL* TDDFT

TDDFT is applied in 3 distinct regimes:

- **Strong fields**, where time-dependence is not perturbative.
  - Properties: double ionization probabilities, momentum distributions, high-harmonic generation
  - Methodology: Must be real time, usually on a grid in real space.
  - Performance: Several problems, including that $n(\mathbf{r}, t)$ is not enough info to get the desired property, and that no good approximations when $n(\mathbf{r}, t)$ is not close to ground state.
- **Excitations**: To extract excitations and optical absorption, only need linear response theory
  - Methodology: Either real time, fourier transform dipole moment, or response equations in frequency space.
  - Performance: Usually quite good (good properties of excited molecules) but growing list of deficiencies, e.g.:
    - Extended systems and non-locality
    - Charge transfer
- **Ground-state approximations**: Via fluctuation-dissipation theorem, can calculate the XC energy from TDDFT (very expensive - RPA cost)

Outline

1. Time-dependent quantum mechanics
2. TDDFT: formalism
3. **Linear response theory**
4. Performance
5. Back to the ground state

Excitations from DFT

- Many approaches to excitations in DFT
- There is no HK theorem from excited-state density (PRL with Rene Gaudoin)
- Would rather have variational approach (ensembles, constrained search, etc.)
- TDDFT yields a response approach, i.e, looks at TD perturbations around ground-state

Linear response theory

We will need the density-density response function:

$$\delta n(\mathbf{r}, t) = \int d^3r' \int dt' \; \chi(\mathbf{r}\mathbf{r}', t - t')\delta v(\mathbf{r}', t')$$

where

- $\delta v(\mathbf{r}, t)$ is a perturbation to the potential,
- $\delta n(\mathbf{r}, t)$ is the density response to this perturbation, and
- χ is the density-density response (susceptibility) function:

$$\chi(\mathbf{r}, \mathbf{r}', t - t') = \frac{\delta n(\mathbf{r}t)}{\delta v(\mathbf{r}'t')}$$

(functional derivative)

Linear response in TDDFT

Equate density change in reality with that of KS system (and Fourier transform):

$$\begin{aligned}\delta n(\mathbf{r}\omega) &= \int d^3r'\ \chi[n](\mathbf{r}\mathbf{r}'\omega)\delta v(\mathbf{r}'\omega)\\ &= \int d^3r'\ \chi_{\mathrm{S}}[n](\mathbf{r}\mathbf{r}'\omega)\delta v_{\mathrm{S}}[n](\mathbf{r}'\omega)\end{aligned}$$

which implies

$$\delta v_{\mathrm{S}}[n](\mathbf{r}\omega) = \delta v(\mathbf{r}\omega) + \int d^3r'\ \left\{\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{XC}}[n](\mathbf{r}\mathbf{r}'\omega)\right\}\delta n(\mathbf{r}'\omega)$$

and the XC kernel is defined in time as

$$f_{\mathrm{XC}}(\mathbf{r}\mathbf{r}', t-t') = \frac{\delta v_{\mathrm{XC}}(\mathbf{r}t)}{\delta n(\mathbf{r}'t')}.$$

Dyson-like equation from equating density responses

Get the real response function from the *ground-state* KS response function plus kernel:

$$\begin{aligned}\chi(\mathbf{r}\mathbf{r}'\omega) &= \chi_{\mathrm{S}}(\mathbf{r}\mathbf{r}'\omega) + \\ &\int d^3r_1 \int d^3r_2\ \chi_{\mathrm{S}}(\mathbf{r}\mathbf{r}'\omega)\left\{\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} + f_{\mathrm{XC}}[n](\mathbf{r}_1\mathbf{r}_2\omega)\right\}\chi(\mathbf{r}\mathbf{r}'\omega)\end{aligned}$$

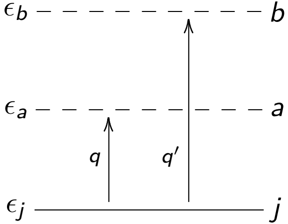
with KS susceptibility

$$\chi_{\mathrm{S}}(\mathbf{r}\mathbf{r}'\omega) = \sum_{jk} f_{jk}\frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega-(\epsilon_j-\epsilon_k)+i0_+}$$

where $f_{jk}=f_j-f_k$, ϵ_j is the KS orbital energy and $\phi_j(\mathbf{r})$ is the orbital.
If adiabatic approximation, the ground-state functional determines all.

Transitions

Look at KS transition frequencies $\omega_q = \epsilon_a - \epsilon_j$, where j is an occupied and a an unoccupied orbital. Thus q is a double index (j, a).



If we consider

$$\Phi_q(\mathbf{r}) = \phi_j^*(\mathbf{r})\phi_a(\mathbf{r}),$$

we can rewrite

$$\chi_{\mathrm{S}}(\mathbf{r}\mathbf{r}'\omega) = 2\sum_q \left\{ \frac{\Phi_q(\mathbf{r})\Phi_q^*(\mathbf{r}')}{\omega - \omega_q + i0_+} - \frac{\Phi_q^*(\mathbf{r})\Phi_q(\mathbf{r}')}{\omega + \omega_q - i0_+} \right\}.$$

TDDFT linear response

- Probe system with AC field of frequency ω
- See at what ω you find a self-sustaining response
- That's a transition frequency!
- Need a new functional, the XC kernel, $f_{\rm XC}[n](\mathbf{rr}\omega)$
- Almost always ignore ω-dependence (called adiabatic approximation)
- Can view as corrections to KS response

Casida's matrix formulation (1996)

Get true transition frequencies ω as eigenvalues of

$$\sum_{q'} \Omega_{qq'}(\omega)\nu_{q'} = \omega^2 \nu_q,$$

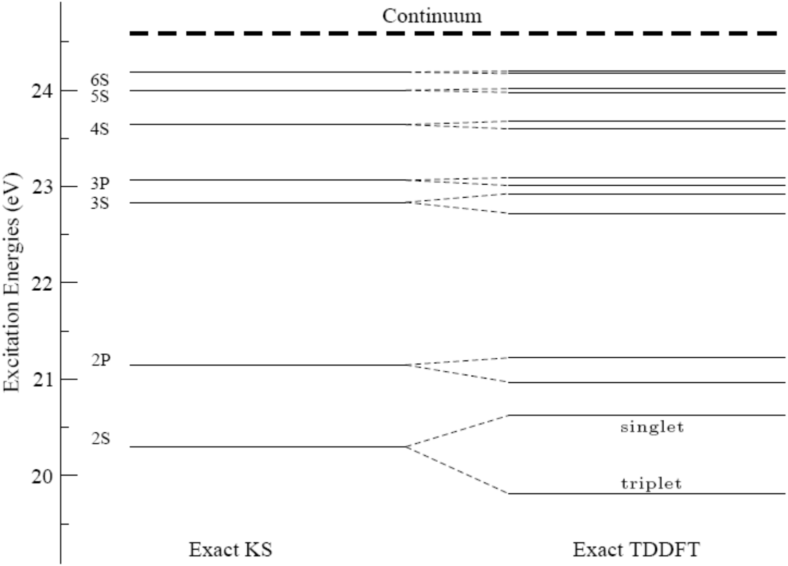
where $\nu_q = ?$,

$$\Omega_{qq'} = \delta_{qq'}\omega_q^2 + 4\sqrt{\omega_q \omega_q'}[q|f_{\rm HXC}(\omega)|q']$$

and

$$[q|f_{\rm HXC}(\omega)|q'] = \iint d^3r\ d^3r'\ \Phi_q^*(\mathbf{r}')f_{\rm HXC}(\mathbf{r}\mathbf{r}'\omega)\Phi_{q'}(\mathbf{r})$$

KS response


Continuum
6S
5S
4S
3P
3S
2P
2S
singlet
triplet
Excitation Energies (eV)
24
23
22
21
20
Exact KS
Exact TDDFT

Outline

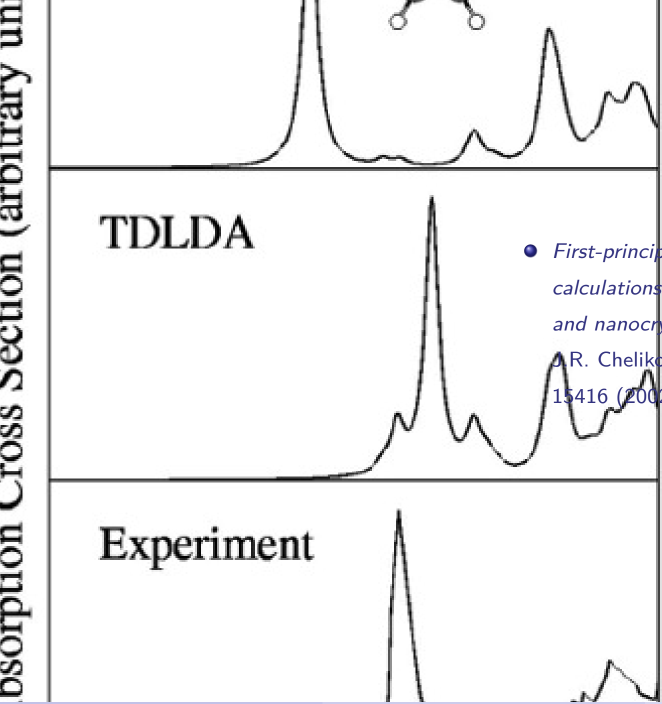
1. Time-dependent quantum mechanics

2. TDDFT: formalism

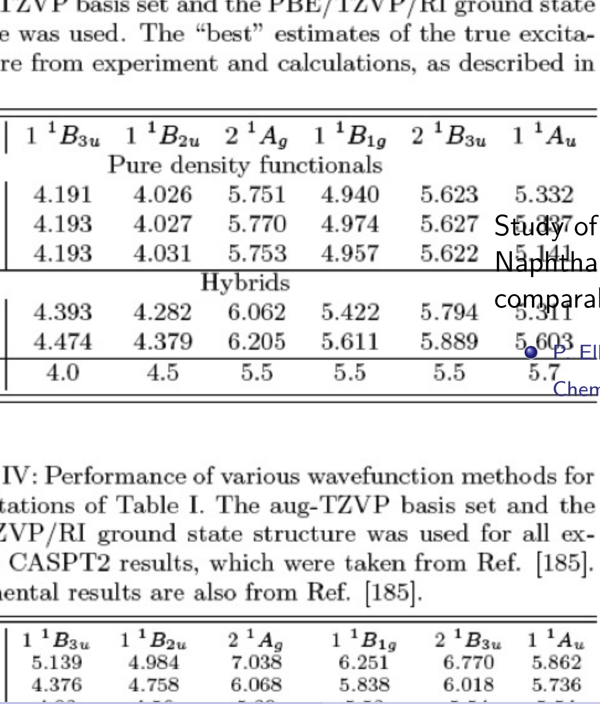
3. Linear response theory

4. Performance

5. Back to the ground state



- *First-principles density-functional calculations for optical spectra of clusters and nanocrystals*, I. Vasiliev, S. Ogut, and J.R. Chelikowsky, Phys. Rev. B 65, 1 15416 (2002).



TZVP basis set and the PBE/TZVP/RI ground state
e was used. The "best" estimates of the true excita-
re from experiment and calculations, as described in

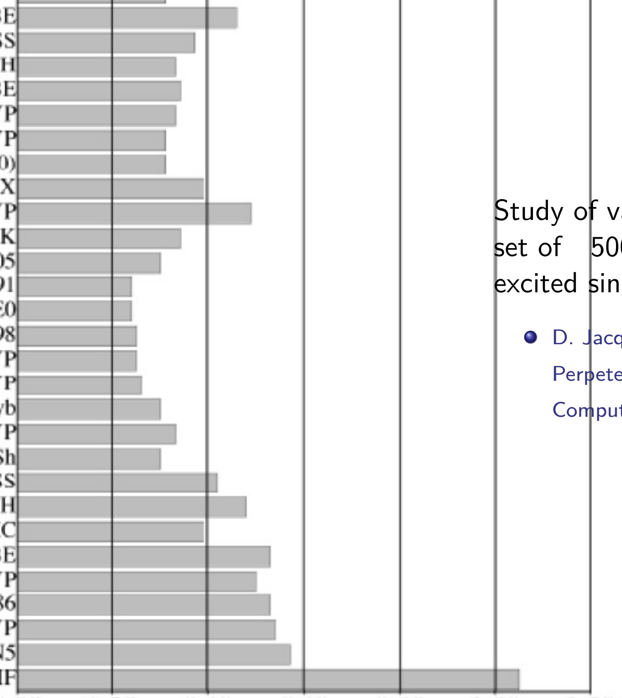
$1\,^1B_{3u}$	$1\,^1B_{2u}$	$2\,^1A_g$	$1\,^1B_{1g}$	$2\,^1B_{3u}$	$1\,^1A_u$
Pure density functionals					
4.191	4.026	5.751	4.940	5.623	5.332
4.193	4.027	5.770	4.974	5.627	5.237
4.193	4.031	5.753	4.957	5.622	5.141
Hybrids					
4.393	4.282	6.062	5.422	5.794	5.311
4.474	4.379	6.205	5.611	5.889	5.603
4.0	4.5	5.5	5.5	5.5	5.7

IV: Performance of various wavefunction methods for
tations of Table I. The aug-TZVP basis set and the
ZVP/RI ground state structure was used for all ex-
CASPT2 results, which were taken from Ref. [185].
ental results are also from Ref. [185].

$1\,^1B_{3u}$	$1\,^1B_{2u}$	$2\,^1A_g$	$1\,^1B_{1g}$	$2\,^1B_{3u}$	$1\,^1A_u$
5.139	4.984	7.038	6.251	6.770	5.862
4.376	4.758	6.068	5.838	6.018	5.736

Study of various functionals for Naphthalene. Variations in $v_{\rm XC}(\mathbf{r})$ comparable to those in $f_{\rm XC}(\mathbf{r},\mathbf{r}')$.

- P. Elliott, F.Furche, KB, Reviews Comp Chem, 2008.



Study of various functionals over a set of 500 organic compounds, 700 excited singlet states

- D. Jacquemin, V. Wathelet, E. A. Perpete, C. Adamo, J. Chem. Theory Comput. (2009).

Typical success of TDDFT for excited states

- Energies to within about 0.4 eV
- Bonds to within about 1%
- Dipoles good to about 5
- Vibrational frequencies good to 5
- Cost scales as N2, vs N5 for CCSD
- Available now in your favorite quantum chemical code

Current challenges in TDDFT

- Rydberg states - know what to do
- Polarizabilities of long-chain molecules
- Optical response of solids
- Double excitations
- Long-range charge transfer
-

Outline

1. Time-dependent quantum mechanics

2. TDDFT: formalism

3. Linear response theory

4. Performance

5. Back to the ground state

Extracting $E_{\mathrm{XC}}[n]$ from TDDFT

From the fluctuation-dissipation theorem:

$$\begin{aligned} E_{\mathrm{XC}}[n] \;=\; & -\frac{1}{2}\int_0^1 d\lambda \int d^3r \int d^3r' \, \frac{1}{|\mathbf{r}-\mathbf{r}'|} \times \\ & \int_0^\infty \frac{d\omega}{\pi} \Big\{ \chi_\lambda[n](\mathbf{r}\mathbf{r}'\omega) + n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \Big\} \end{aligned}$$

Plug in ground-state $n(\mathbf{r})$ to obtain E_{XC}.

- Combine with TDDFT Dyson-like equation to get new approximations from old functionals, but demanding response calculation.
- For separated systems, gives van der Waals coefficients.
- Approximate frequency integration and factorization of response functions yields Langreth-Lunqvist van der Waals function—a non-local ground-state density functional.
  - M Dion et al, PRL **92**, 24601 (2004).

Lessons about TDDFT

- A way to extract electronic excitations using new theorem, from ground-state DFT calculation.
- Only real game in town for excitations in chemistry for decent-sized molecules.
- Cost comparable to single-point ground-state calculation.
- Uses adiabatic approximation.
- Problems for large systems due to locality of approximate functionals.