

Basics of DFT

Kieron Burke and Lucas Wagner

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

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Outline

- 1 General background
- 2 DFT
- 3 Common functionals

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1 General background

2 DFT

3 Common functionals

Electronic structure problem

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

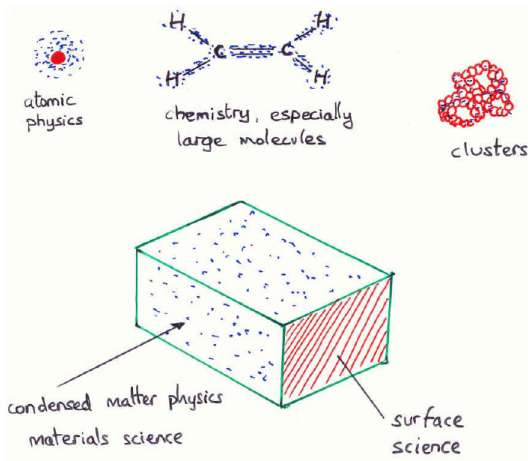


Figure: My first ever DFT transparency

Atomic units

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

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 electrons 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 $v(\mathbf{r})$:

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

where the kinetic and elec-elec repulsion energies are

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

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 \mathbf{E} and \mathbf{B} fields.

Schrödinger equation

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

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

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

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

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

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

where Ψ is normalized and antisym.

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- 1 General background
- 2 DFT**
- 3 Common functionals

References for ground-state DFT

- **DFT in a nutshell**, with Lucas Wagner, and **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 $X\alpha$ 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, $E_{XC}[n]$.
- **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):

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

where

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

- ▶ 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).

- Define *fictitious* non-interacting electrons satisfying:

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

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

- Define T_s as the kinetic energy of the KS electrons, U as their Hartree energy and

$$T + V_{ee} = T_s + U + E_{xc}$$

the remainder is the exchange-correlation energy.

- Most important result of exact DFT:

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r}), \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

Kohn-Sham energy components

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

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

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

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

- 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_C is everything else.

Kohn-Sham elementary facts

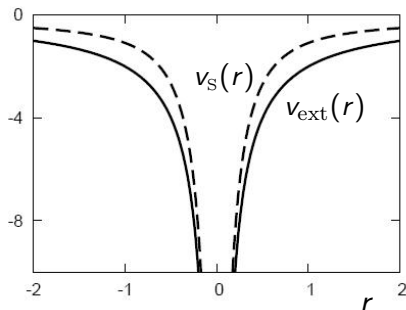
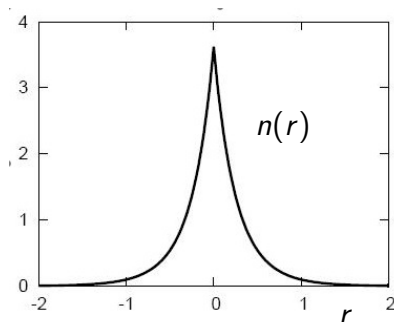
- T and V_{ee} are both positive, trying to rip system apart, but overcome by more negative V .
- Kinetic energies are positive, and $T > T_S$ by definition.
- U is positive and dominates the electron-electron repulsion.
- E_X only has contributions from same-spin electrons and is negative. This part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

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

- E_C contains both kinetic and potential contributions:

$$\begin{aligned} E_C &= \langle \Psi[n] | \hat{T} + \hat{V}_{ee} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{V}_{ee} | \Phi[n] \rangle \\ &= (T - T_S) + (V_{ee} - U - E_X) = T_C + U_C \end{aligned}$$

KS potential of He atom



Every density has (at most) one KS potential.¹

Dashed line: $v_s(r)$ 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)

Energy components of small spherical atoms

	T	V_{ext}	V_{ee}	T_{S}	U	E_{X}	T_{C}	U_{C}	E_{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_{XC} , then energy can go *below* the exact ground-state energy.
- Any given formula for E_{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
 - ▶ $\Delta = I - A$ (= 24.6 eV for He)
- The exact Kohn-Sham gap:
 - ▶ $\Delta_S = \epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}$ (= $\epsilon_{1s} - \epsilon_{2s} = 21.16$ 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 $E_{\text{XC}}[n]$ produces a KS gap different from the fundamental gap.

- 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_{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 $E_{\text{xc}}[n]$.
 - ▶ approximate in practice.
- Exact DFT tells us what we can and cannot expect our functionals to be able to do.
- $v_{\text{s}}(\mathbf{r})$ 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 $v_{\text{s}}(\mathbf{r})$ is dangerous.

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Functionals in common use

- Local density approximation (LDA)

- ▶ Uses only $n(\mathbf{r})$ at a point,

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

- Generalized gradient approx (GGA)

- ▶ Uses both $n(\mathbf{r})$ and $|\nabla n(\mathbf{r})|$

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

- ▶ Examples are PBE and BLYP

- Hybrid:

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

- ▶ 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.
-
- | | |
|---|--|
| <ul style="list-style-type: none">• Empirical<ul style="list-style-type: none">▶ GGA: BLYP▶ Hybrid: B3LYP• Names:<ul style="list-style-type: none">▶ B=B88 exchange▶ LYP = Lee-Yang-Parr correlation | <ul style="list-style-type: none">• Non-empirical<ul style="list-style-type: none">▶ GGA:PBE▶ Meta-GGA: TPSS▶ Hybrid: PBE0 |
|---|--|

Local density approximation (LDA)

- Exchange is trivial (Dirac, 1931)

$$e_x^{\text{unif}}(n) = A_x n^{4/3}, \quad A_x = -0.738$$

- Correlation energy known:
 $e_c^{\text{unif}}(n)$ 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.

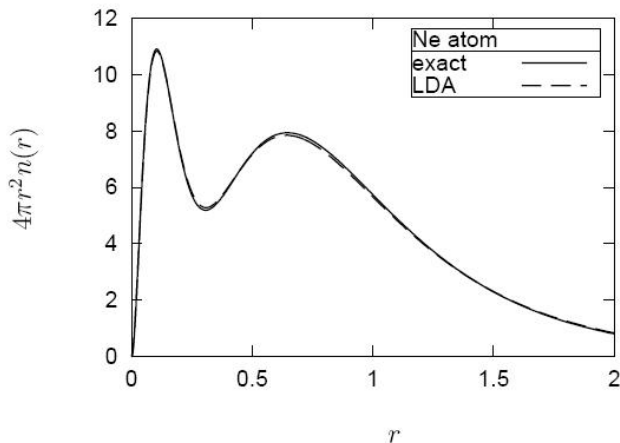


Figure: Exact and LDA radial densities of the Ne atom.

Easy conditions

- **Size-consistency:**

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

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 $q \leq 2k_F$.
- **Lieb-Oxford bound:** Magnitude of E_{XC} cannot be greater than $2.3 E_{\text{X}}^{\text{LDA}}$.

Uniform coordinate scaling

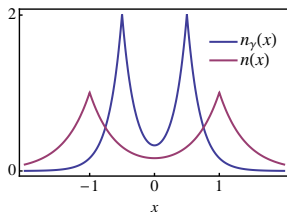


Figure: A one-dimensional density (red) being squeezed by $\gamma = 2$ (blue)

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

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

- ▶ For $\gamma > 1$, squeezes up the density, preserving norm; for $\gamma < 1$, stretches it out.
- Exchange: Require $E_x[n_\gamma] = \gamma E_x[n]$
- Correlation: $E_c[n_\gamma] = B[n] + C[n]/\gamma + \dots$ 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_x^{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 $E_C[n]$ (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.

- Correlation:

- ▶ In slowly varying limit, $E_C \rightarrow E_C^{\text{GEA}}$.
- ▶ In rapidly varying limit, $E_C \rightarrow E_C^{\text{LDA}}$.
- ▶ In high-density limit, $E_C \rightarrow -\text{const.}$

- Exchange:

- ▶ Under uniform scaling, $E_x[n_\gamma] = \gamma E_x[n]$.
- ▶ Under spin-scaling, $E_x[n_\uparrow, n_\downarrow] = (E_x[2n_\uparrow] + E_x[2n_\downarrow])/2$.
- ▶ Linear response same as LDA.
- ▶ Lieb-Oxford bound: $E_{\text{xc}} \geq 2.3 E_x^{\text{LDA}}$.

Leads to enhancement factor:

$$F_x(s) = 1 + \kappa - \kappa/(1 + \mu s^2/\kappa), \quad \kappa \leq 0.804.$$

- Performance

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

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.

Applications of DFT

- Tens of thousands of papers every year.
- Appearing in every branch of science:
 - ▶ Solid-state physics
 - ▶ Chemistry
 - ▶ Biochemistry
 - ▶ Geology
 - ▶ Astrophysics
- Traditionally divided into finite systems (molecules) and extended (solids), but distinction is breaking down.
- Codes divided into either using localized basis functions (usually Gaussians) or plane waves.