

ABC of ground-state DFT

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

1 General background

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Electronic structure problem

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

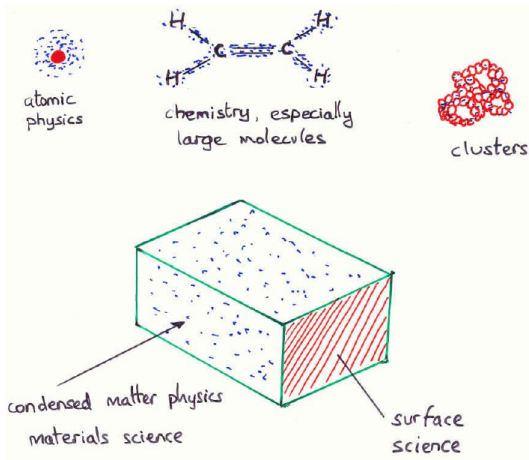


Figure: My first ever DFT transparency

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 nuclear \times electronic to an excellent approximation.
- Because electronic energies are in eV and much greater than 300K, electrons always in ground state.
- Yields

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

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 $v(\mathbf{r})$:

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

where the kinetic and elec-elec repulsion energies are

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

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

- $4N$ -dimensional Schrödinger equation for stationary states

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

- 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

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

where Ψ is normalized and antisym.

First principles

- Aim: Predict properties just by solving the Schrödinger equation
- Physics: Usually use model Hamiltonians with empirical parameters (e.g. Hubbard)
- Chemistry: Systematic expansion either of wavefunction or Hamiltonian

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References for ground-state DFT

- *DFT: A theory full of holes?*, Aurora Pribram-Jones, David Gross, KB, *Ann Rev Phys Chem*, **66**, 283-304 (2015)
- *DFT in a nutshell*, by KB and Lucas Wagner, *IJQC* **113**, 96, (2013)
- *ABC of DFT*, by KB and Rudy Magyar, <http://dft.uci.edu/>
- *Perspective on DFT*, by KB, *JCP* **136**, 150901, (2012)
- *A Primer in Density Functional Theory*, edited by C. Fiolhais et al. (Springer-Verlag, NY, 2003)
- *Density Functional Theory: An advanced course*, Engel and Dreizler, (Springer-Verlag, Berlin, 2011); see also Dreizler and Gross (1990).
- *A Chemist's Guide to Density Functional Theory*, Koch and Holthausen (Wiley-VCH, Weinheim, 2000)

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):

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

where

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

- ▶ 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:

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

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

$$T + V_{ee} = T_S + U + E_{XC}$$

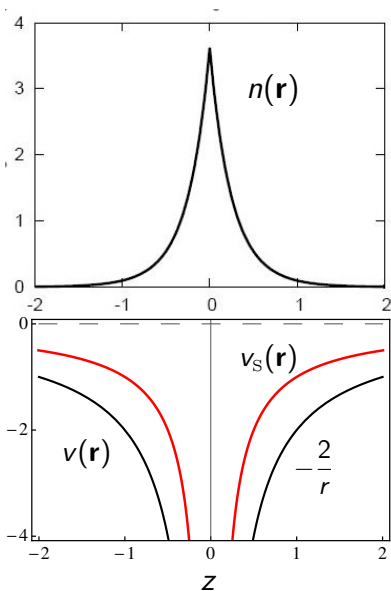
the remainder is the exchange-correlation energy.

- Most important result of exact DFT:

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

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

KS potential of He atom



Every density has (at most) one KS potential.^a
Red line: $v_S(\mathbf{r})$ is the *exact* KS potential.

^a *Accurate exchange-correlation potentials and the helium isoelectronic series*, C. J. Umrigar and 3827 (1994).

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

$$E_x = -\frac{1}{2} \sum_{\sigma} \sum_{\substack{i,j \\ occ}} \int d^3r \int d^3r' \frac{\phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}^*(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}') \phi_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} < 0$$

- E_C is everything else, < 0

Simple 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, $n_\alpha(\mathbf{r})$ and $n_\beta(\mathbf{r})$, with two different KS potentials (but some subtleties).
- 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 \mathbf{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

Local density approximation (LDA)

- Exchange is trivial (Dirac, 1931)

$$e_X^{\text{unif}}(n) = -A_X n^{4/3}, \quad A_X = \frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} = 0.738$$

- 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 accurate parametrizations in use (all very similar):
 - ▶ 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.

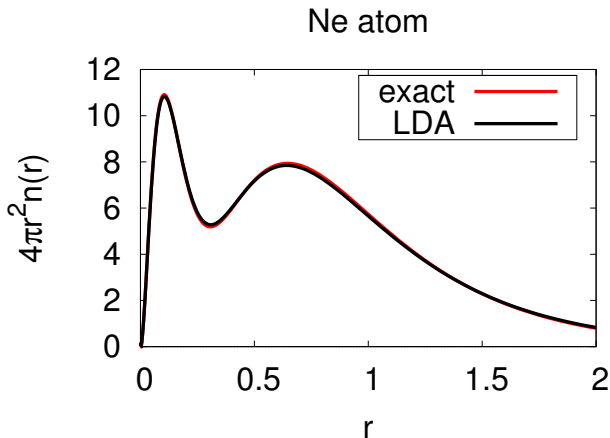


Figure: Exact and LDA radial densities of the Ne atom.

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 $2.3 E_{\text{X}}^{\text{LDA}}$.

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

PBE – a VERY misleading derivation

- PBE works because of the accuracy of the XC hole, which quantifies the antisocial behavior of electrons.
- Accurate XC hole
 - ⇒ accurate pair distribution of electrons:
$$P(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}) (n(\mathbf{r}') + n_{\text{XC}}(\mathbf{r}, \mathbf{r}'))$$
 - ⇒ accurate XC energies.
- Plotting the GEA XC hole made need for GGAs apparent.
- Numerical GGAs, precursors to PBE, modeled the XC hole.
- PBE paper gives simplified derivation based on energy, not XC hole.

- **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, $E_x[n_\alpha, n_\beta] = (E_x[2n_\alpha] + E_x[2n_\beta])/2$.
- ▶ 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%.

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**, 115, (1996)
 - ▶ Perdew, Ernzerhof, and Burke, J. Chem. Phys. **105**, 9982, (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.
- Mysteriously, 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.