Tutorial: Introduction to Hartree-Fock and DFT

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Outline

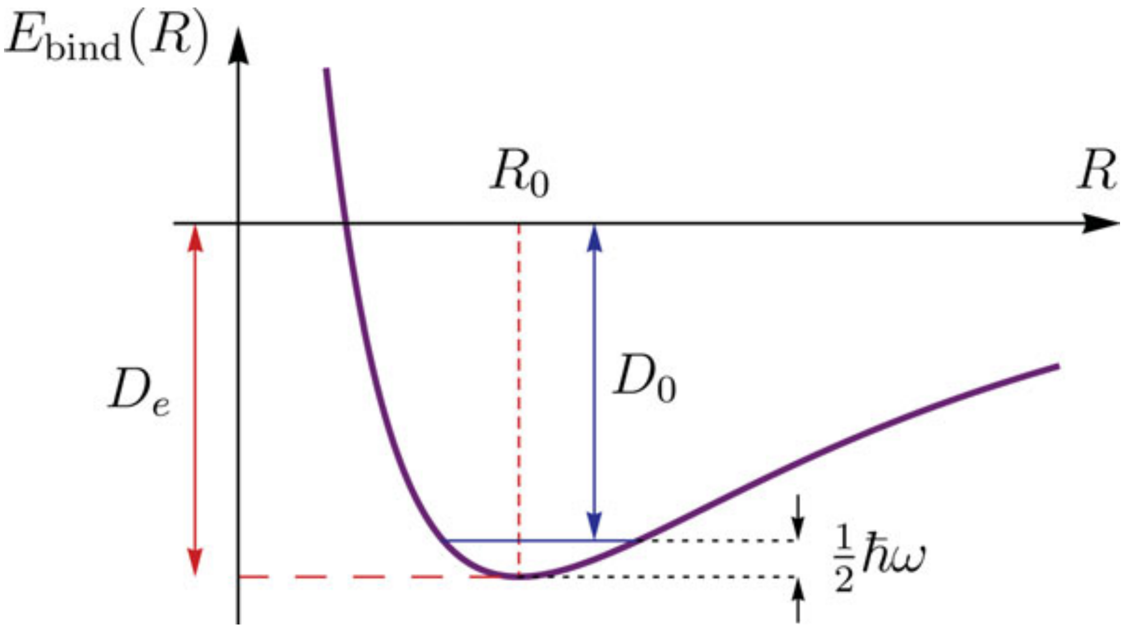
- HF theory and MB theory
- DFT
- Advanced issues in DFT
- Jianfeng Lu: Math behind HF/DFT (Tu 11)

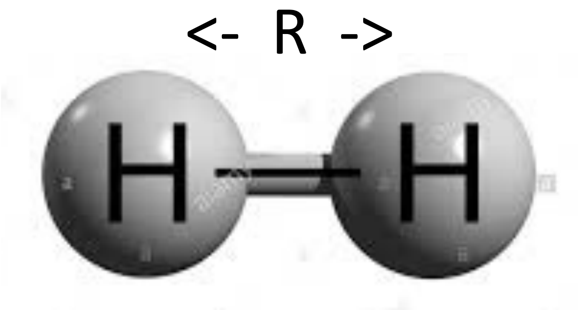
Basic problem

- Non-relativistic
- Born-Oppenheimer approximation
- No external B field
- First principles
- Ab initio?

Basic Electronic Structure Problem

- Just want E(R), mostly (fixed nuclei, electrons in ground state):





Dominance of ground-state energy

- Determines which molecules and solids exist and many of their most basic properties
- Bond lengths / lattice parameters
- Vibrational frequencies / phonons
- Reaction rates via transition-state barriers
- Vital in chemistry, increasingly so in materials
- Often care more about response properties in physics

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.

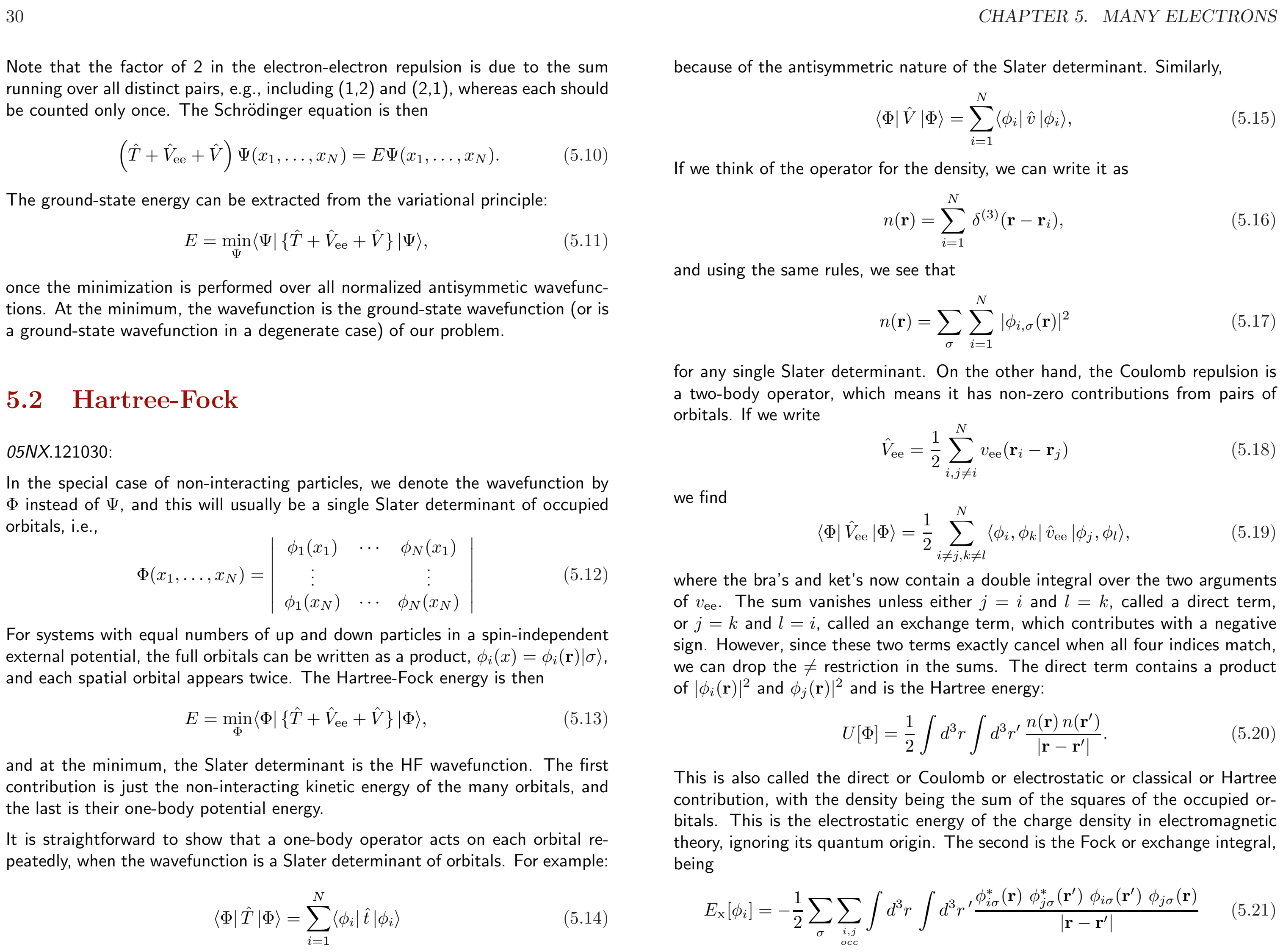
$$\{\hat{T} + \hat{V}_{\rm ee} + \hat{V}\}\,\Psi = E\,\Psi$$

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

.Hartree-Fock approximation

- Assume wavefunction is a single Slater determinant of occupied orbitals: satisfies Pauli exclusion
- Minimize energy with orthonormal orbitalss
- Yields HF equations for those orbitals
- Solve self-consistently
- Rebuild interacting energy from orbitals and eigenvalues
- Names:
  - HF theory, HF equations
  - Self-consistent field theory (SCF)
  - Molecular orbital theory
  - HOMO, LUMO, frontier orbitals

HF energy function



Note that the factor of 2 in the electron-electron repulsion is due to the sum running over all distinct pairs, e.g., including (1,2) and (2,1), whereas each should be counted only once. The Schrödinger equation is then

$$\left(\hat{T} + \hat{V}_{\rm ee} + \hat{V}\right) \Psi(x_1, \ldots, x_N) = E\Psi(x_1, \ldots, x_N). \tag{5.10}$$

The ground-state energy can be extracted from the variational principle:

$$E = \min_{\Psi} \langle \Psi | \{\hat{T} + \hat{V}_{\rm ee} + \hat{V}\} | \Psi \rangle, \tag{5.11}$$

once the minimization is performed over all normalized antisymmetic wavefunctions. At the minimum, the wavefunction is the ground-state wavefunction (or is a ground-state wavefunction in a degenerate case) of our problem.

5.2 Hartree-Fock

05NX.121030:

In the special case of non-interacting particles, we denote the wavefunction by Φ instead of Ψ, and this will usually be a single Slater determinant of occupied orbitals, i.e.,

$$\Phi(x_1, \ldots, x_N) = \begin{vmatrix} \phi_1(x_1) & \cdots & \phi_N(x_1) \\ \vdots & & \vdots \\ \phi_1(x_N) & \cdots & \phi_N(x_N) \end{vmatrix} \tag{5.12}$$

For systems with equal numbers of up and down particles in a spin-independent external potential, the full orbitals can be written as a product, $\phi_i(x) = \phi_i(\mathbf{r})|\sigma\rangle$, and each spatial orbital appears twice. The Hartree-Fock energy is then

$$E = \min_{\Phi} \langle \Phi | \{\hat{T} + \hat{V}_{\rm ee} + \hat{V}\} | \Phi \rangle, \tag{5.13}$$

and at the minimum, the Slater determinant is the HF wavefunction. The first contribution is just the non-interacting kinetic energy of the many orbitals, and the last is their one-body potential energy.

It is straightforward to show that a one-body operator acts on each orbital repeatedly, when the wavefunction is a Slater determinant of orbitals. For example:

$$\langle \Phi | \hat{T} | \Phi \rangle = \sum_{i=1}^{N} \langle \phi_i | \hat{t} | \phi_i \rangle \tag{5.14}$$

because of the antisymmetric nature of the Slater determinant. Similarly,

$$\langle \Phi | \hat{V} | \Phi \rangle = \sum_{i=1}^{N} \langle \phi_i | \hat{v} | \phi_i \rangle, \tag{5.15}$$

If we think of the operator for the density, we can write it as

$$n(\mathbf{r}) = \sum_{i=1}^{N} \delta^{(3)}(\mathbf{r} - \mathbf{r}_i), \tag{5.16}$$

and using the same rules, we see that

$$n(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{N} |\phi_{i,\sigma}(\mathbf{r})|^2 \tag{5.17}$$

for any single Slater determinant. On the other hand, the Coulomb repulsion is a two-body operator, which means it has non-zero contributions from pairs of orbitals. If we write

$$\hat{V}_{\rm ee} = \frac{1}{2} \sum_{i,j \neq i}^{N} v_{\rm ee}(\mathbf{r}_i - \mathbf{r}_j) \tag{5.18}$$

we find

$$\langle \Phi | \hat{V}_{\rm ee} | \Phi \rangle = \frac{1}{2} \sum_{i \neq j, k \neq l}^{N} \langle \phi_i, \phi_k | \hat{v}_{\rm ee} | \phi_j, \phi_l \rangle, \tag{5.19}$$

where the bra's and ket's now contain a double integral over the two arguments of $v_{\rm ee}$. The sum vanishes unless either $j = i$ and $l = k$, called a direct term, or $j = k$ and $l = i$, called an exchange term, which contributes with a negative sign. However, since these two terms exactly cancel when all four indices match, we can drop the $\neq$ restriction in the sums. The direct term contains a product of $|\phi_i(\mathbf{r})|^2$ and $\phi_j(\mathbf{r})|^2$ and is the Hartree energy:

$$U[\Phi] = \frac{1}{2} \int d^3r \int d^3r' \, \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{5.20}$$

This is also called the direct or Coulomb or electrostatic or classical or Hartree contribution, with the density being the sum of the squares of the occupied orbitals. This is the electrostatic energy of the charge density in electromagnetic theory, ignoring its quantum origin. The second is the Fock or exchange integral, being

$$E_{\rm x}[\phi_i] = -\frac{1}{2} \sum_{\sigma} \sum_{\substack{i,j \\ occ}} \int d^3r \int d^3r' \, \frac{\phi_{i\sigma}^*(\mathbf{r})\ \phi_{j\sigma}^*(\mathbf{r}')\ \phi_{i\sigma}(\mathbf{r}')\ \phi_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \tag{5.21}$$

HF equations

To find the orbitals in Hartree-Fock, we must minimize the energy as a functional of each orbital $\phi_i(\mathbf{r})$, subject to the constraint of orthonormal orbitals. Doing this, using the techniques of chapter 2 yields the Hartree-Fock equations

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\rm H}(\mathbf{r})\right)\phi_i(\mathbf{r}) + f_{F,i}[\{\phi_i\}](\mathbf{r}) = \epsilon_i\,\phi(\mathbf{r}) \qquad (5.22)$$

where the last contribution to the potential is due to the Fock operator, and is defined by

$$f_{F,i}[\{\phi_i\}](\mathbf{r}) = -\sum_j^N \int d^3r'\,\frac{\phi_j^*(\mathbf{r}')\,\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\phi_j(\mathbf{r}). \qquad (5.23)$$

Note that this odd-looking animal is *orbital*-dependent, i.e., it is a different function of $\mathbf{r}$ for each occupied orbital. Also, for just one electron, the Hartree and Fock terms in the potential cancel, as they should. In order to discuss the pro's and con's of HF calculations, we must first discuss the errors it makes.

Single-particle basis sets

- LCAO most common in chemistry
- Mostly Gaussians
- Very few use Slater-type orbitals (exponential decay with cusp at nucleus)
- Use planewaves for periodic codes
- Also grids, wavelets, etc.

Performance

- HF often gets 99% of total energy accurately.
- Remainder is $E_C = E - E^{HF} \leq 0$
- But HF terrible for most energy differences
- Not great for bond lengths
- Underestimates vibrational frequencies

Greatest failure: Binding energy curve

- Try to calculate entire binding energy curve of H_2
- As molecule is stretched, gap with triplet state gets very small
- As limit approached, exact wavefunction is 50:50 combination of 2 Slater determinants
- Restricted HF goes to wrong limit
- Unrestricted HF gets energy right in limit but wrong spin densities

Modern quantum chemistry

- Start from HF solution
- Each occupation is a 'configuration'
- Label states by number of excitations
- Full CI: Include as many excitations as needed to converge – impractical
- Coupled cluster: CCSD(T)
- MP2, MP4,..
- CAS=minimize coefficients and orbitals within limited subspace
- Narang: Ab initio QC for non-equilibrium (Tu4)

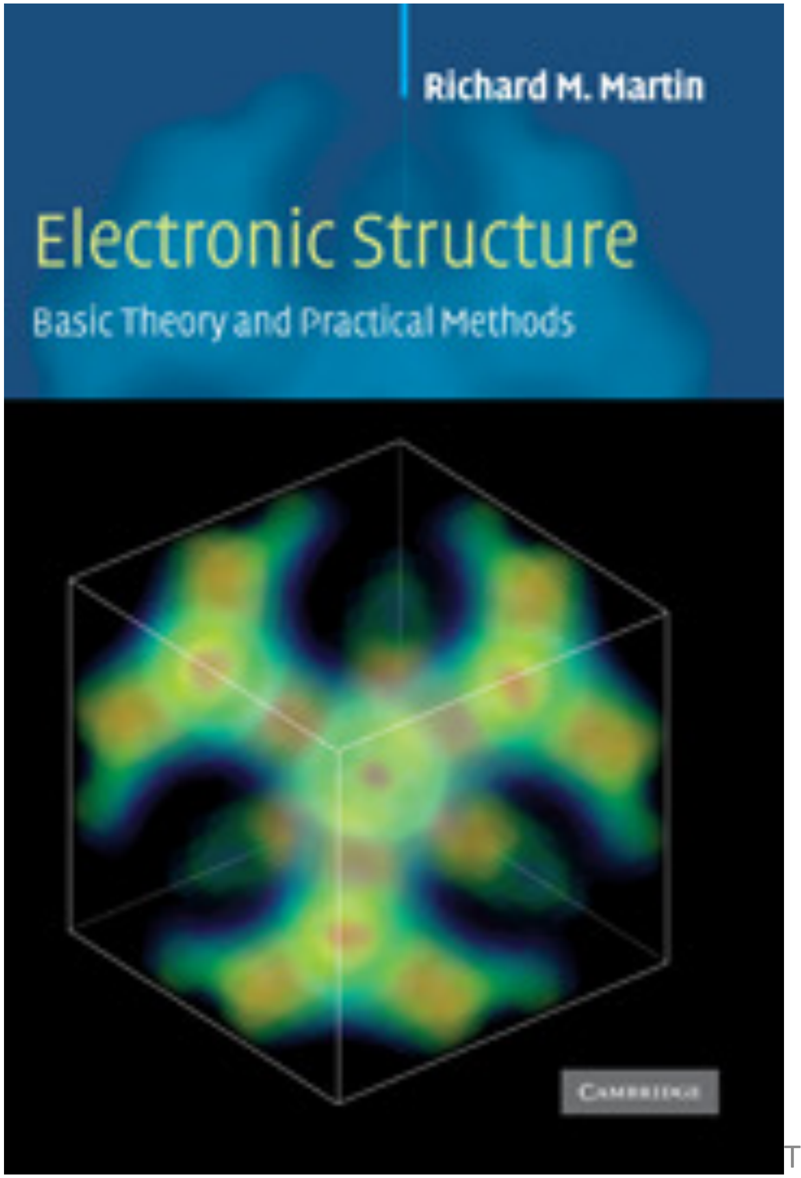
Quantum Monte Carlo

- Start from HF wavefunction and build ‘better’ one
  - Use MC to estimate parameters
  - Many different flavors
- Used in materials and warm dense matter
- Beginning to be more common in molecular calculations
- See other talks:
  - Webber: math for random methods (W9)
  - Ceperley: Intro to MC (W11)
  - Rossi: statistical methods – MD,MC,ML (Th 9)

Green's function approaches

- Start from non-interacting G
  - Add Hartree, gives G^{HF}
  - Add all many-body diagrams, get exact G
- For weakly-correlated systems:
  - Some flavor of GW
  - Zgid: Green's function methods (W 2)
  - Lindsey: MBPT and GF (Th 11)
- For strongly correlated systems:
  - Dynamical mean field theory
  - Poor man's version: DFT + U

Useful books for materials

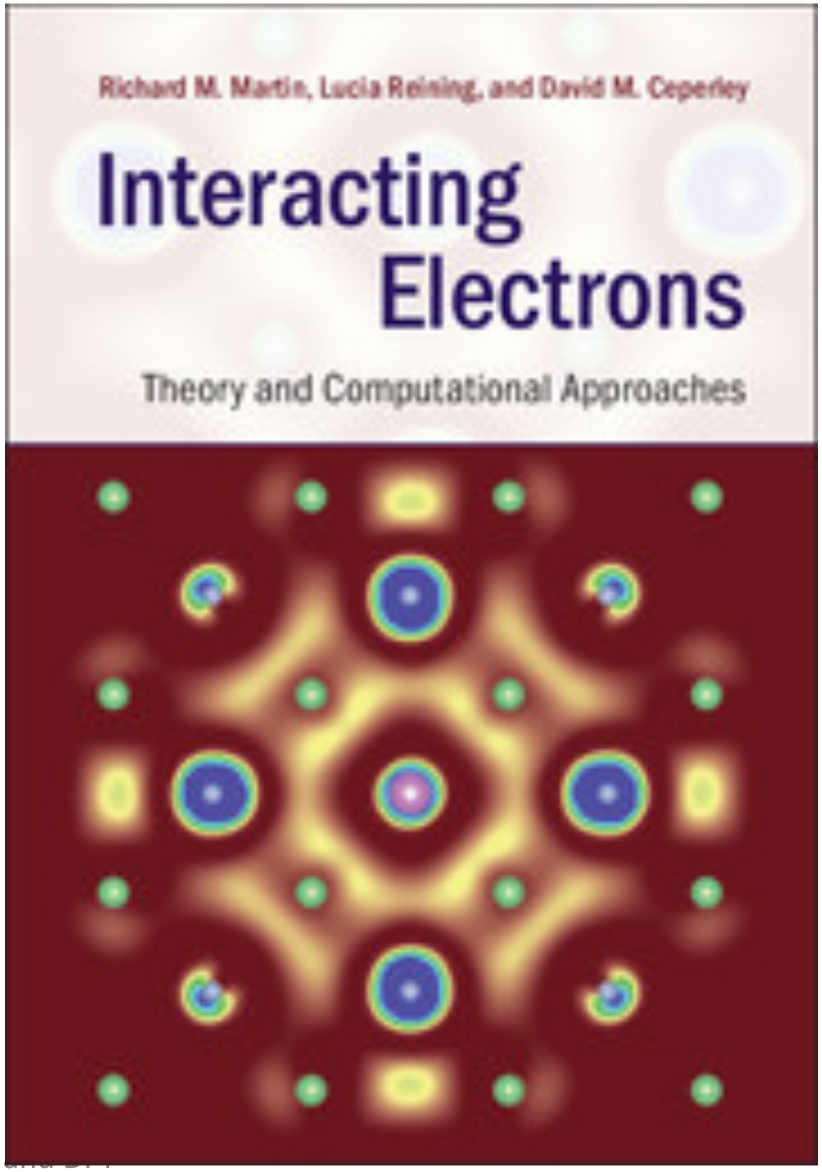


Richard M. Martin

Electronic Structure

Basic Theory and Practical Methods

Cambridge



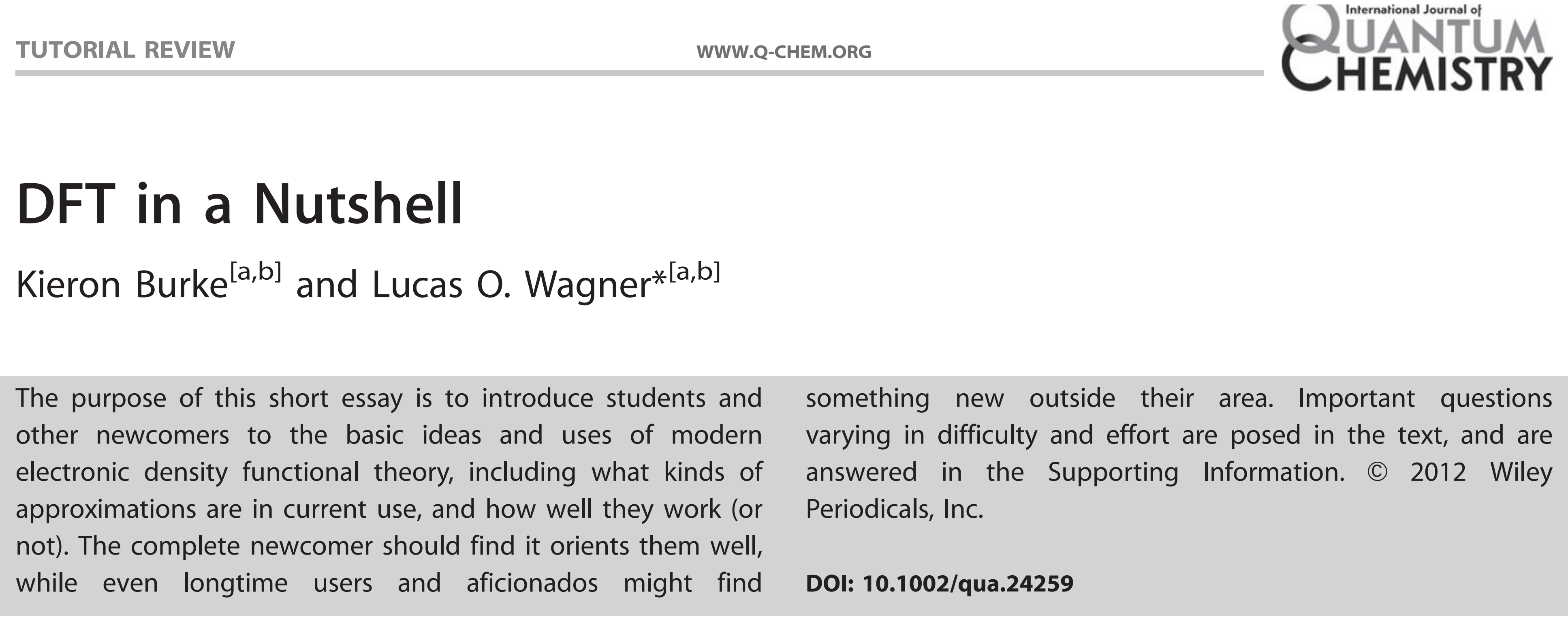
Richard M. Martin, Lucia Reining, and David M. Ceperley

Interacting Electrons

Theory and Computational Approaches

DFT

Useful intro for anyone



TUTORIAL REVIEW

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International Journal of QUANTUM CHEMISTRY

DFT in a Nutshell

Kieron Burke[a,b] and Lucas O. Wagner*[a,b]

The purpose of this short essay is to introduce students and other newcomers to the basic ideas and uses of modern electronic density functional theory, including what kinds of approximations are in current use, and how well they work (or not). The complete newcomer should find it orients them well, while even longtime users and aficionados might find something new outside their area. Important questions varying in difficulty and effort are posed in the text, and are answered in the Supporting Information. © 2012 Wiley Periodicals, Inc.

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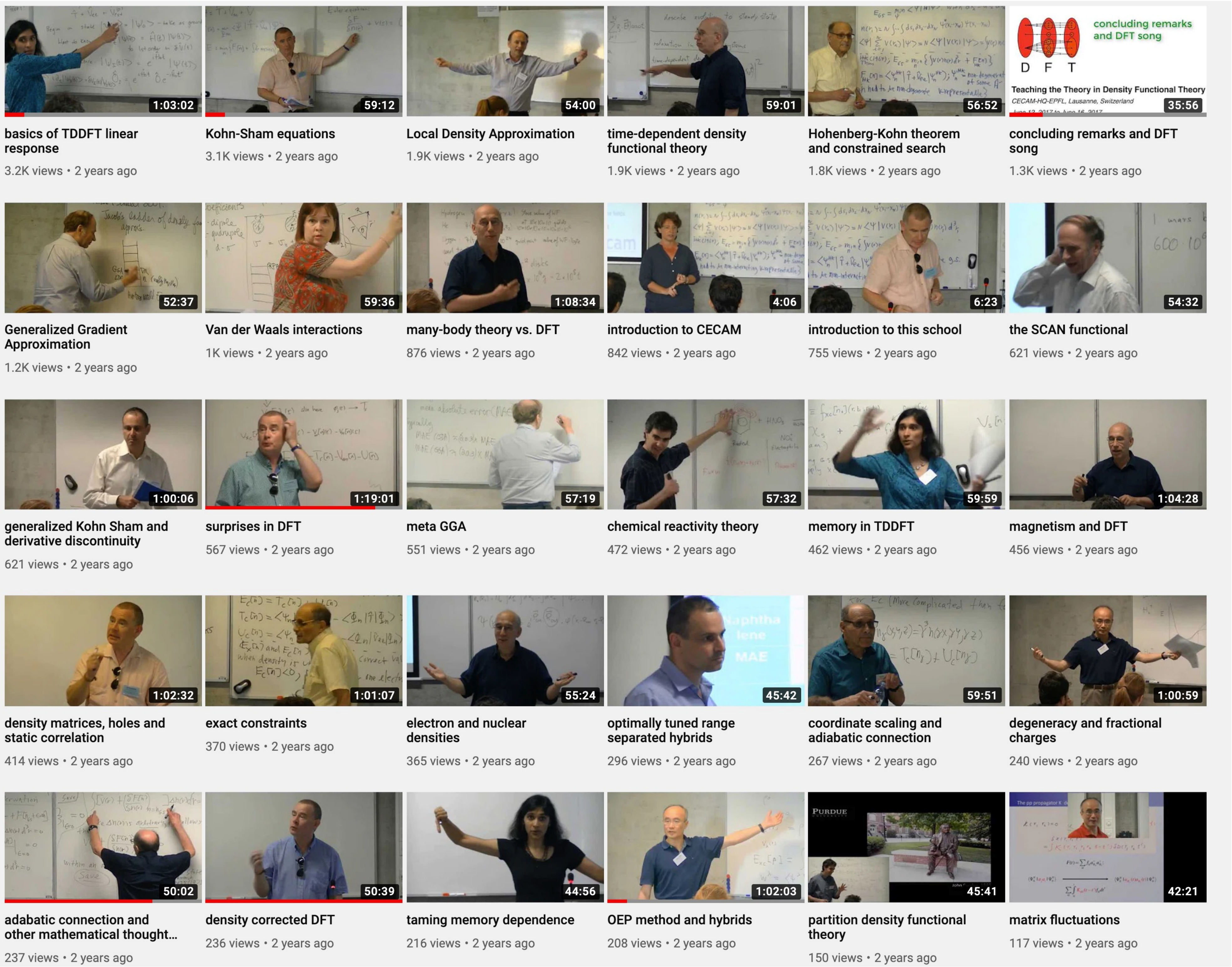

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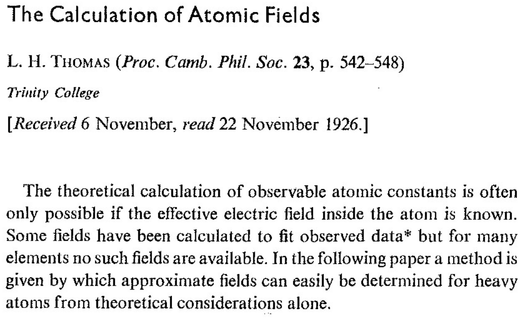
Thomas/Fermi Theory 1927

- Derived in 1926 without Schrodinger eqn.



The Calculation of Atomic Fields

L. H. Thomas (*Proc. Camb. Phil. Soc.* **23**, p. 542–548)

Trinity College

[*Received* 6 November, *read* 22 November 1926.]

The theoretical calculation of observable atomic constants is often only possible if the effective electric field inside the atom is known. Some fields have been calculated to fit observed data* but for many elements no such fields are available. In the following paper a method is given by which approximate fields can easily be determined for heavy atoms from theoretical considerations alone.

- Thomas-Fermi Theory (TF):
  - $T \approx T^{TF}$
  - $V_{ee} \approx U$ = Hartree energy
  - $V = \int d\mathbf{r}\, \rho(\mathbf{r})\, v(\mathbf{r})$
  - $E_0 = T + V_{ee} + V$
  - Minimize $E_0[n]$ for fixed N

$$T_s^{loc} = \frac{3(3\pi)^{2/3}}{10} \int d^3r\, n^{5/3}(r)$$

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

- Properties:
  - Typical error of order 10%
  - Teller's unbinding theorem: Molecules don't bind.

Hohenberg-Kohn theorems (1964)

- HK I:1-1 between n(**r**) and v(**r**)
- HK II: F[n] is independent of v(**r**) [universal]
- HK III: Minimize F+V for fixed N to find n(**r**)
- Constrained searc

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

where

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

- TF a crude approximation to exact theory

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

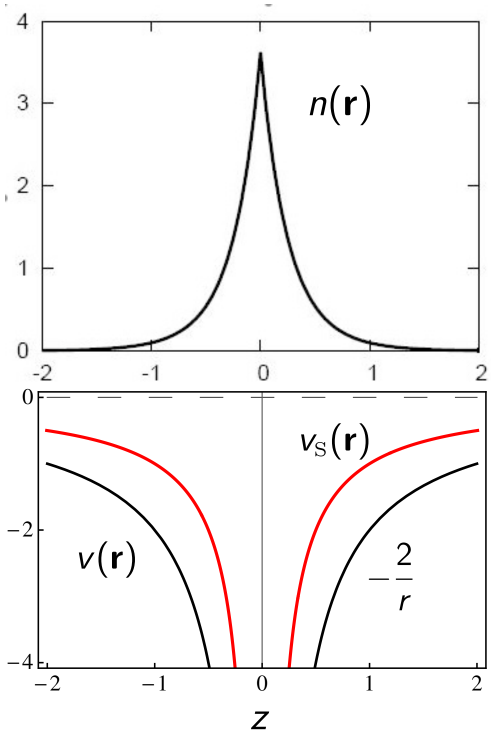
$$\boxed{F = T + V_{\rm ee} = T_{\rm S} + U + E_{\rm XC}}$$

the remainder is the exchange-correlation energy.

Most important result of exact DFT:

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

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



Today's basic XC approximations

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

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

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

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

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

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

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

Cost

- With GGA, KS cheaper than HF, scales N^3
- CCSD(T) scales N^7
- Moderate cluster, a week for CCSD(T) 20 atoms
- Decent desktop, a morning for 200 atoms HF or DFT.

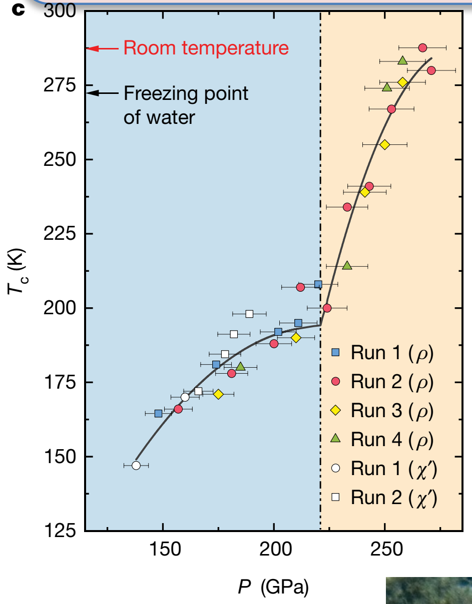
Performance

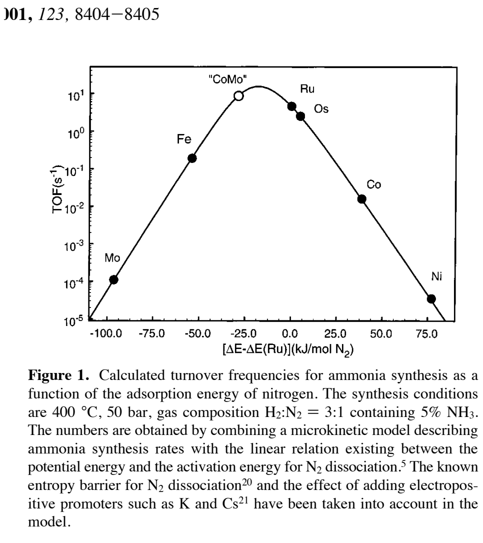
- Most cases, CCSD(T) gives chemical accuracy (error < 1 kcal/mol) for main group chemistry if converged

- Gives signal if there are known unknowns

- Dissociates H_2 correctly, but not N_2 because of single-reference starting point

Cool DFT applications

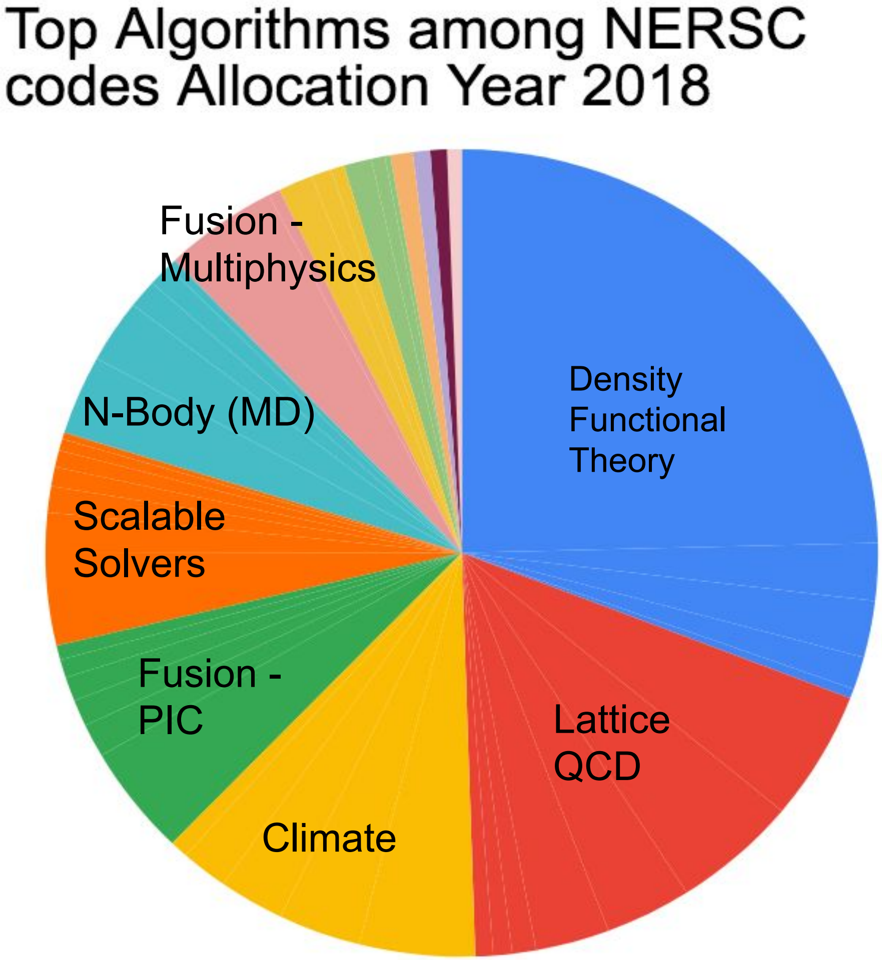




01, *123*, 8404−8405

Figure 1. Calculated turnover frequencies for ammonia synthesis as a function of the adsorption energy of nitrogen. The synthesis conditions are 400 °C, 50 bar, gas composition H_2:N_2 = 3:1 containing 5% NH_3. The numbers are obtained by combining a microkinetic model describing ammonia synthesis rates with the linear relation existing between the potential energy and the activation energy for N_2 dissociation.[5] The known entropy barrier for N_2 dissociation[20] and the effect of adding electropositive promoters such as K and Cs[21] have been taken into account in the model.

Many codes implement similar algorithms.



Regrouped top 50 codes by similar algorithms.

A small number of benchmarks can represent a large fraction of the workload.

More modern XC approximations

- Weak interactions
  - Tchatchenko: MBPT (Tu 2, F11)
- Range-separated hybrids eg HSE06
- Random Phase Approximation (RPA), eg Furche, Goerling, Scuseria,…
- Meta-GGA, eg Perdew's SCAN
- Local hybrid, eg DM21

Orbital-free DFT

- If we had accurate-enough approximation to $T_S[n]$, bypass solving KS equations.
- Could allow much larger systems.
- Original TF theory is of this kind
- But errors too large on absolute scale, so no-one has ever produced a generally useful approximation
- Genius of KS was overcoming this difficulty by re-introducing orbitals (Slater)
- Work by Trickey, Carter, Wesolwski, …

Time-dependent DFT

- Applies same methodology, but different theorem (Runge-Gross theorem)
- Create TDKS equations for v(r,t)
- In linear response, get low-lying optical excitations usefully accurately
- Built in to most quantum chemical codes
- Misses non-locality in solids
- Used in 1000’s papers/year.
- See Maitra’s recent Perspective JCP

Thermal DFT and WDM

- Mermin generalized HK to equilibrium at finite temperature (1965).
- Can solve KS equations at finite T with XC free energy
- WDM is about 30kK to 1MK, in between ‘normal’ phases and pure plasmas
- DFT proven very useful for simulating shocks, planetary interiors, fusion reactions, etc.

Common DFT failures

- Hard to get below 1 kcal/mol even for main group atomization energies
- Much less accurate for transition metal complexes
- Fails for stretched bonds
- Fails for multiple stretched bonds (thermodynamic limit)
- …

Delocalization error

- Semilocal functionals are too smooth (convex up)
- HF too sharp (convex down)
- Should be straight line segments
- Recently, SCAN @ HF yields very accurate water clusters
- Explained by DC-DFT.

Other tutorials

- Lin Lin: Embedding (W4)
- Stamm: Error analysis (Th 2)
- Gori: Field theory methods (Th 4)
- Grigori: Large scale lin alg (F9)

Chemistry versus materials physics

- Primary focus in materials: Response properties
  - Optical versus photoemission, etc.
- Primary focus in quantum chemistry: Ground-state energies to high accuracy
  - Tells you what bonds are formed and reaction rates
  - Chemical accuracy (1 kcal/mol)
  - CCSD(T) fails for multireference systems
  - Accuracy for weak bonds 0.1 kcal/mol
- Given method and basis set, any good code reproduces numbers to about 10 digits

Reproducibility and benchmarking

- In quantum chemistry, Pople created the concept of a ‘model chemistry’
- Model chemistry=a method plus a basis set
- Can get the same result to about 10 digits anywhere, anytime, with any professional-level code.
- The G2 data set is benchmark experimental and calculated data agreeing within 0.05 eV.
- In famous 1993 paper, Pople et al showed DFT could yield about 0.15 eV accuracy for covalent bond energies.

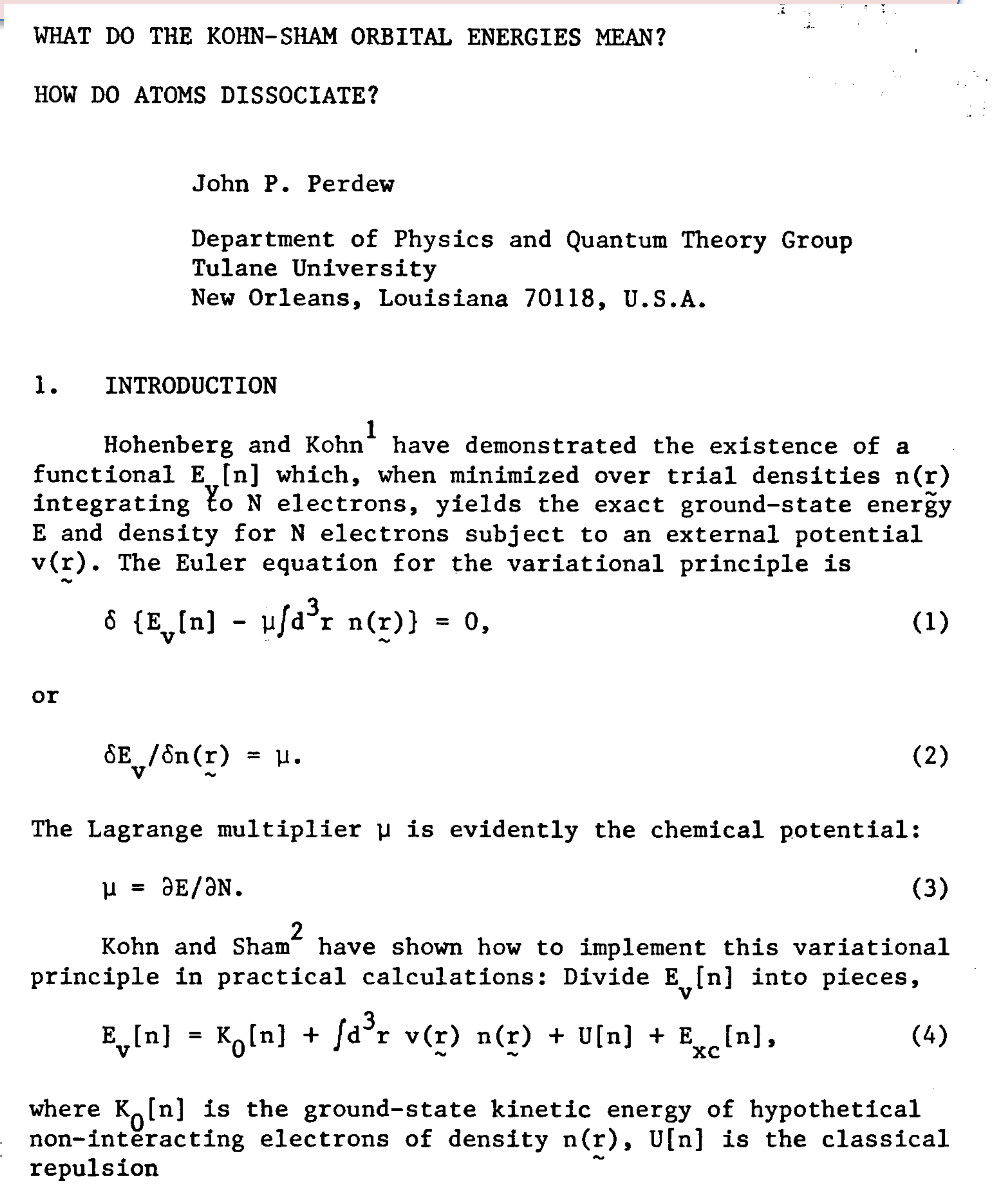
Basic successes ground-state DFT

- Local, semi-local, hybrid, vdw-corrected approximations yield useful accuracy for weakly correlated systems
- Works for both solids and molecules
- Some find functionals from general rules of quantum mechanics (eg Perdew), some from fitting databases (eg Truhlar)
- Perdew functionals work comparably well for solids and molecules simultaneously
- Many fitted functionals work only for molecules

Properties messed up by semilocal DFT

J.P. Perdew. “What do the Kohn-Sham orbitals mean? How do atoms dissociate?” In: Density Functional Methods in Physics. Ed. by R.M. Dreizler and J. da Providencia. NY: Plenum, 1985, p. 265.

See also much recent work by Weitao Yang, generalizing to spin DFT



WHAT DO THE KOHN-SHAM ORBITAL ENERGIES MEAN?

HOW DO ATOMS DISSOCIATE?

John P. Perdew

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1. INTRODUCTION

Hohenberg and Kohn[1] have demonstrated the existence of a functional $E_v[n]$ which, when minimized over trial densities $n(\underset{\sim}{r})$ integrating to N electrons, yields the exact ground-state energy E and density for N electrons subject to an external potential $v(\underset{\sim}{r})$. The Euler equation for the variational principle is

$$\delta\,\{E_v[n] - \mu\int d^3r\; n(\underset{\sim}{r})\} = 0, \tag{1}$$

or

$$\delta E_v/\delta n(\underset{\sim}{r}) = \mu. \tag{2}$$

The Lagrange multiplier μ is evidently the chemical potential:

$$\mu = \partial E/\partial N. \tag{3}$$

Kohn and Sham[2] have shown how to implement this variational principle in practical calculations: Divide $E_v[n]$ into pieces,

$$E_v[n] = K_0[n] + \int d^3r\; v(\underset{\sim}{r})\; n(\underset{\sim}{r}) + U[n] + E_{xc}[n], \tag{4}$$

where $K_0[n]$ is the ground-state kinetic energy of hypothetical non-interacting electrons of density $n(\underset{\sim}{r})$, U[n] is the classical repulsion

Derivative discontinuity

As a function of N, the energy is a sequence of straight line segments

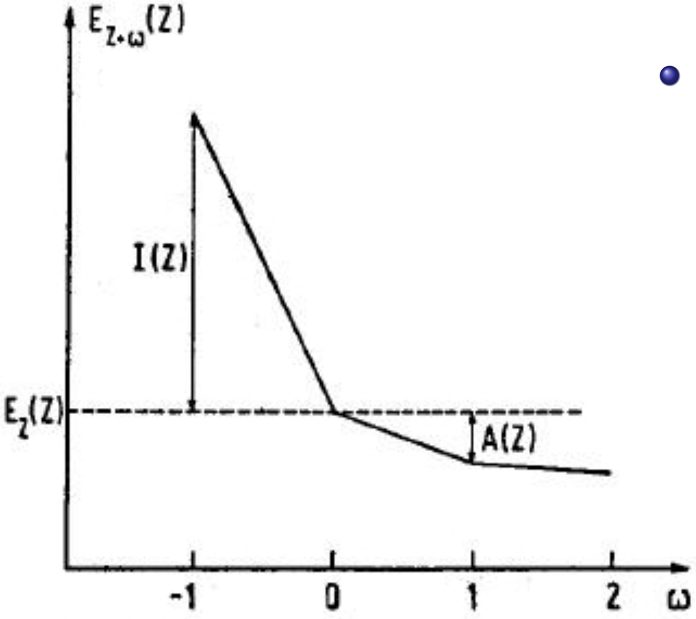


Fig. 2.2. Ground state energy of an atom with nuclear charge Z and $(Z+\omega)$ electrons

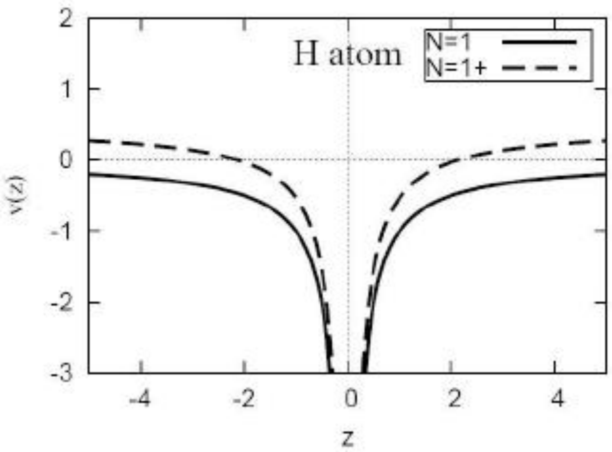
- R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).

$$\begin{aligned}\mu &= \frac{\partial E}{\partial N} \\ &= -\begin{cases} I, & N \le Z \\ A, & N > Z \end{cases}\end{aligned}$$

Jumps in potential

- When you add a tiny fraction of an electron to a system, the KS potential shifts uniformly, since before, $\epsilon_{\rm HOMO}(N) = -I$, but now, $\epsilon_{\rm HOMO}(N+\delta) = -A$
- Thus $v_{\rm S}(\mathbf{r})$ must jump by

$$\Delta_{\rm XC} = (I - A) + (\epsilon_{\rm HOMO} - \epsilon_{\rm LUMO}) = -\epsilon_{\rm LUMO} - A$$



- Very important in DFT calculations of:
  - molecules approaching each other, before they bond covalently.
  - single-molecule transport if molecule is weakly bound to leads.

Three gaps: All 'HOMO-LUMO'

- Fundamental (or charge) gap: (I=24.6 eV for He)
  - Voltage needed to get solid to conduct.
  - Can also be found from I-A, but tricky for periodic codes
  - AKA quasiparticle gap, well-approximated by GW, seen in photoemission. experiments
- Optical gap: (1s->2s singlet in He, 20.6 eV)
  - Lowest excitation by light, without changing N
  - Matches fundamental gap if no excitons
- Kohn-Sham gap: (1s->2s in He, 20.3 eV)
  - Energy difference between KS HOMO and LUMO for neutral system
  - Typically a great underestimate of I-A for solids

Mott-Hubbard gap

- Classic prototype of condensed matter
- Infinite chain of H atoms
- When lattice spacing is large, must be an insulator
- But with one electron per site, always a band metal

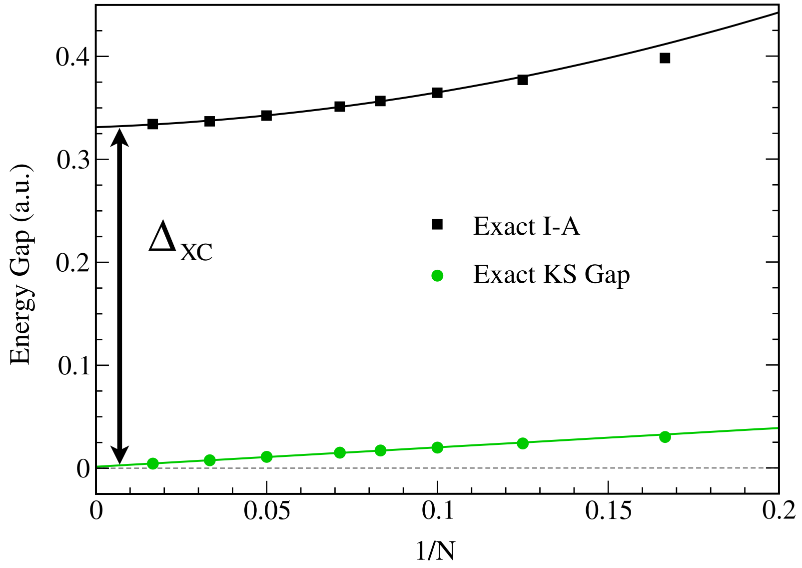


FIG. 3 (color online). Exact gaps for chains of N soft hydrogen atoms with atomic separation $b = 4$ (error bars are less than symbol sizes). The upper curve is a quadratic fit of exact gaps of the largest six systems and extrapolates to a finite value $E_g \simeq 0.33$. The exact Kohn-Sham gaps, in contrast, extrapolate to zero showing that for $N \to \infty$ the true KS system is metallic (lower curve is a linear fit of exat KS gaps of the largest six systems).

One-Dimensional Continuum Electronic Structure with the Density-Matrix Renormalization Group and Its Implications for Density-Functional Theory E.M. Stoudenmire, Lucas O. Wagner, Steven R. White, Kieron Burke, Phys. Rev. Lett. **109**, 056402 (2012).

Steps in KS potential

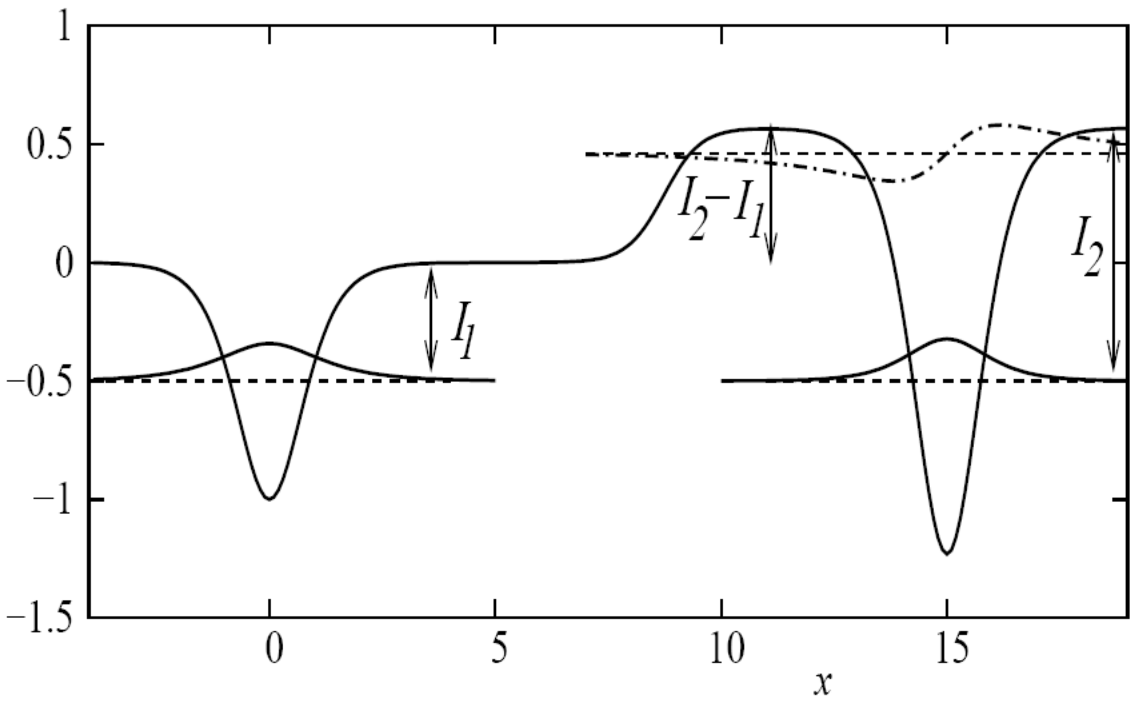


Figure: Cartoon of step in KS potential between two well-separated open-shell fragments.

- N. T. Maitra, J. Chem. Phys. 122, 234104 (2005).

Orbital-dependent functionals

- Perdew-Zunger self-interaction correction (1981) improves LDA, not GGA.
- Hybrids have some fraction of exact exchange
- Orbital-dependence cures many errors of semilocal approximations
- But key principle is that semilocal X mimics C, so cancellation of errors destroyed by 100% X.
- Fraction in hybrid must be fixed and determined by ground-state energetics

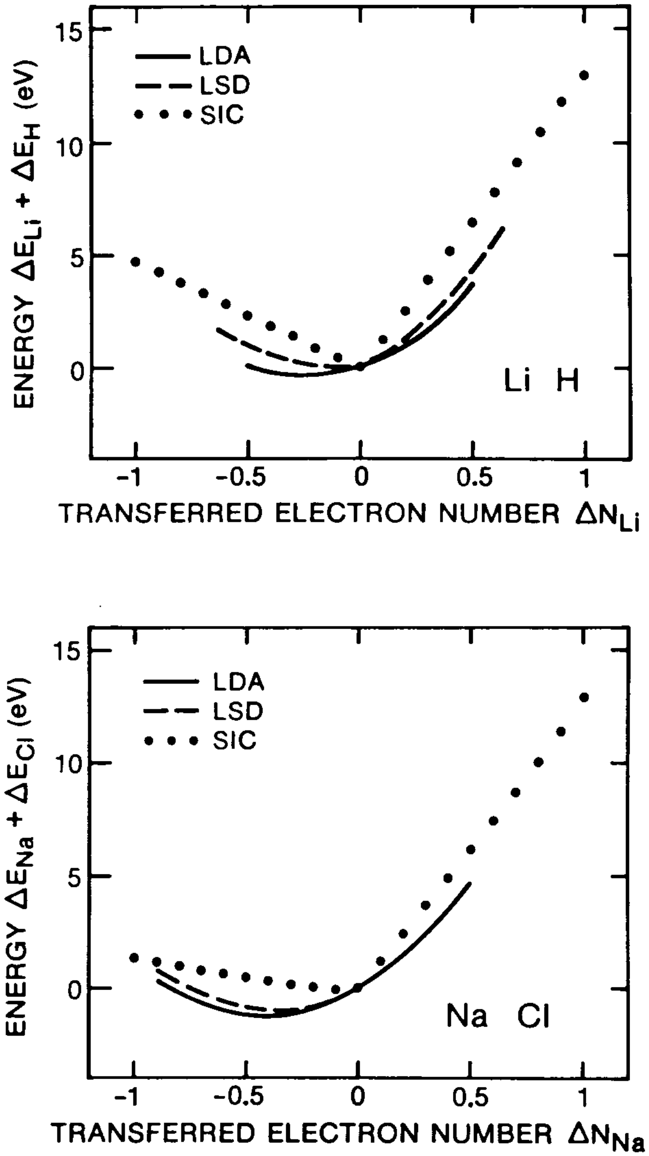


Fig. 6. Total energy of a separated diatomic system $\alpha\beta$, as a function of the number of electrons transferred from atom β to atom α.

KS versus GKS

- When dealing with orbital-dependent functionals, can treat as HF or pure KS (OEP)
- GKS treats as HF
- Both legitimate
- For ground-state energy, it typically makes almost no difference
- Makes large differences to eigenvalues spectrum!

Confusions

The word universal

- Always mis-applied
- Applies to exact functional, says that it does not depend on v(**r**), only n(**r**)
- All our approximations beyond LDA are hard-wired to Coulomb one-body potentials
- LDA *is* a universal functional as LDA becomes relatively exact for all systems in certain large-*N* limit.
- HF *is* a universal approximation as HF becomes relatively exact for all systems as strength of interaction goes to zero.

*All properties are functionals of n(**r**)*

- One of the HK theorems, certainly true.
- Means, e.g, the entire excitation spectrum.
- But the ground-state energy functional (and its universal piece, F[n]) is very special, because we can use it to find the density and then E.
- Even knowing exact $E_{XC}[n]$ only gives E, n, and properties that can be extracted from them.
- Can regard linear response TDDFT as a way of finding the functional for excited states (Hardy I)

Purity of functionals

- Word ‘empirical’ in DFT has little to do with semi-empirical models of quantum chemistry.
- B88 has an ‘empirical’ parameter that we derived 18 years later.
- Once a recipe is given in terms of the density, no matter where it comes from, it is a density functional that can be applied to any system.
- Intellectual purity is in the eye of the beholder.
- Do not read papers of empiricists to understand DFT.

Ambiguity of energy density

- Given a functional (eg LDAX), the energy density is not unique, but usually there's a standard one.
- Given an prescription for an energy density (eg the XC hole), then if a functional models the hole, energy densities are unique
- Local Lieb-Oxford bound never existed, but now appears in literature. Based on a misinterpretation of use in PBE.

Role of exact conditions

- Different kinds: Coordinate scaling of $E_X[n]$ against E_C=-42mH for He.
- Can classify by direct application to approximate functional versus need to calculate for a specific system
- Can impose for all possible densities versus check for real (ie Coulomb potential) densities
- Cannot construct useful functional from exact conditions alone (please read PBE paper)

Conclusions

- HF Is starting point of both traditional approaches
  - Wavefunction, eg CCSD(T), QMC, …
  - Green's function, eg GW

- KS-DFT is totally different approach to problem
  - Much lower cost allows larger systems
  - Unreliable, only moderate accuracy, failures for strong correlation