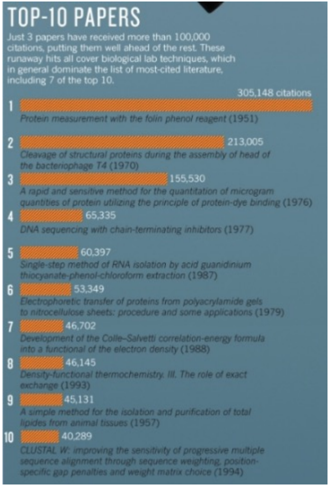
Density Functional Theory

Motivation



TOP-10 PAPERS

Just 3 papers have received more than 100,000 citations, putting them well ahead of the rest. These runaway hits all cover biological lab techniques, which in general dominate the list of most-cited literature, including 7 of the top 10.

Density Functional Theory extremely influential

- 1926: Schrödinger’s equation
- 1927: Thomas-Fermi
- 1965: Kohn-Sham

R. Van Noorden, B. Maher, R. Nuzzo, Nature, 2014.

Recap

Known: Obtaining observables from quantum mechanics (Born-Oppenheimer)

$$\hat{H} = \hat{H}\left(\underbrace{Z_i}_{\text{Nuclear charges}}, \underbrace{\mathsf{R}_i}_{\text{Nuclear coordinates}}, \overbrace{N_e}^{\text{Number of electrons}}, \overbrace{\sigma}^{\text{Spin}}\right) \tag{50}$$

Steps:

- System defines Hamiltonian $\hat{H}$
- Solving Schrödinger's equation yields wave function $\hat{H}\,\Psi = E\,\Psi$
- Operator yields observable $\langle \hat{A} \rangle = \langle \Psi \mid \hat{A} \mid \Psi \rangle$

Recap

$$\hat{H} = \underbrace{\hat{T}}_{\text{Kinetic energy}} + \underbrace{\hat{V}}_{\text{Potential energy}} = \underbrace{\hat{T}_{\text{e}}}_{\text{Kinetic energy electrons}} + \underbrace{\hat{V}_{\text{en}}}_{\text{Electron-nuclei interaction}} + \overbrace{\hat{V}_{\text{ee}}}^{\text{Electron-electron interaction}} + \overbrace{\hat{V}_{\text{nn}}}^{\text{Nuclei-nuclei}} \tag{51}$$

with

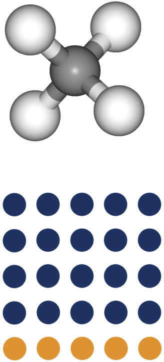
$$\hat{H} = -\sum_{i} \frac{\hbar^2}{2m_e} \nabla^2_{r_i} - \sum_{i,j} \frac{Z_i e^2}{4\pi\varepsilon_0 |\mathbf{R}_i - \mathbf{r}_j|} + \sum_{i,j>i} \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,j>i} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 |\mathbf{R}_i - \mathbf{R}_j|} \tag{52}$$

Resulting wave function

$$\Psi = \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_n)$$

has $3N_e$ dimensions!

Example



Example

- Methane, i.e. 10 electrons
- Grid with 5 points along each dimension

Wave function

- $5^{3 \cdot 10}$ grid points
- 6 ZB
- 7 times ALL data

Core idea of DFT

Replace 3N-dimensional wave function Ψ with a 3-dimensional electron density ρ

$$\Psi = \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_n) \longrightarrow \rho = \rho(\mathbf{r}) \tag{53}$$

Motivation for equivalence

E.B. Wilson[1]: this contains the same information

$$\rho \to Z_i, \mathsf{R}_i, N_e, \sigma \to \hat{H} \to \Psi$$

$$\hat{H}\left(\underbrace{Z_i}_{\text{Nuclear charges}}, \underbrace{\mathsf{R}_i}_{\text{Nuclear coordinates}}, \overbrace{N_e}^{\text{Number of electrons}}, \overbrace{\sigma}^{\text{Spin}}\right) \to \Psi \tag{54}$$

Tricks:

- Coordinates: local maxima in ρ
- Nuclear charges: Kato's Theorem[2]
- Number electrons and spin: $N_e = \int d\mathsf{r}\rho(\mathsf{r})$

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[1] P.O. Löwdin, Int. J. Quant. Chem. 1986. [2] T. Kato, Commun. Pure Appl. Math., 1957.

Hohenberg-Kohn Theorem I

The ground state electron density uniquely defines the external potential.[1]

Proof through contradiction: Let's assume, one density would be valid for two external potentials V_i

$$\underbrace{E_1}_{\text{Energy for potential 1}} = \langle \underbrace{\Psi_1}_{\text{Wave function for potential 1}} | \hat{H}_1 | \Psi_1 \rangle = \int \overbrace{V_1}^{\text{External potential}}(\mathbf{r})\, \overbrace{\rho}^{\text{Electron density for both systems}}(\mathbf{r})\, \mathrm{d}\mathbf{r} + \langle \Psi_1 | \underbrace{\hat{T}}_{\text{Kinetic energy}} + \underbrace{\hat{U}}_{\text{Universal (HK) functional}} | \Psi_1 \rangle \tag{55}$$

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[1] P. Hohenberg, W. Kohn, Phys. Rev. 1964.

Hohenberg-Kohn Theorem I (cont’d)

Variational principle ⇒ For all other wave functions, energy is strictly higher

$$E_1 < \langle \underbrace{\Psi_2}_{\text{Wave function for potential 2}} | \underbrace{\hat{H}_1}_{\text{Hamiltonian system 1}} | \Psi_2 \rangle = \langle \Psi_2 | \overbrace{\hat{H}_2}^{\text{Hamiltonian system 2}} | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle = E_2 + \int \left[V_1(\mathbf{r}) - V_2(\mathbf{r}) \right] \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{56}$$

Due to symmetry between indices 1 and 2:

$$E_2 < E_1 + \int \left[V_2(\mathbf{r}) - V_1(\mathbf{r}) \right] \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{57}$$

Contradiction from summation

$$E_1 + E_2 < E_1 + E_2 \tag{58}$$

Hohenberg-Kohn Theorem II

The ground state electron density has the lowest energy of all densities.[1]

Proof: For other wave functions, the energy is strictly larger.

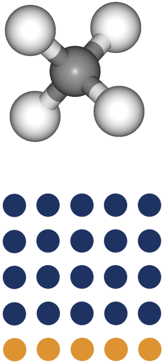
$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle, \qquad E_0 < \langle \Psi | \hat{H} | \Psi \rangle \;\; (\Psi \neq \Psi_0) \tag{59}$$

Since each wave function has exactly one energy.

$$E_0 = E[\rho_0] < E[\rho], \qquad \rho \neq \rho_0 \tag{60}$$

[1] P. Hohenberg, W. Kohn, Phys. Rev. 1964.

Example



Example

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Wave function

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- 6 ZB
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Electron density

- 5^3 grid points
- 1 KB
- half a page of text

Solutions

What we have

- Unknown universal functional $F[\rho]$ (universal: does not depend on geometry)
- Trial densities ρ

What we need

- some functional F
- procedure to find optimal ρ_0

System

- Take geometry, obtain V_{ext}
- Choose functional and basis set (see later)
- Minimize $E[\rho]$ by varying density self-consistently

Kohn-Sham DFT

$$E[\rho] = F[\rho] + \int V_{\text{ext}} \rho \, d\mathbf{r} \tag{61}$$

Challenge: Hard to find F. Kohn and Sham proposed[1]

$$F[\rho] = \underbrace{T_s}_{\text{Kinetic energy non-interacting particles}}[\rho] + \overbrace{E_{\text{H}}}^{\text{Hartree energy functional}}[\rho] + \overbrace{E_{\text{XC}}}^{\text{Exchange correlation functional}}[\rho] \tag{62}$$

$$T_s[\rho] = \langle \overbrace{\Phi}^{\text{Kohn-Sham wave function}}[\rho] \mid \underbrace{\hat{T}}_{\text{Kinetic energy operator } -\nabla^2/2} \mid \Phi[\rho] \rangle; \qquad E_{\text{H}}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\, \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \tag{63}$$

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[1] W. Kohn and L. J. Sham, Phys. Rev., 1965.

Kohn-Sham Equations

$$E[\underbrace{\{\varphi_i\}}_{\text{Kohn-Sham orbitals}}] = \sum_{i=1}^{N} \int \varphi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) \right) \varphi_i(\mathbf{r})\, d\mathbf{r} + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho] \qquad (64)$$

Where the orbitals are found by solving (self-consistently)

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \frac{\delta\left[E_{\text{H}}[\rho] + E_{\text{xc}}[\rho]\right]}{\delta\rho(\mathbf{r})}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \underbrace{\varepsilon_i}_{\text{Kohn-Sham orbital energies}} \varphi_i(\mathbf{r}) \qquad (65)$$

$$\underbrace{v_{\text{H}}(\mathbf{r})}_{\text{Hartree potential}} \equiv \frac{\delta E_{\text{H}}[\rho]}{\delta\rho(\mathbf{r})}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'; \; \underbrace{v_{\text{xc}}(\mathbf{r})}_{\text{Exchange-correlation potential}} \equiv \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}(\mathbf{r}) \qquad (66)$$

How to solve? See Hartree-Fock (later)

Functionals

Recent developments in LIBXC — A comprehensive library of functionals for density functional theory

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ABSTRACT

LIBXC is a library of exchange–correlation functionals for density-functional theory. We are concerned with semi-local functionals (or the semi-local part of hybrid functionals), namely local-density approximations, generalized-gradient approximations, and meta-generalized-gradient approximations. Currently we include around 400 functionals for the exchange, correlation, and the kinetic energy, spanning more than 50 years of research. Moreover, LIBXC is by now used by more than 20 codes, not only from the atomic, molecular, and solid-state physics, but also from the quantum chemistry communities.

Local Density Approximation (LDA)

Idea

- Assumes (almost) same density everywhere
- Exact for the uniform electron gas *Jellium*
- Used for materials, deprecated
- Strictly local

$$E_{xc}^{\mathrm{LDA}} = \int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r})\, \epsilon_{xc}^{\mathrm{LDA}}[\rho(\mathbf{r})] \tag{67}$$

Popular choice: VWN

Generalized-Gradient Approximation (GGA)

Idea

- Includes local gradient
- *semi-local* nature: gradient tells a bit about close proximity
- Widely used, both for materials and molecules

$$E_{xc}^{\mathrm{GGA}} = \int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r})\, \epsilon_{xc}^{\mathrm{GGA}}\big(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\big) \tag{68}$$

Popular choice: PBE

Meta-GGA

Idea

- Next derivative and/or kinetic energy density τ
- Sensitive to numerical integration through Laplacian
- Default settings sometimes not good enough

$$E_{xc}^{\mathsf{GGA}} = \int \mathsf{d}\mathbf{r}\, \rho(\mathbf{r})\, \epsilon_{xc}^{\mathsf{GGA}}\big(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau\big), \qquad \tau \equiv \sum_i^{\mathsf{occ}} |\nabla\psi_i(\mathbf{r})|^2 \tag{69}$$

Popular choices: SCAN (built on constraints!), M06, TPSS

Hybrid functional

Idea

- Commonly improved band gaps and relative energies between spin states
- Popular choices: B3LYP, PBE0

$$E_{xc}^{\mathrm{hyb}} = a\,E_x^{\mathrm{HF}} + (1-a)\,E_x^{\mathrm{DFT}} + E_c^{\mathrm{DFT}} \tag{70}$$

$$E_x^{\mathrm{HF}} = -\frac{1}{2}\sum_{i,j}\iint \psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\,\frac{1}{r_{12}}\,\psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \tag{71}$$

Range-separated hybrid

Idea

- Computationally more efficient
- Popular choice: HSE06

$$\frac{1}{r_{12}} = \frac{1 - \left[\alpha + \beta\big(1 - \omega_{\mathsf{RSF}}(\gamma, r_{12})\big)\right]}{r_{12}} + \frac{\alpha + \beta\big(1 - \omega_{\mathsf{RSF}}(\gamma, r_{12})\big)}{r_{12}} \tag{72}$$

Can be tuned in many cases to specific system based on Koopman's condition

$$-\varepsilon_{\mathsf{HOMO}}(N_e) = \mathsf{IE}(N_e) = E(N_e - 1) - E(N_e) \tag{73}$$

Summary

Implications

- Replace the 3N-dimensional wave function with 3D electron density.
- There is one functional (function of functions) yielding the energy, hence the name density functional theory: $E[\rho]$
- This functional is...
  - Universal: Does not depend on the system!
  - Unknown: Topic of current research
- We can obtain the electron density by minimizing the energy.