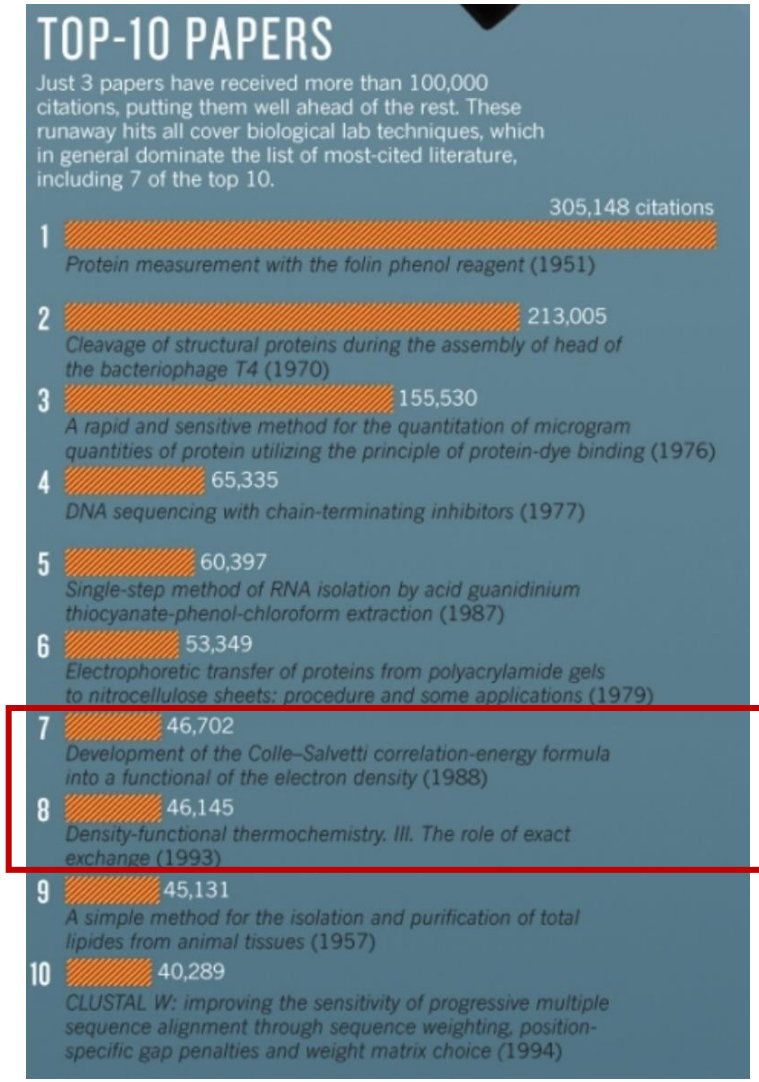
Density Functional Theory

Motivation



Density Functional Theory extremely influential

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

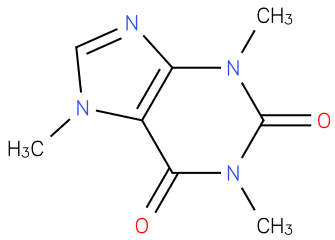
R. Van Noorden, B. Maher, R. Nuzzo, *Nature*, 2014.

Recap

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

1. System defines Hamiltonian $\hat{\mathrm{H}} = \hat{\mathrm{H}}(Z_i, \mathbf{R}_i, N_e, \sigma)$

   $\hat{\mathrm{H}} = \hat{\mathrm{T}} + \hat{\mathrm{V}}$



$\longrightarrow \quad \hat{\mathrm{H}}$

2. Solving Schrödinger's equation yields wave function Ψ

   $\hat{\mathrm{H}}\,\Psi = E\Psi$

$\hat{\mathrm{H}} \longrightarrow \Psi$

3. Operator yields observable $\hat{\mathrm{A}}$

   $\langle \hat{\mathrm{A}} \rangle = \langle \Psi | \hat{\mathrm{A}} | \Psi \rangle$

$\Psi \longrightarrow$ property

Recap

System defines Hamilton operator $\hat{\mathrm{H}}$

$$\hat{\mathrm{H}} = \hat{\mathrm{T}} + \hat{\mathrm{V}} = \hat{\mathrm{T}}_{\mathrm{e}} + \hat{\mathrm{V}}_{\mathrm{en}} + \hat{\mathrm{V}}_{\mathrm{ee}} + \hat{\mathrm{V}}_{\mathrm{nn}}$$

$$= -\sum_i \frac{\hbar^2}{2m_e} \nabla^2_{\mathbf{r}_i}$$ Kinetic energy of the electrons

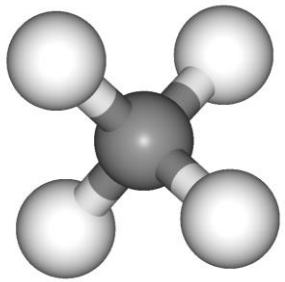
$$-\sum_{i,j} \frac{Z_i e^2}{4\pi\varepsilon_0 \left|\mathbf{R}_i - \mathbf{r}_j\right|}$$ Coulomb nuclei-electrons

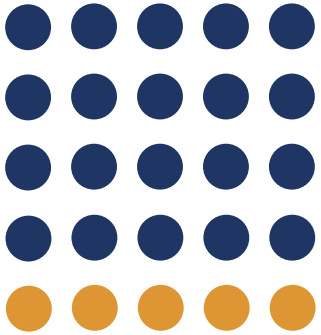
$$+\sum_{i,j>i} \frac{e^2}{4\pi\varepsilon_0 \left|\mathbf{r}_i - \mathbf{r}_j\right|}$$ Coulomb electrons-electrons

$$+\sum_{i,j>i} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 \left|\mathbf{R}_i - \mathbf{R}_j\right|}$$ Coulomb nuclei-nuclei

Resulting wave function $\Psi = \Psi\left(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_n\right)$ Impractical: 3N-dimensional!

Example





$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_n)$$

Methane: 10 electrons
Grid with 5 points along each dimension

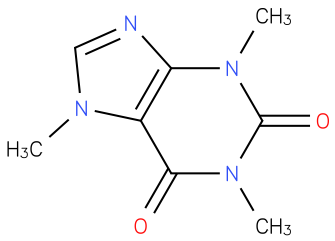
Wave function: $5^{3 \times 10}$ grid points 6 ZB 7 times ALL data

Core idea

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

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_n) \longrightarrow \rho = \rho(\mathbf{r})$$

E.B. Wilson: Same information!



$\longrightarrow \hat{\mathrm{H}} = \hat{\mathrm{H}}(Z_i, \mathbf{R}_i, N_e, \sigma)$

$\longrightarrow \Psi$

$\mathbf{R}_i$ Nuclear coordinates from local maxima

Z_i Nuclear charges: Kato's Theorem

N_e, σ Number electrons: $N_e = \int \mathrm{d}\mathbf{r}\rho(\mathbf{r})$

$$\rho \longrightarrow Z_i, \mathbf{R}_i, N_e, \sigma \longrightarrow \hat{\mathrm{H}} \longrightarrow \Psi$$

P.O. Löwdin, *Int. J. Quant. Chem.* **1986**. T. Kato, *Commun. Pure Appl. Math.*, **1957**.

Hohenberg-Kohn-Theorem 1

The ground state electron density uniquely defines the electrostatic potential.

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

$$E_1 = \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle = \int V_1(\mathbf{r}) \rho(\mathbf{r}) \, \mathrm{d}\mathbf{r} + \langle \Psi_1 | \hat{T} + \hat{U} | \Psi_1 \rangle$$

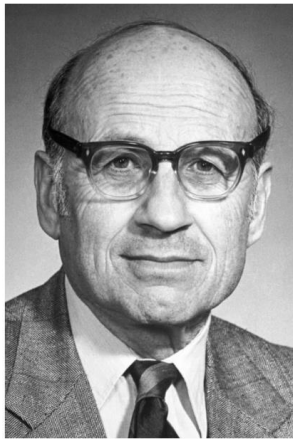
Variationsprinzip: Für andere Wellenfunktionen ist die Energie strikt größer

$$E_1 < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \underline{\langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle} + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle =$$

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

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

$$E_1 + E_2 < E_1 + E_2$$ Widerspruch!



W. Kohn
Nobelpreis Chemie 1998

P. Hohenberg, W. Kohn, *Phys. Rev.* **1964**.

Hohenberg-Kohn-Theorem 2

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

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

$$E_0 = \langle \Psi_0 | \hat{\mathrm{H}} | \Psi_0 \rangle$$

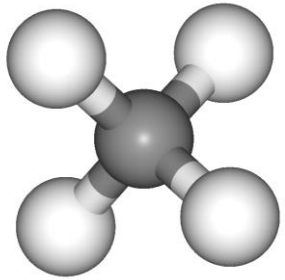
$$E_0 < \langle \Psi | \hat{\mathrm{H}} | \Psi \rangle \qquad \Psi \neq \Psi_0$$

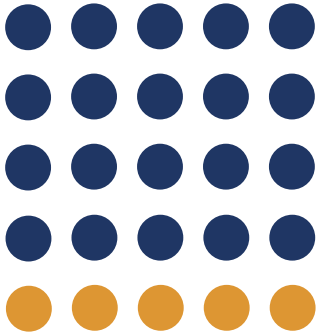
Since each wave function has exactly one energy.

$$E_0 = E[\rho_0] < E[\rho] \qquad \rho \neq \rho_0$$

P. Hohenberg, W. Kohn, *Phys. Rev.* **1964**.

Example





$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_n)$$

Methane: 10 electrons
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Wave function:	$5^{3 \times 10}$ grid points	6 ZB	7 times ALL data
Electron density:	5^3 points	1 KB	½ page of text

Implications

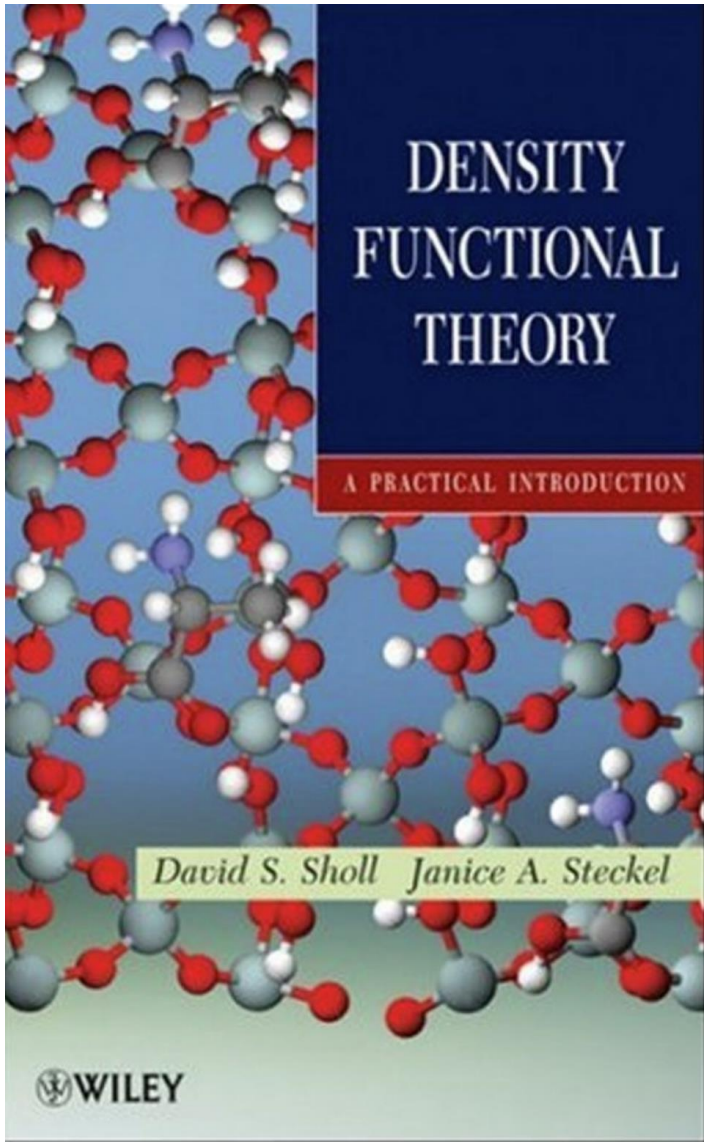
- Replace the 3N-dimensional wave function with 3D electron density.

- 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.

Suggested Literature



- “How to”: examples of practical methods
- Easy to follow, high-level picture
- Enough details to obtain reliable setups
- A bit dated on choice of functionals (more on that later)