Molecular Dynamics

Propagation

Ergodicity: time average = ensemble average

$$\frac{\mathbf{F}}{m} = \mathbf{a} = \frac{d}{dt}\mathbf{v} = \frac{d^2}{dt^2}\mathbf{r}$$

Stepwise integration
- Long steps
- Reversible = conservation of energy
- No high derivatives
- Access to instantaneous velocities
- Metric: global error: long term error from integration

Verlet Integrator

- Two Taylor expansions, one forward, one backward

$$\mathbf{x}(t+\Delta t) = \mathbf{x}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2 + \frac{1}{6}\mathbf{j}(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

$$\mathbf{x}(t-\Delta t) = \mathbf{x}(t) - \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2 - \frac{1}{6}\mathbf{j}(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

- Add them up

$$\mathbf{x}(t+\Delta t) + \mathbf{x}(t-\Delta t) = 2\mathbf{x}(t) + \mathbf{a}(t)\Delta t^2 + \mathcal{O}(\Delta t^4)$$

Verlet Integrator

$$\mathbf{x}(t + \Delta t) + \mathbf{x}(t - \Delta t) = 2\mathbf{x}(t) + \mathbf{a}(t)\Delta t^2 + \mathcal{O}(\Delta t^4)$$

- No instantaneous velocities: finite differences required
- Needs two past positions and initial boundary conditions

$$\mathbf{x}(t_0 + \Delta t) = \mathbf{x}(t_0) + \mathbf{v}(t_0)\Delta t + \mathbf{a}(t_0)\Delta t^2$$

- Global error $\mathcal{O}(\Delta t^2)$
- Time reversible

Velocity Verlet Integrator

- Like Verlet, explicitly calculate velocities via a half-step

$$\mathbf{x}(t+\Delta t) = \mathbf{x}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2$$

$$\mathbf{v}(t+\frac{1}{2}\Delta t) = \mathbf{v}(t) + \frac{1}{2}\mathbf{a}(t)\Delta t$$

$$\mathbf{v}(t+\Delta t) = \mathbf{v}(t+\frac{1}{2}\Delta t) + \frac{1}{2}\mathbf{a}(t+\Delta t)\Delta t$$

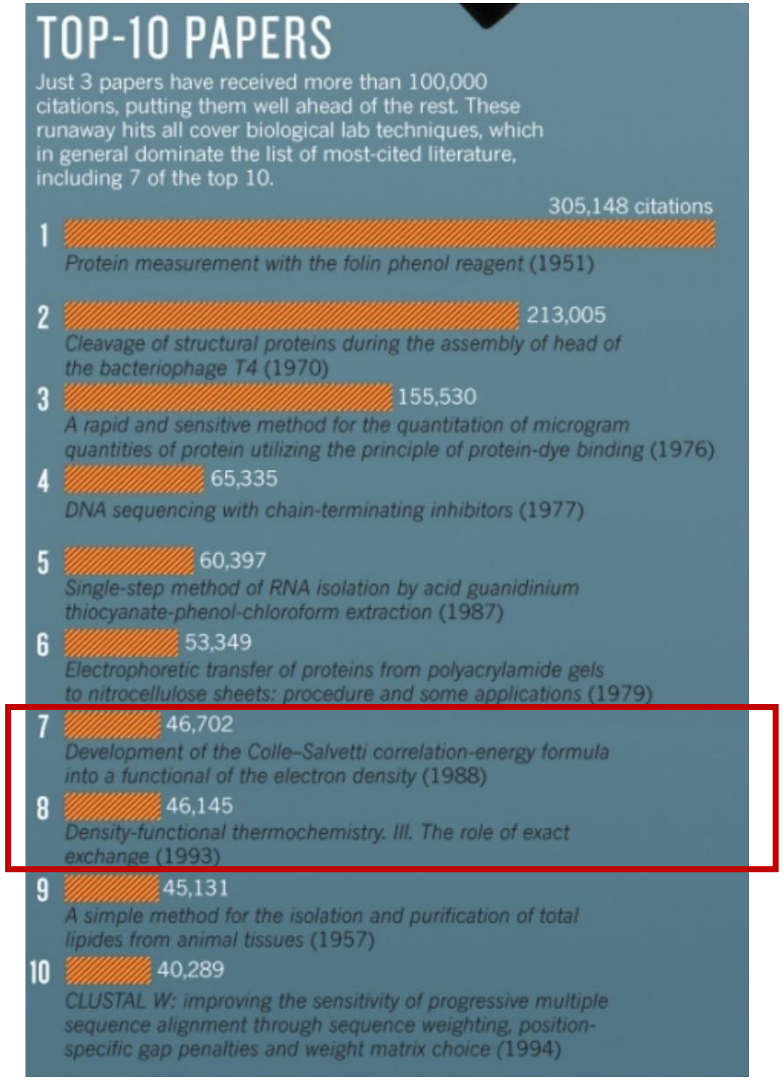
$$\mathbf{v}(t+\Delta t) = \mathbf{v}(t) + \frac{1}{2}\left[\mathbf{a}(t+\Delta t) + \mathbf{a}(t)\right]\Delta t$$

Edge Cases

- Initial velocities: flying ice cube
- Interfaces: thermalisation
- Ensembles
  - NVT, NPT, NVE, …
- Periodic boundary conditions and minimum image convention

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.

1 305,148 citations
Protein measurement with the folin phenol reagent (1951)

2 213,005
Cleavage of structural proteins during the assembly of head of the bacteriophage T4 (1970)

3 155,530
A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding (1976)

4 65,335
DNA sequencing with chain-terminating inhibitors (1977)

5 60,397
Single-step method of RNA isolation by acid guanidinium thiocyanate-phenol-chloroform extraction (1987)

6 53,349
Electrophoretic transfer of proteins from polyacrylamide gels to nitrocellulose sheets: procedure and some applications (1979)

7 46,702
Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density (1988)

8 46,145
Density-functional thermochemistry. III. The role of exact exchange (1993)

9 45,131
A simple method for the isolation and purification of total lipides from animal tissues (1957)

10 40,289
CLUSTAL W: improving the sensitivity of progressive multiple sequence alignment through sequence weighting, position-specific gap penalties and weight matrix choice (1994)

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

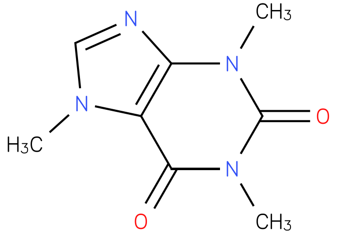
$$\hat{\mathrm{H}} = \hat{\mathrm{T}} + \hat{\mathrm{V}}$$

2. Solving Schrödinger's equation yields wave function Ψ

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

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

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



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

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

$\Psi \longrightarrow$ 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

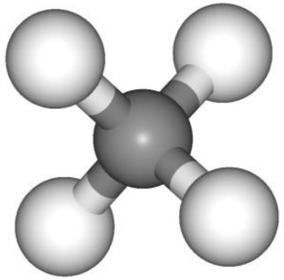
$$-\sum_{i,j} \frac{Z_i e^2}{4\pi\varepsilon_0 \left|\mathbf{R}_i - \mathbf{r}_j\right|}$$ Coulomb nuclei-electrons

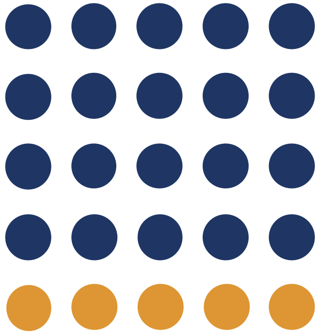
$$+\sum_{i,j>i} \frac{e^2}{4\pi\varepsilon_0 \left|\mathbf{r}_i - \mathbf{r}_j\right|}$$ Coulomb electrons-electrons

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

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

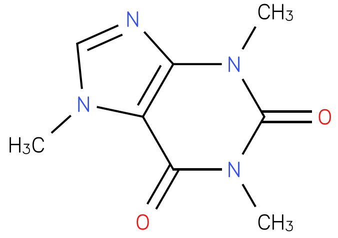
Wave function: $5^{3 \times 10}$ grid points 6 ZB 7 times ALL data

Core idea

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

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

E.B. Wilson: Same information!



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

$$\longrightarrow \quad \Psi$$

$\mathbf{R}_i$	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

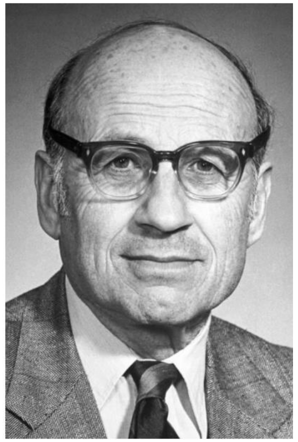
$$E_1 < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \underline{\langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle} + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle =$$

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

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

$$E_1 + E_2 < E_1 + E_2$$

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.

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

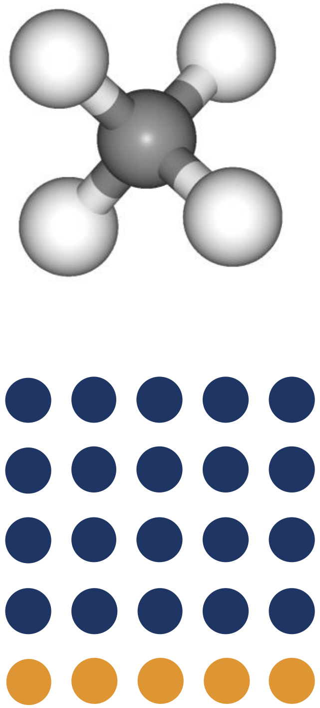
$$E_0 < \langle \Psi | \hat{\mathrm{H}} | \Psi \rangle \qquad \Psi \neq \Psi_0$$

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



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

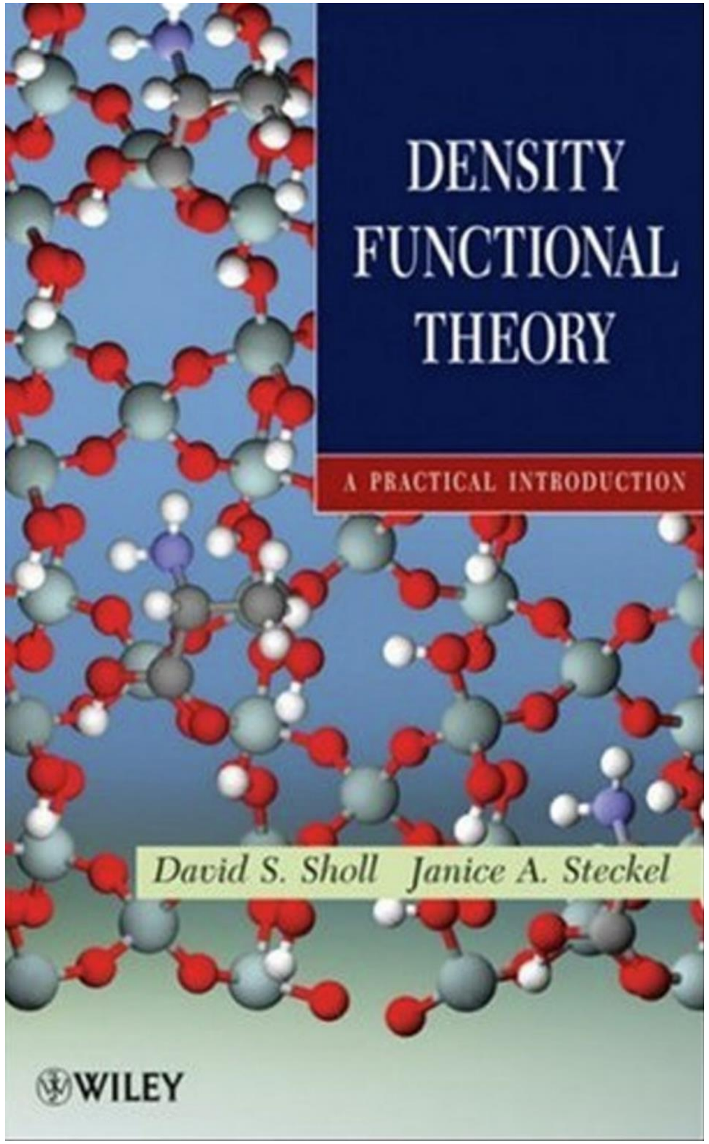
Methane: 10 electrons
Grid with 5 points along each dimension

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


DENSITY FUNCTIONAL THEORY

A PRACTICAL INTRODUCTION

David S. Sholl Janice A. Steckel

WILEY

- “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)