

General Introduction: Theory, Approximations and Methods

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Part I: Theoretical Foundations

Part II: Quantum-Level Methods

Part III: Classical & Multiscale Methods

Part IV: Implementation & Applications

The Need for Quantum Mechanics

Limitations of Classical Mechanics

- Blackbody radiation
- Photoelectric effect
- Atomic Structure

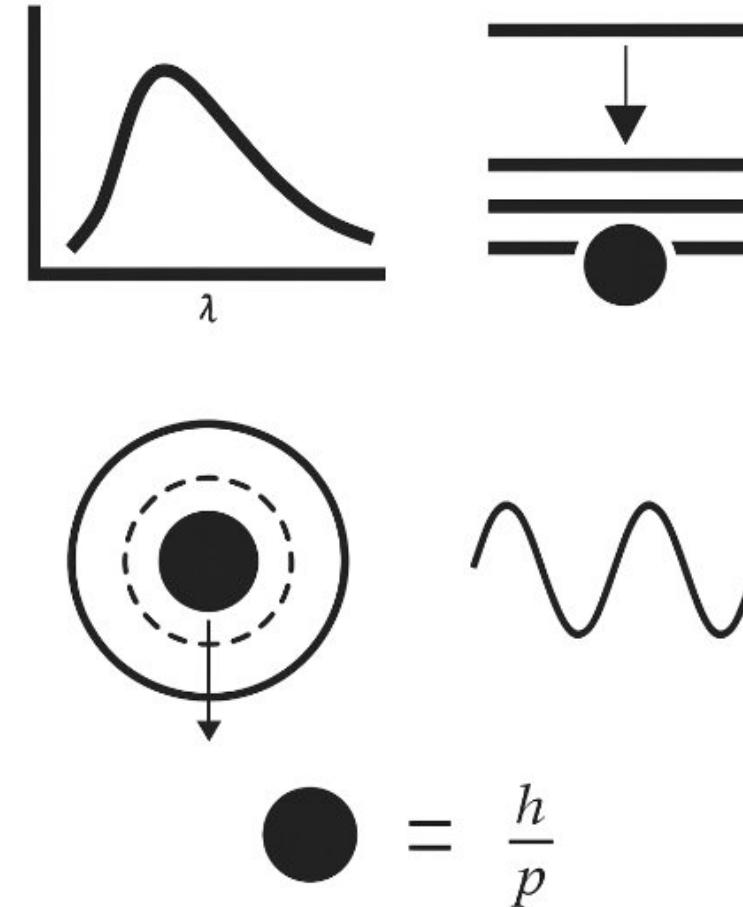
Birth of Quantum Theory

- Planck (1900): Energy is quantized
- Einstein (1905): Light is made of photons
- Bohr (1913): Quantized orbits explain hydrogen spectrum

Wave-Particle Duality

- Matter behaves as both particles and waves
- de Broglie relation:

$$\lambda = \frac{h}{p}$$



The Quantum Mechanical Framework

The Wavefunction $\psi(r, t)$

- Contains all information about a quantum system
- $|\psi(r, t)|^2$: Probability density

The Schrödinger Equation

- Time-independent form:

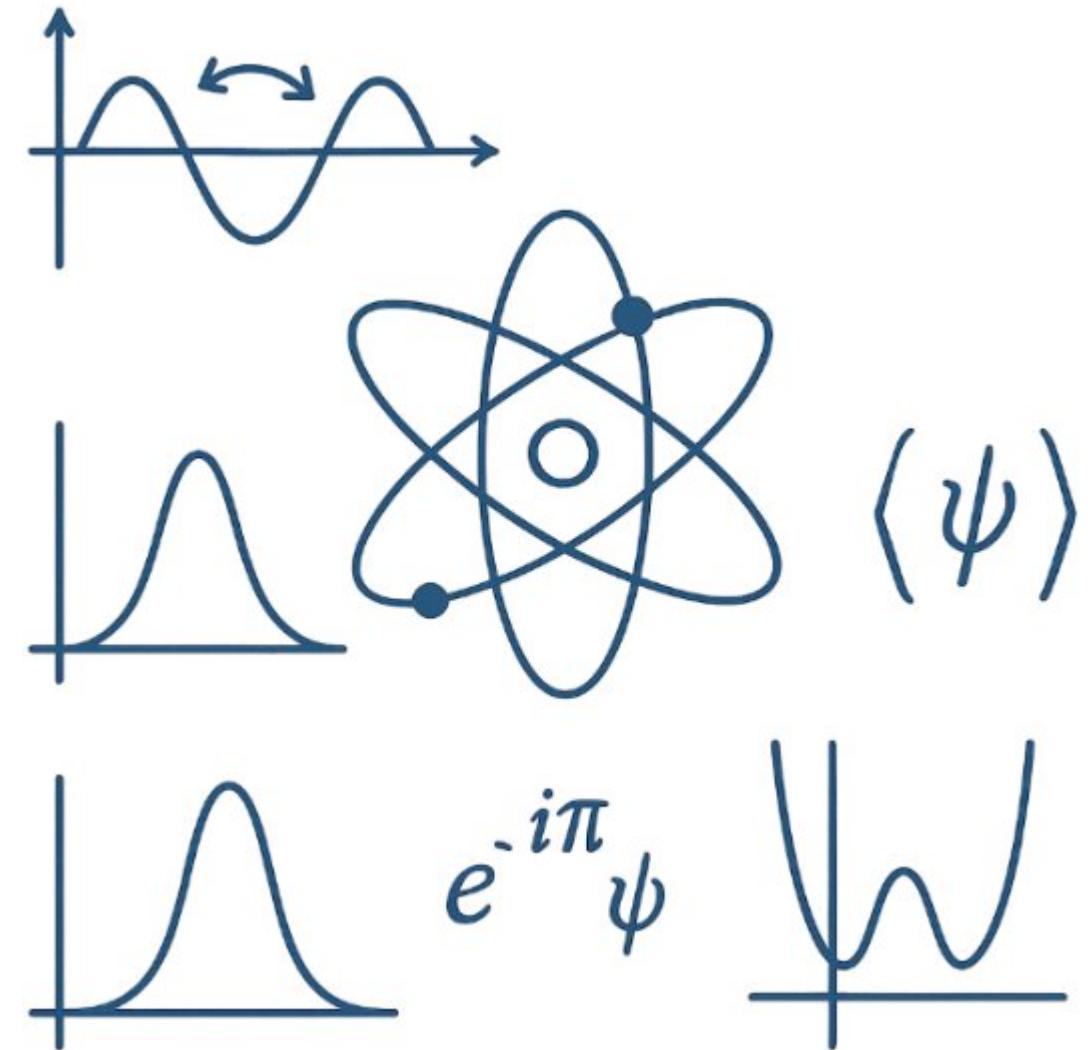
$$\hat{H}\psi(r) = E\psi(r)$$

- Hamiltonian Operator

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r)$$

The Challenge:

- Solvable only for simple systems
- For realistic atoms/molecules we need approximations



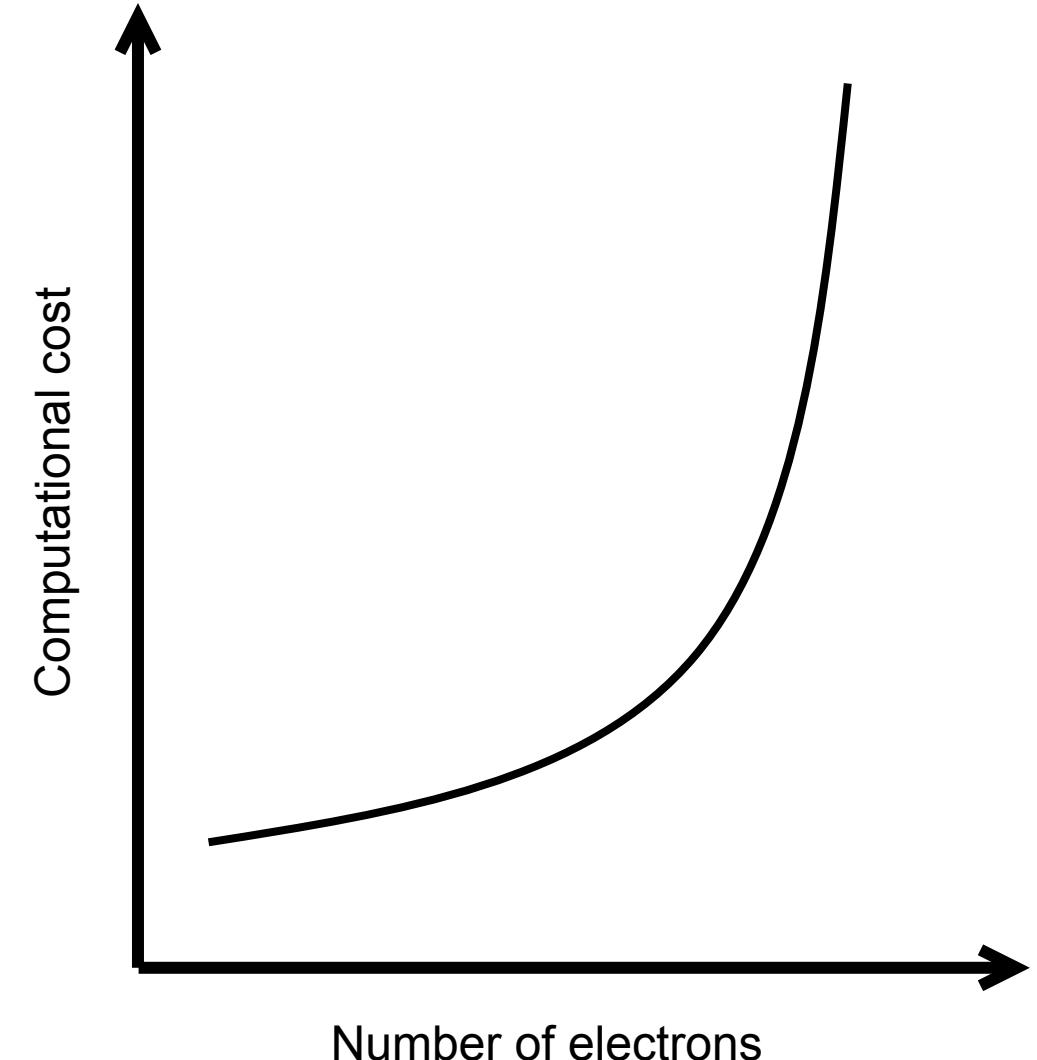
The Need for Approximation in Quantum Mechanics

The Many-Body Problem

- Schrödinger equation for multi-particle systems
- $$\hat{H}\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = E\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$$
- No analytical solution for systems with $N > 1$
 - Full wavefunction lives in a $3N$ -dimensional space

Why It Matters:

- Realistic systems: molecules, materials, proteins = many electrons
- Must use approximate methods to make calculations feasible



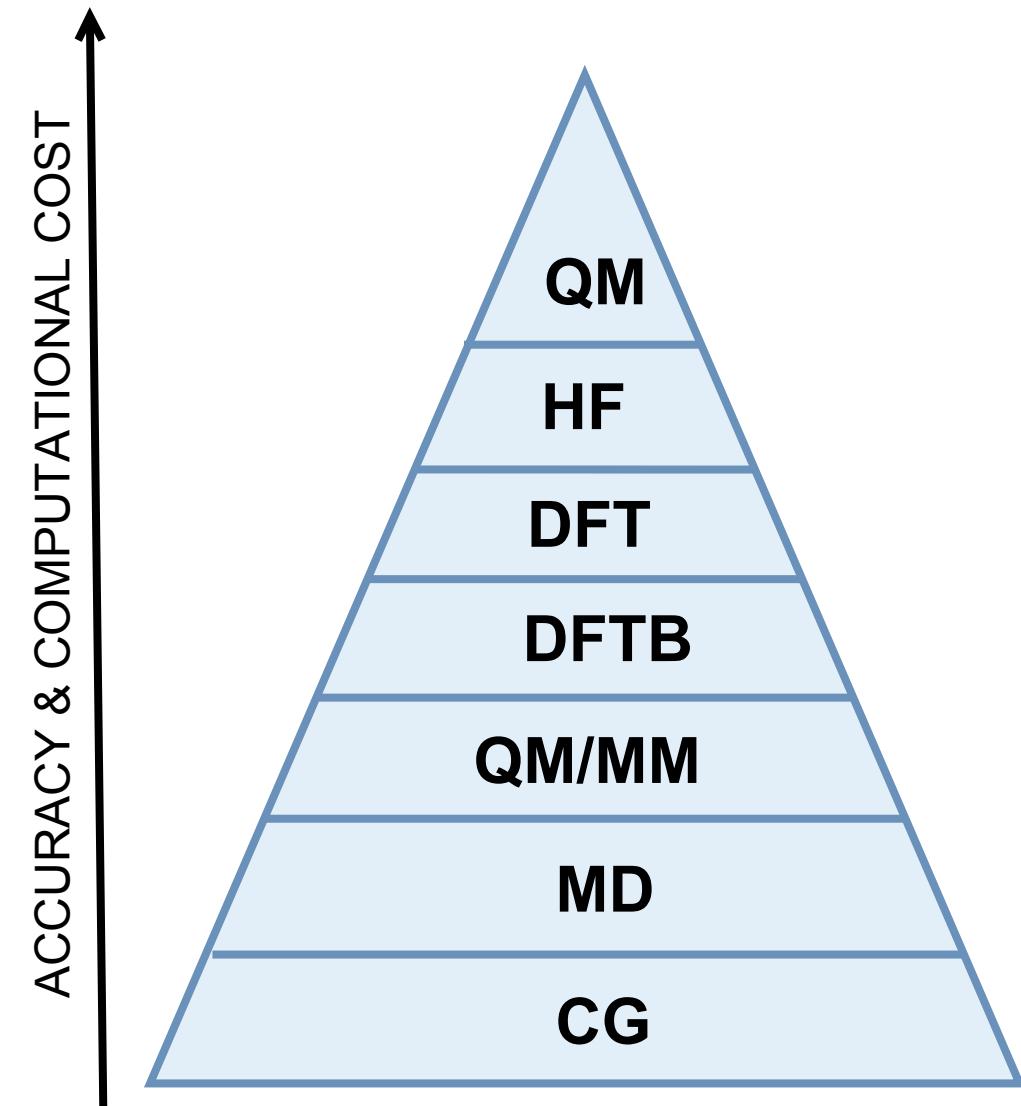
A Hierarchy of Methods: Accuracy vs Efficiency

The Fundamental Trade-off

- Accurate methods are slow and costly
- Efficient methods are fast but approximate

Hierarchy of Methods

- **Exact QM** (full wavefunction): only for 1-2 electron systems
- **Ab Initio**: Hartree-Fock, Post-HF (MP2, CCSD)
- **DFT**: Focus on electron density instead of wavefunction
- **DFTB**: Approximate DFT using precomputed parameters
- **QM/MM**: Hybrid of quantum and classical regions
- **Molecular Dynamics (MD)**: Classical atoms, no electrons
- **Coarse-Grained (CG)**: Group atoms into larger particles



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What are Ab Initio Methods?

- Latin: “from the beginning”
- No empirical parameters
- Start from: $\hat{H}\psi = E\psi$

Hartree-Fock (HF) Theory

- Electrons move in the average field of others
- Wavefunction = Slater determinant

$$\psi_{HF}(r_1, r_2, \dots, r_N) = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \phi_1(r_1) & \cdots & \phi_N(r_1) \\ \vdots & \ddots & \vdots \\ \phi_1(r_N) & \cdots & \phi_N(r_N) \end{bmatrix}$$

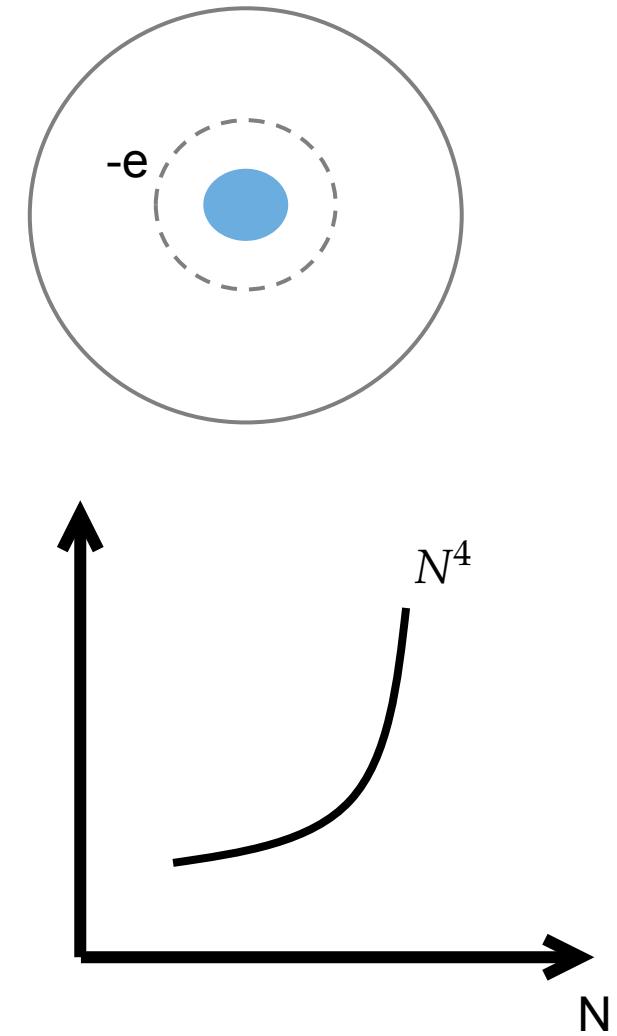
- Includes exchange but, not correlation

Limitations:

- Misses electron correlation
- Computational cost is very high

Softwares:

- Gaussian
- ORCA
- Q-chem



Post Hartree-Fock Methods

What's Missing from HF?

- Electron correlation
- HF includes exchange but not correlation

Post-HF Methods Add Correlation

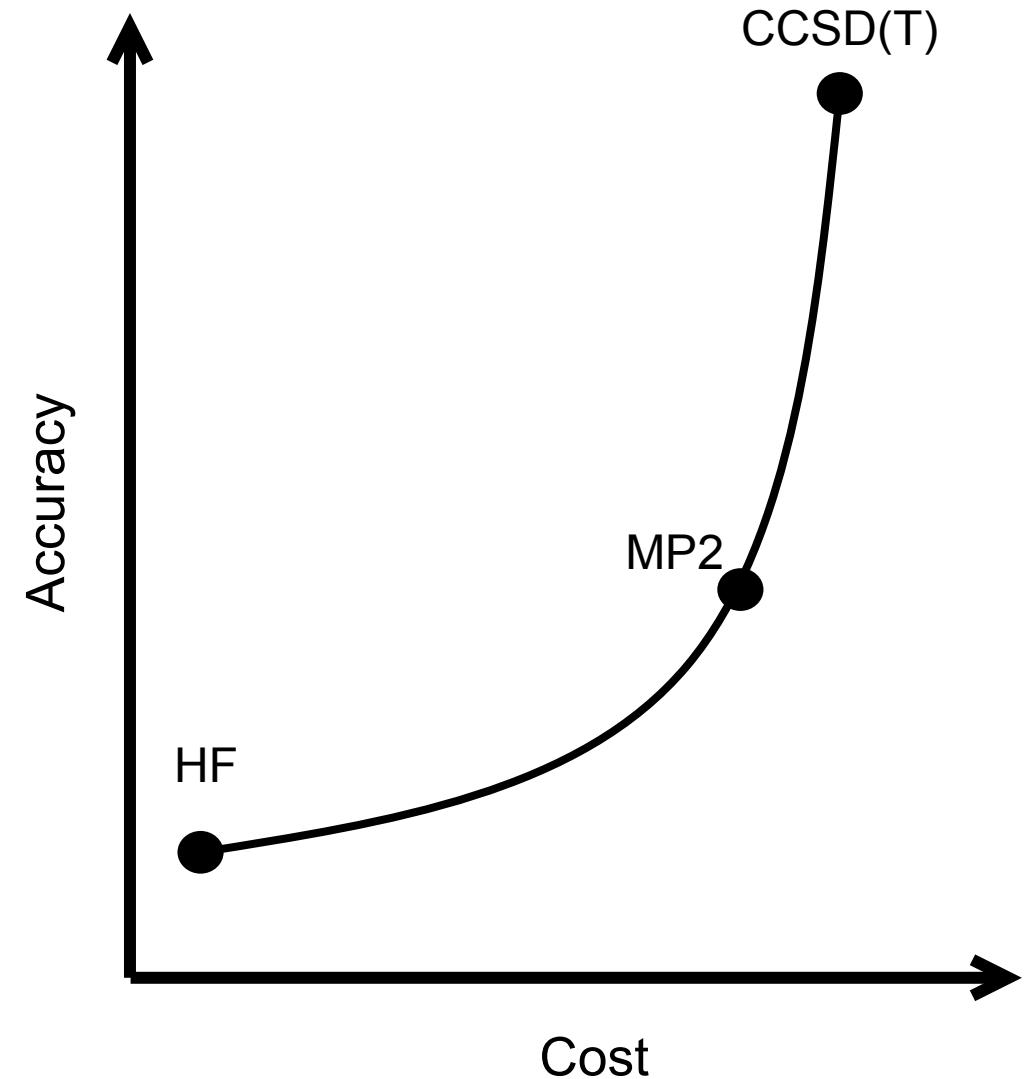
- MP2: Perturbation theory on HF
- CI: Expands wavefunction with excited states
- CCSD(T): Coupled-cluster

Limitations:

- Extremely high computational cost
- Not practical for large systems
- Mostly used for benchmarking and small molecules

Softwares:

- Gaussian
- ORCA
- Q-chem



Density Functional Theory (DFT)

Key Idea

- Use electron density $n(r)$ instead of wavefunction ψ
- Based on Hohenberg-Kohn theorems

Kohn-Sham Equations

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(r) \right] \phi_i = \phi_i \epsilon_i$$

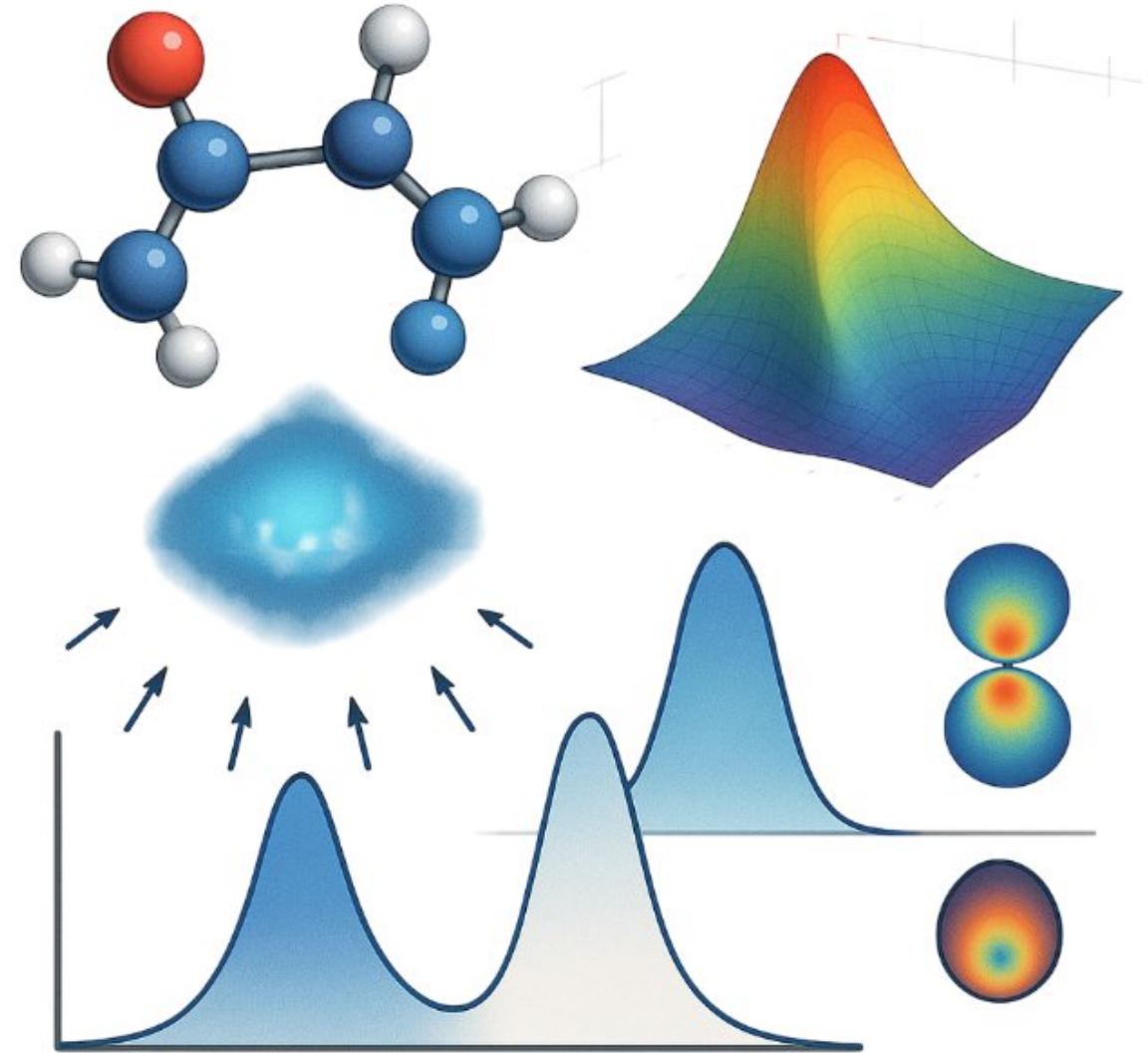
- Effective potential includes:
 - External + Coulomb + Exchange-Correlation (XC)

XC Functionals:

- LDA, GGA, Hybrid
- Scales to 100s-1000s of atoms

Softwares:

- VASP
- QE
- CP2K
- FHI-aims
- ...



Density Functional Tight Binding (DFTB)

Key Idea

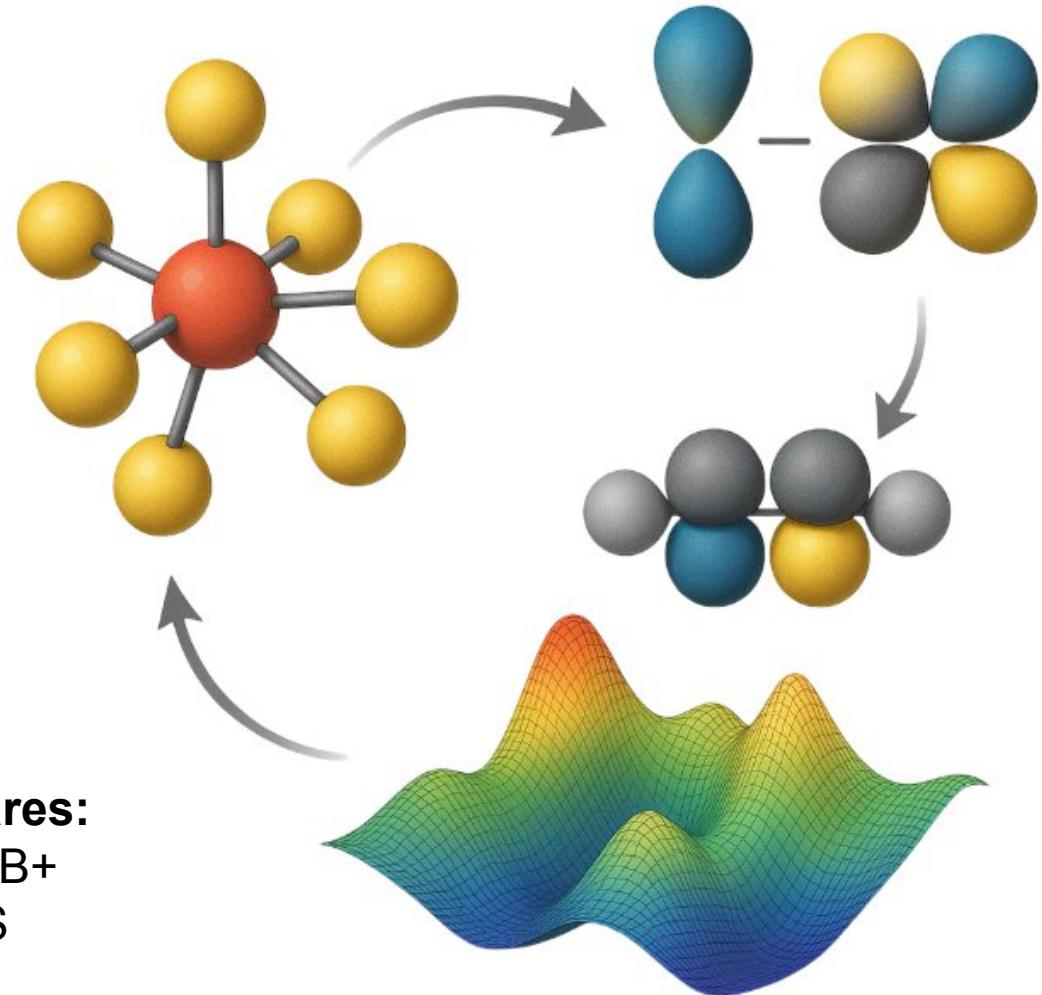
- Approximate version of DFT using precomputed integrals
- Expands energy around a reference density:
$$E_{DFTB} = E_{BS} + E_{coul} + E_{rep}$$
- Keeps quantum effects, and 100-1000x faster than DFT

Use Cases

- Ideal for large molecules, nanostructures
- Good for experimenting
- Very fast but not accurate as much as DFT

Softwares:

- DFTB+
- AMS



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Classical & Multiscale Methods

QM/MM Hybrid Methods

Core Idea

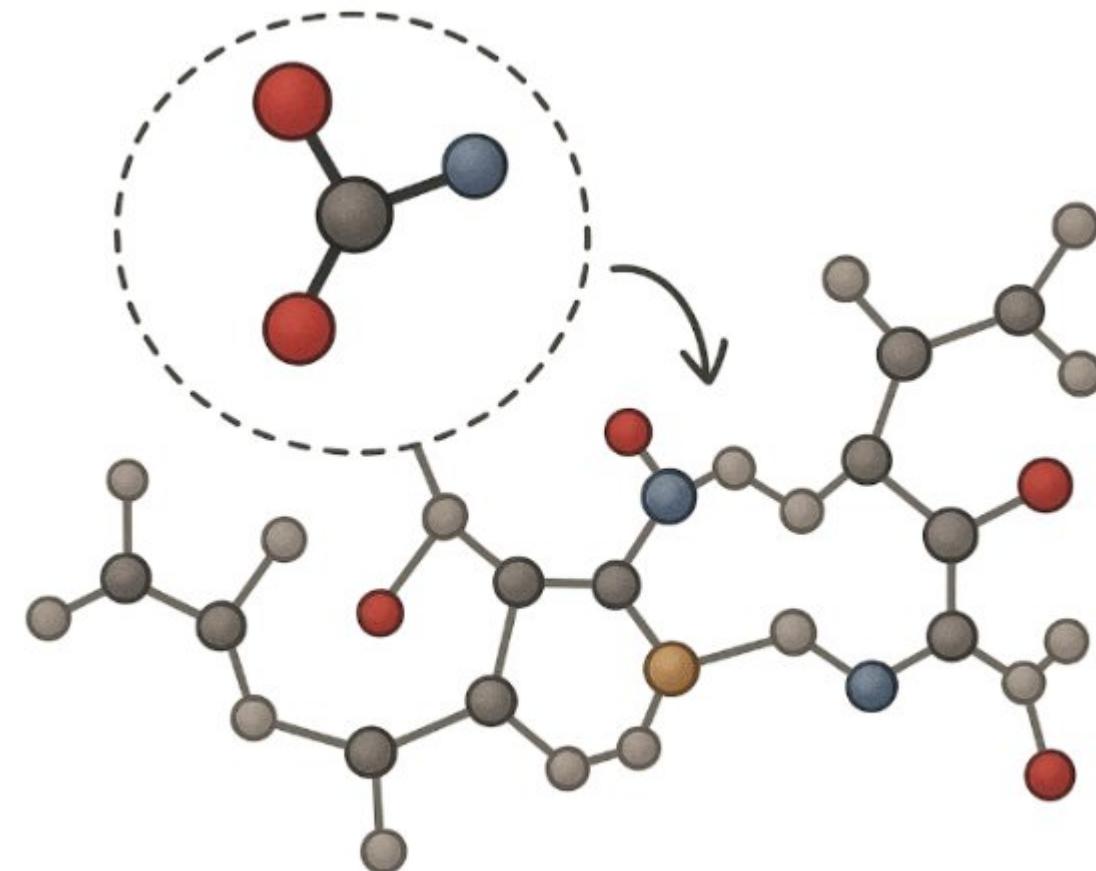
- Divide system into two regions:
 - QM region: reactive site, modeled with DFT or semi-empirical methods
 - MM region: surroundings, modeled with classical force fields

Why Use QM/MM?

- Enables simulation of large systems
- Focuses on QM accuracy where needed

Total Energy in QM/MM

$$E_{total} = E_{QM} + E_{MM} + E_{QM/MM}$$



Softwares:

- ONIOM
- Amber-QM/MM
- CHARMM

Classical & Multiscale Methods

Molecular Dynamics

Core Idea

- Simulate the motion of atoms using Newton's laws over time

$$m_i \frac{d^2 r_i}{dt^2} = -\nabla_i U(r_1, r_2, \dots, r_n)$$

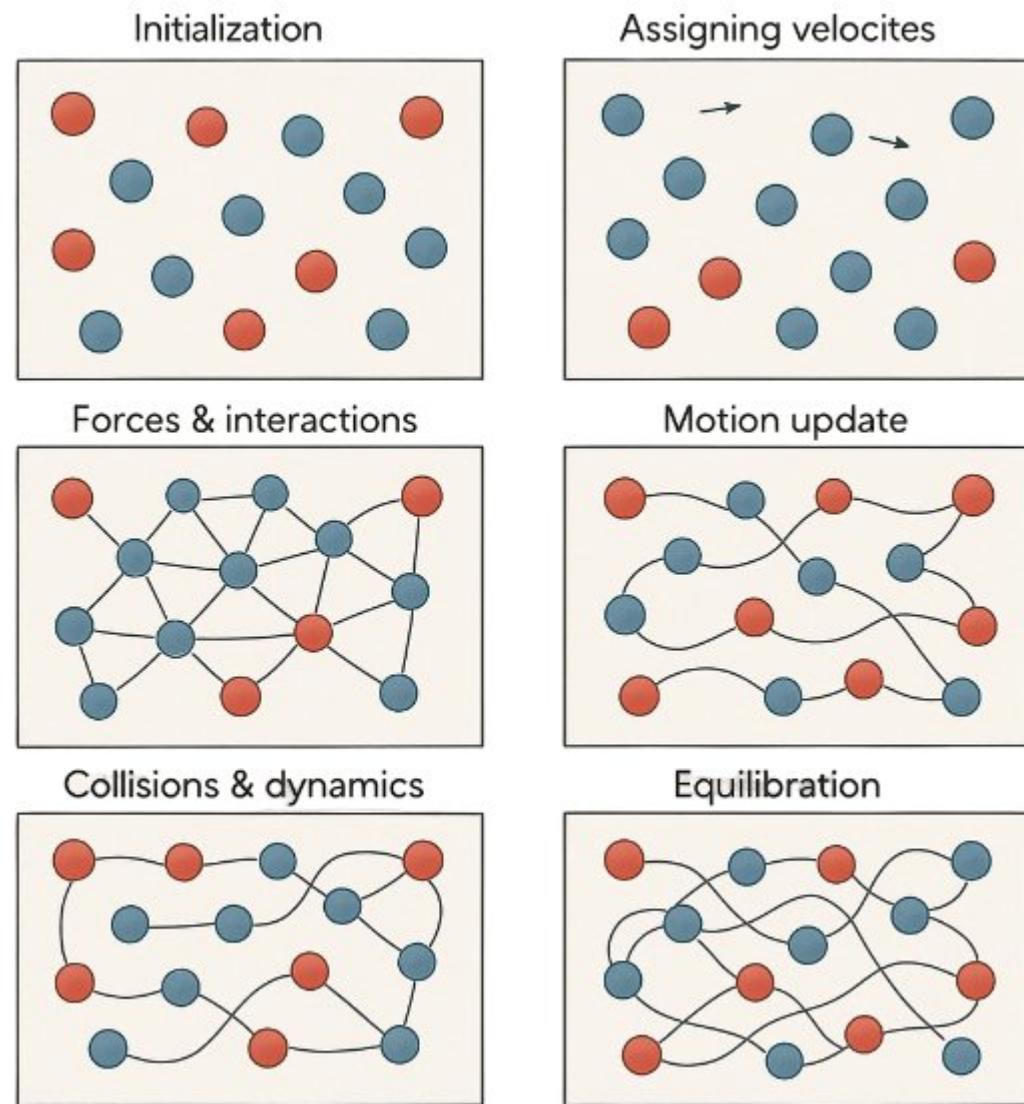
- No electrons; atoms treated as classical particles

Simulation Output

- Atom positions over time : trajectories
- Calculate dynamics, thermodynamics, diffusion, conformational changes

Softwares:

- GROMACS
- LAMMPS
- AMBER



Classical & Multiscale Methods

Coarse-Grained Modeling

Core Idea

- Reduce complexity by grouping atoms into “beads”
- Example: 4 heavy atoms: 1 bead (Martini model)
- Captures large-scale dynamics, loses atomistic details

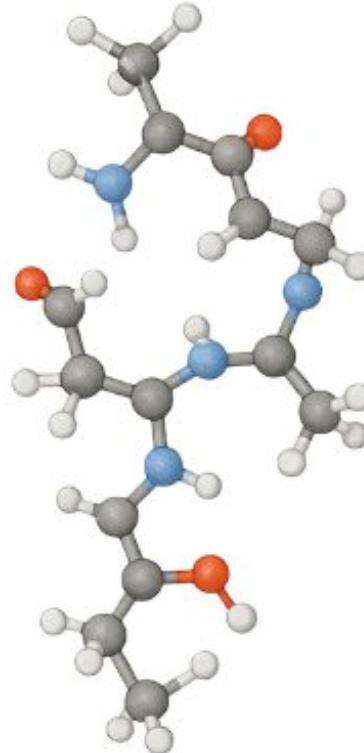
Effective Potential

- Derived from averaging over atomistic details
- Potential of Mean Force (PMF):
$$U_{CG}(R) = -k_B T \ln P(R)$$

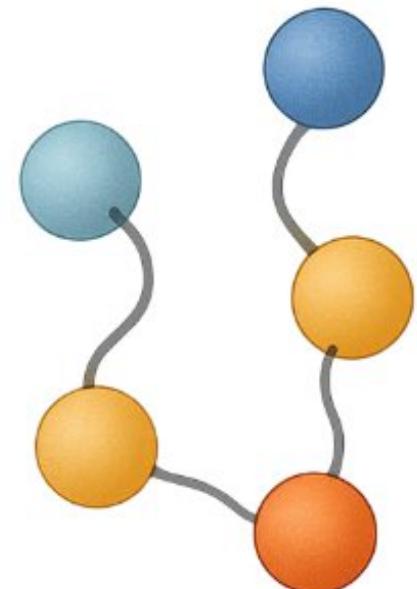
Advantages

- Simulate larger systems
- Access longer timescales (ms)
- Useful for membranes, protein-protein interactions, self-assembly

Fine-grained



Coarse-grained



Softwares:

- Martini
- SDK
- OpenMM

Classical & Multiscale Methods

Machine Learning Potentials (MLPs)

Core Idea

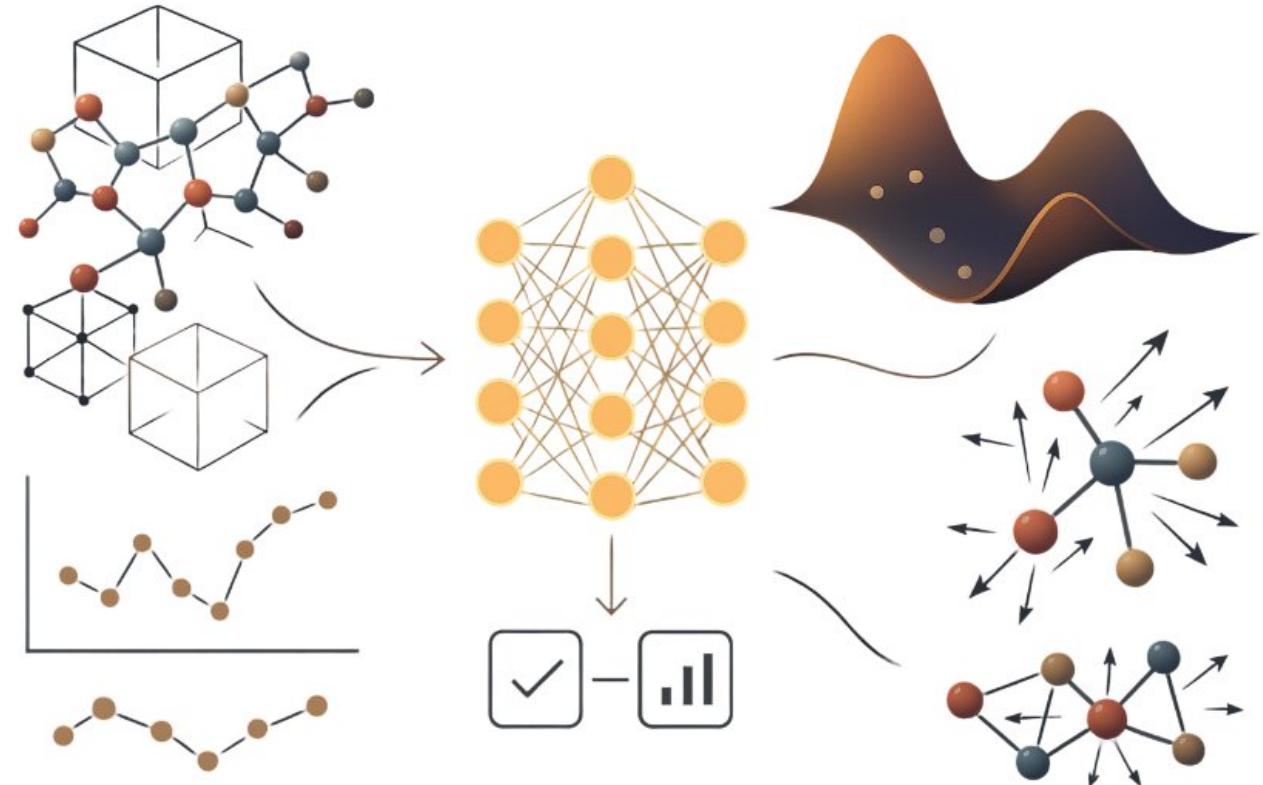
- ML models trained on Quantum data (e.g., DFT)
- Predict energies and forces from atomic coordinates
- Combine near-DFT accuracy with MD-level efficiency

How They Work

- Input: atomic environments (distances, angles, descriptors)
- Output: predicted total energy & forces
- Models: Neural Networks, GAP, Graph Neural Networks

Advantages

- Near-DFT accuracy
- Much faster than QM
- Scalable to big systems



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Real-World Applications

Quantum Mechanics / DFT / QM/MM

- Models chemical reactions and electronic structures
- Predicts molecular and material properties
- Studies catalytic and spectroscopic behavior

Molecular Dynamics

- Simulates atomic motions and structural changes
- Examines molecular interactions over time
- Explores complex biological and material systems

Coarse-Grained Modeling

- Captures large-scale molecular organization
- Studies collective behavior in soft matter
- Connects atomic and macroscopic models

Quantum mechanics is essential

- Accurately describes atoms, molecules, and reactions
- Core equation: Schrödinger (hard to solve exactly)

Approximations are necessary

- Many-body systems are intractable without simplifications.
- We trade off between accuracy and computational cost

Wide spectrum of methods exist

- Ab Initio → DFT → DFTB → QM/MM → MD → CG
- Each method serves different scales and purposes

Tools make it practical

- Powerful software exists at every level
- Real systems can be modeled from electrons to entire assemblies

Thank You!

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- **Special Thanks:**
 - Computational X Support Group at LRZ
 - Everyone attending today!