An Introduction to Density Functional Theory
And the Quantum Many-body Problem

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Outline

Quantum Chemistry

Why quantum chemistry?

- Systems at scales small-enough to be governed by quantum mechanics
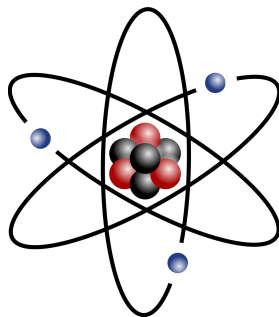- Scale of a few Ångstöms $\approx 10^{-10} m$

Figure: source:
https://en.wiktionary.org/wiki/atom

Ab-Initio Quantum Chemistry

"From First Principles": given atoms in molecule, can calculate
macroscopic properties **using only quantum mechanics**

- Chemistry $\implies$ molecules, bonding
- Materials Science $\implies$ solids, material properties
- Biology $\implies$ interaction of protiens

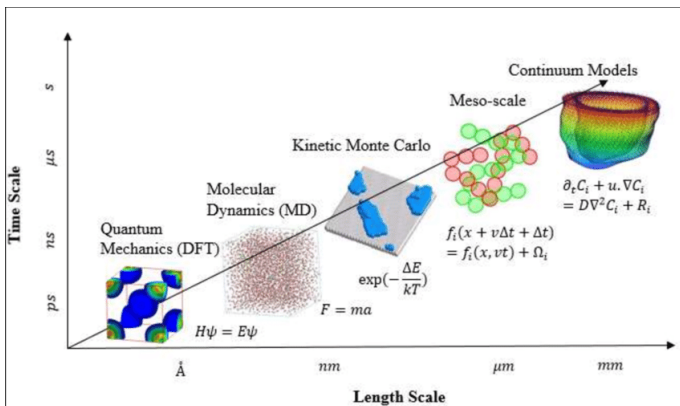## Density Functional Theory to Molecular Dynamics

Figure: Source [1]

Many-Body Problems

Given many interacting particles, derive salient properties of system

- Classical problems $\rightarrow$ position and momenta given exactly
- Quantum problems $\rightarrow$ wave-function

Many questions to ask, and lots of solutions (Perturbation Theory, Quantum Monte Carlo, DFT, etc.)

Electronic structure: understand motion of electrons in molecule

Wave Functions

- Position and momenta not known exactly, but determined by **wave function** denoted $\Psi(\mathbf{x})$
- Assume $\Psi(x) \in L^2(\mathbb{R}^3)$
- Wave function of system with N particles is $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \in \mathcal{H}$
- $\mathbf{x} = (\mathbf{r}, \sigma)$, σ is **spin**
- Normalized: $\|\Psi\|_{\mathcal{H}} = 1$

Wave Functions

- Probabilistic intuition:

$$|\mathbf{\Psi}(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2 dx_1 \ldots dx_N$$

Probability of finding particle 1 in volume $|x_1 + dx_1|$, particle 2 in volume $|x_2 + dx_2|$, etc.

Operators and Measurements

In a quantum system,

- Observables are self-adjoint operators on the state space, $\hat{A} : \mathcal{H} \to \mathcal{H}$, $\langle \hat{A}x, y \rangle = \langle x, \hat{A}y \rangle$
- Eigenvalues of $\hat{A}$ are real
- Result of measurement is eigenvalue of operator

Why?

- Measurement inherently **affects** a quantum system
- "Quantum" in quantum mechanics: measurements are only eigenvalues of operators

Operators and Measurements

"A measurement always causes
the system to jump into an
eigenstate of the dynamical
variable that is being measured,
the eigenvalue this eigenstate
belongs to being the result of
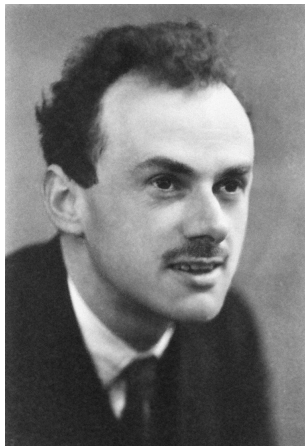that measurement" - Paul Dirac

Figure: Source https://en.
wikipedia.org/wiki/Paul_Dirac

Operators

QM Operators

- Momentum operator $\hat{p} = -i\hbar\nabla \implies \hat{p}\psi(x) = -i\hbar\nabla\psi(x)$
- Position operator $\hat{x} \implies (\hat{x}\psi)(x) = x\psi(x)$
- Kinetic energy operator $\hat{T} = \frac{1}{2m}\hat{p}\cdot\hat{p} = \frac{-\hbar^2}{2m}\nabla^2$

Notation

Given $\hat{A} : \mathcal{H} \to \mathcal{H}$, self-adjoint

Bra-Ket Notation

Quantum state $|x\rangle \in \mathcal{H}$, observable (operator) $\hat{A}$

- $\langle \hat{A}x, x \rangle = \langle x, \hat{A}x \rangle := \langle x|\hat{A}|x\rangle$
- $\langle x, y \rangle := \langle x|y\rangle$

Probabilistic Interpretation, Revisited

Expected Value

The **expected value** of operator $\hat{A}$ in a state $|x\rangle$ is defined as

$$\langle\hat{A}\rangle_x = \langle x|\hat{A}|x\rangle$$

Assume $\hat{A}$, self-adjoint, has a complete set of eigenstate $|\phi_j\rangle$

- Any state $|x\rangle$ can be written as a **superposition** of eigenstates

$$|x\rangle = \sum_j \gamma_j |\phi_j\rangle$$

- The expected value of that state is

$$\begin{aligned}
\langle\hat{A}\rangle_x &= \langle x|A|x\rangle \\
&= \sum_j \underbrace{\lambda_j}_{\text{Outcome}} \underbrace{|\langle x|\phi_j\rangle|^2}_{\text{Probability}}
\end{aligned}$$

Hamiltonian

- One important operator: **Hamiltonian**, $\hat{H}$ represents the total energy of a system
- Two parts:

$$\hat{H} = \underbrace{\hat{T}}_{\text{Kinetic}} + \underbrace{\hat{V}}_{\text{Potential}}$$

One particle, mass m,

$$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2 \nabla^2}{2m}$$

$$\hat{p} = -i\hbar\nabla$$

$\hat{p}$ **momentum operator**

Time-independent Schrödinger Equation

The Time-indepedent Schrödinger Equation

Given Hamiltonian operator $\hat{H}$

$$\hat{H} \left| \mathbf{\Psi} \right\rangle = E \left| \mathbf{\Psi} \right\rangle$$

- Energy of the system $\hat{H}$ $\implies$ Eigenvalue problem
- Smallest eigenvalue E_0 is the **ground-state energy**
- Ground-state is important: $e^{-\beta E_i}/Z$

Variational Form for Ground-state Energy

Variational Form

$$E_0 = \min_{\boldsymbol{\Psi}} \frac{\langle \boldsymbol{\Psi} | \hat{H} | \boldsymbol{\Psi} \rangle}{\langle \boldsymbol{\Psi} | \boldsymbol{\Psi} \rangle} = \min_{\substack{\boldsymbol{\Psi} \\ \|\boldsymbol{\Psi}\|=1}} \langle \boldsymbol{\Psi} | \hat{H} | \boldsymbol{\Psi} \rangle$$

- Quantum Mechanics $\rightarrow$ Variational Principle
- Applied Mathematics $\rightarrow$ Rayleigh Quotient
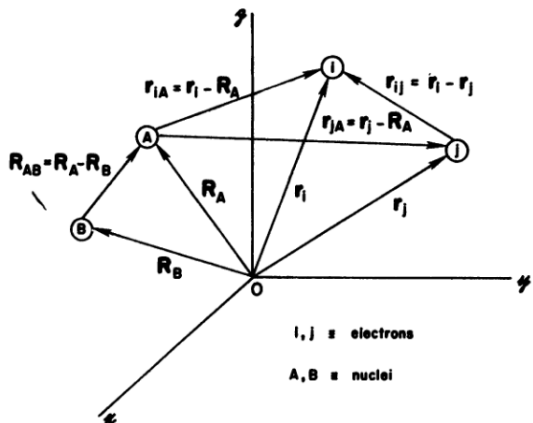
Electron Problem

Figure: Source: [9]

Quantum Many-body Hamiltonian

The Hamiltonian for a Quantum system with M nuclei at positions $\{\mathbf{R}_i\}$ and N electrons at positions $\{\mathbf{r}_i\}$ is:

Many-Body Hamiltonian

$$\hat{H} = -\sum_{i=1}^{M} \frac{\hbar^2 \nabla_{\mathbf{R}_i}^2}{2M_i} + \frac{1}{2} \sum_{\substack{i,j<M \\ i\neq j}}^{M} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} - \sum_{i=1}^{N} \frac{\hbar \nabla_{\mathbf{r}_i}^2}{2m}$$

$$- \sum_{i=1}^{M}\sum_{j=1}^{N} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{\substack{i,j<N \\ i\neq j}}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- M_i is mass of ith nucleus, and m is mass of electron
- $\hbar$ is the reduced Planck constant
- Z_i is charge of ith nucleus, e is charge of electron

Quantum Many-Body Hamiltonian

Many-Body Hamiltonian

$$\hat{H} = \underbrace{-\sum_{i=1}^{M}\frac{\hbar^2\nabla_{\mathbf{R}_i}^2}{2M_i}}_{\text{Kinetic energy nuclei}} + \underbrace{\frac{1}{2}\sum_{\substack{i,j<M \\ i\neq j}}^{M}\frac{Z_iZ_je^2}{|\mathbf{R}_i-\mathbf{R}_j|}}_{\text{Ion-ion interaction}} - \underbrace{\sum_{i=1}^{N}\frac{\hbar\nabla_{\mathbf{r}_i}^2}{2m}}_{\text{Kinetic energy electrons}}$$

$$\underbrace{-\sum_{i=1}^{M}\sum_{j=1}^{N}\frac{Z_ie^2}{|\mathbf{R}_i-\mathbf{r}_j|}}_{\text{Ion-electron interaction}} + \underbrace{\frac{1}{2}\sum_{\substack{i,j<N \\ i\neq j}}^{N}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}}_{\text{Electron-electron interaction}}$$

Quantum vs Classical Many-Body

Classical system with N particles: momenta and position are known exactly

Quantum system with 10 particles

- Discretize wave function with just 100 points in each x, y, z coordinate ($100^3 = 10^6$ points)
- 10^6 points for each coordinate $= (10^6)^{10} = 10^{60}$ dimensions
- Need to approximate

Born-Oppenheimer Approximation

- Nuclei are significantly more massive than electrons
- Regard nuclei positions $\{\mathbf{R}_i\}$ as fixed. **Born-Oppenheimer (B-O) Approximation**
- Constant Ion-ion interaction

$$\frac{1}{2} \sum_{\substack{i,j < M \\ i \neq j}}^{M} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} = E_{II}$$

- Nuclear kinetic energy

$$-\sum_{i=1}^{M} \frac{\hbar \nabla_{\mathbf{R}_i}^2}{2M_i} = 0$$

Born-Oppenheimer Approximation

Many-Body Hamiltonian Under B-O Approximation

$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar \nabla_{\mathbf{r}_i}^2}{2m} - \sum_{i=1}^{M} \sum_{j=1}^{N} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{\substack{i,j<N \\ i \neq j}}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + E_{II}$$

- We can add constant E_{II} before or after solving
- This approximation **isn't enough** to make Schrödinger's Equation tractable

Many-Body Hamiltonian Under B-O Approximation

$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar \nabla_{\mathbf{r}_i}^2}{2m} - \sum_{i=1}^{M} \sum_{j=1}^{N} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{\substack{i,j < N \\ i \neq j}}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + E_{II}$$

$$= T + V_{en} + V_{ee} + E_{II}$$

We can write

$$V_{en} = \sum_{i=1}^{M} \sum_{j=1}^{N} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|}$$

$$= \sum_{i=1}^{N} V_{ext}(\mathbf{r}_i; \{\mathbf{R}_{j=1}^{M}\})$$

Independent-electron Approximation

- The electron-electron interaction term $\sum \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$ is tricky

- "The role of correlation among electrons stands out as defining the great questions and challenges of the field of electronic structure today" - Richard Martin
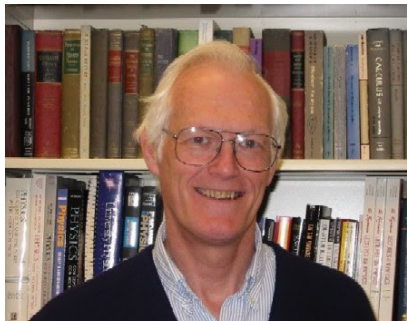

Figure: Richard Martin, American Condensed Matter Theorist

Independent-electron Approximation

- Electron-electron interactions are difficult
- What if we ignored them?

$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar\nabla_{\mathbf{r}_i}^2}{2m} - \sum_{i=1}^{M}\sum_{j=1}^{N} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|}$$

$$= -\sum_{j=1}^{N} \left(\frac{\hbar\nabla_{\mathbf{r}_j}^2}{2m} - \sum_{i=1}^{M} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} \right)$$

Now Schrödinger's Equation becomes:

$$\hat{H}\mathbf{\Psi} = -\sum_{j=1}^{N} \left(\underbrace{\frac{\hbar\nabla_{\mathbf{r}_j}^2}{2m} - \sum_{i=1}^{M} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|}}_{H^j} \right) \mathbf{\Psi}$$

Independent-electron Approximation

System with $\hat{H}$ as above admits seperable eigenfunctions of form

$$\mathbf{\Psi}(x_1, x_2, \ldots, x_N) = \psi_1(x_1)\psi_2(x_2)\ldots\psi_N(x_N)$$
$$H^j\psi_j(x) = E_j\psi_j(x)$$

- Total Ground-state Energy $E = E_1 + E_2 + \cdots + E_N$
- Wave Functions under this approximation don't satisfy the **Pauli Exclusion Principle**

Pauli-Exclusion Principle

- **Pauli-Exclusion Principle**: two fermions cannot occupy same quantum state
- $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ is anti-symmetric:
  1. $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots \mathbf{x}_N) = 0$ if $\mathbf{x}_i = \mathbf{x}_j$
  2. $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots \mathbf{x}_N) = -\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_i, \ldots \mathbf{x}_N)$

Variational Principle, Revisited

Variational Form

$$E = \min_{\mathbf{\Psi} \in \mathcal{A}_N} \frac{\langle \mathbf{\Psi}|\hat{H}|\mathbf{\Psi}\rangle}{\langle \mathbf{\Psi}|\mathbf{\Psi}\rangle} = \min_{\substack{\mathbf{\Psi} \in \mathcal{A}_N \\ \|\mathbf{\Psi}\|=1}} \langle \mathbf{\Psi}|\hat{H}|\mathbf{\Psi}\rangle$$

- $\mathcal{A}_N =$ Set of N-electron antisymmetric wavefunctions
- $\mathcal{A}_N$ is large and complex

Variational Approximation

$$E^V = \min_{\substack{\mathbf{\Psi} \in \mathcal{B}_N \\ \|\mathbf{\Psi}\|=1}} \langle \mathbf{\Psi}|\hat{H}|\mathbf{\Psi}\rangle$$

With $\mathcal{B}_N \subset \mathcal{A}_N$. Note $E^V \geq E$

One idea of antisymmetric function: a determinant

Slater Determinant

Slater Determinant

Define $\mathcal{A}_N^0 \subset \mathcal{A}_N$ as the set of all Slater Determinant wavefunctions

$$\Psi(x_1,\ldots,x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \ldots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \ldots & \psi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(x_1) & \psi_N(x_2) & \ldots & \psi_N(x_N) \end{vmatrix}$$

Such that the N spin-orbital functions $\{\psi_i\}_{i=1}^N$ satisfy

- $\psi_i \in L^2$
- $\langle \psi_i | \psi_j \rangle = \delta_{ij}$

Variational Principle, Revisited

Hartree-Fock Variational Form

$$E^{HF} = \min_{\boldsymbol{\Psi} \in \mathcal{A}_N^0} \frac{\langle \boldsymbol{\Psi} | \hat{H} | \boldsymbol{\Psi} \rangle}{\langle \boldsymbol{\Psi} | \boldsymbol{\Psi} \rangle} = \min_{\substack{\boldsymbol{\Psi} \in \mathcal{A}_N^0 \\ \|\boldsymbol{\Psi}\|=1}} \langle \boldsymbol{\Psi} | \hat{H} | \boldsymbol{\Psi} \rangle$$

Since $\mathcal{A}_N^0 \subset \mathcal{A}_N$ we have that $E^{HF} \geq E$

So, solving for

$$\begin{aligned} E^{HF} &= \min_{\substack{\boldsymbol{\Psi} \in \mathcal{A}_N^0 \\ \|\boldsymbol{\Psi}\|=1}} \langle \boldsymbol{\Psi} | \hat{H} | \boldsymbol{\Psi} \rangle \\ &= \min_{\substack{\boldsymbol{\Psi} \in \mathcal{A}_N^0 \\ \|\boldsymbol{\Psi}\|=1}} \langle \boldsymbol{\Psi} | T + V_{en} + V_{ee} + E_{II} | \boldsymbol{\Psi} \rangle \end{aligned}$$

Hartree-Fock Approximation

Hartree-Fock Energy

Define the following functional $F^{HF}(\boldsymbol{\Psi}) = F^{HF}(\{\psi_i\}_{i=1}^N)$

$$
\begin{aligned}
F^{HF}(\{\psi_i\}_{i=1}^N) = & \sum_{i=1}^N \int \left(\frac{1}{2}|\nabla_{\mathbf{r}}\psi_i|^2 + V_{ext}|\psi_i|^2 \right) dx \\
& + \frac{1}{2} \sum_{i,j} \int \int \frac{|\psi_i(x)|^2 |\psi_j(x)|^2}{|r - r'|} dx dx' \\
& - \frac{1}{2} \sum_{i,j} \int \int \frac{\psi_i^*(x)\psi_j^*(x')\psi_j(x)\psi_i(x')}{|r - r'|} dx dx' + E_{II}
\end{aligned}
$$

$$
E^{HF} = \min_{\substack{\{\psi_i\}_{i=1}^N \\ \langle \psi_i | \psi_j \rangle = \delta_{ij}}} F^{HF}(\{\psi_i\}_{i=1}^N)
$$

Parametrizations for Ψ

Aside: approximation methods in quantum many-body problems

Variational Approximation

$$E^V = \min_{\substack{\Psi \in \mathcal{B}_N \\ \|\Psi\|=1}} \langle \Psi | \hat{H} | \Psi \rangle$$

With $\mathcal{B}_N \subset \mathcal{A}_N$. Note $E^V \leq E$

Variational Approximation (Parametrization)

$$E^P = \min_{\theta \in \Theta} \langle \Psi_\theta | \hat{H} | \Psi_\theta \rangle$$

θ could be parameters in a tensor network or neural network

Could also make **convex relaxations** to this problem
(See intro of [4])

Electron Density and Wavefunction

Electron Density

Given a Slater-Determinant wavefunction $\boldsymbol{\Psi}$,

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

Probability that an electron lies in an infinitesimal area around $\mathbf{r}$

- $\boldsymbol{\Psi}(x_1, \ldots x_N) \implies$ determines $\rho(\mathbf{r})$
- $\rho(\mathbf{r}) \underbrace{\implies}_{?}$ determines $\boldsymbol{\Psi}(\mathbf{r})$
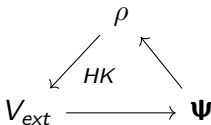
Hohenberg-Kohn Theorems

Theorem (Hohenberg-Kohn)

For any system of interacting particles in an external potential V_{ext}, the potential V_{ext} is determined uniquely, except for a constant, by the ground state particle density ρ (Original Paper: [3])

Corollary

Ψ *is a* <u>*functional*</u> *of the electron* <u>*density*</u>*:*

$$\Psi = \Psi[\rho]$$

$$\rho$$

$$V_{ext} \xrightarrow{\quad\quad\quad} \Psi$$

HK

Variational Principle and HK

$$
E = \min_{\substack{\mathbf{\Psi} \in \mathcal{A}_N \\ \langle \mathbf{\Psi} | \mathbf{\Psi} \rangle = 1}} \langle \mathbf{\Psi} | \hat{H} | \mathbf{\Psi} \rangle
$$

$$
= \min_{\rho \in \mathcal{J}_N} \left\{ \min_{\substack{\mathbf{\Psi} \in \mathcal{A}_N \\ \mathbf{\Psi} \mapsto \rho}} \langle \mathbf{\Psi} | \hat{H} | \mathbf{\Psi} \rangle \right\}
$$

$$
= \min_{\rho \in \mathcal{J}_N} \left\{ \min_{\substack{\mathbf{\Psi} \in \mathcal{A}_N \\ \mathbf{\Psi} \mapsto \rho}} \langle \mathbf{\Psi} | T + V_{en} + V_{ee} + E_{II} | \mathbf{\Psi} \rangle \right\}
$$

$$
= \min_{\rho \in \mathcal{J}_N} \left\{ \min_{\substack{\mathbf{\Psi} \in \mathcal{A}_N \\ \mathbf{\Psi} \mapsto \rho}} \langle \mathbf{\Psi} | T + V_{ee} | \mathbf{\Psi} \rangle + \langle \mathbf{\Psi} | V_{en} | \mathbf{\Psi} \rangle \right\} + E_{II}
$$

External Potential Term

Lemma

$\langle \Psi | V_{en} | \Psi \rangle$ can be expressed solely in terms of density

Proof.

$$
\begin{aligned}
\langle \Psi | V_{en} | \Psi \rangle &= \langle \Psi | \sum_{i=1}^{N} V_{ext}(\mathbf{r}_i; \{\mathbf{R}_{k=1}^{M}\}) | \Psi \rangle = \sum_{i=1}^{N} \langle \Psi | V_{ext}(\mathbf{r}_i) | \Psi \rangle \\
&= \sum_{i=1}^{N} \int \Psi^*(x_1, \ldots, x_N) V_{ext}(\mathbf{r}_i) \Psi(x_1, \ldots, x_N) dx_1 \ldots dx_N \\
&= N \int |\Psi(x_1, \ldots, x_N)|^2 V_{ext}(r_1) dx_1 \ldots dx_N \\
&= \int \rho(r) V_{ext}(r) dr
\end{aligned}
$$

$\square$

Levy-Lieb Functional

$$
E = \min_{\rho \in \mathcal{J}_N} \left\{ \min_{\substack{\mathbf{\Psi} \in \mathcal{A}_N \\ \mathbf{\Psi} \mapsto \rho}} \langle \mathbf{\Psi} | T + V_{ee} | \mathbf{\Psi} \rangle + \langle \mathbf{\Psi} | V_{en} | \mathbf{\Psi} \rangle \right\} + E_{II}
$$

$$
= \min_{\rho \in \mathcal{J}_N} \left\{ \min_{\substack{\mathbf{\Psi} \in \mathcal{A}_N \\ \mathbf{\Psi} \mapsto \rho}} \langle \mathbf{\Psi} | T + V_{ee} | \mathbf{\Psi} \rangle + \int \rho(r) V_{ext}(r) dr \right\} + E_{II}
$$

Definition (Levy-Lieb Functional)

The **Levy-Lieb Functional**, $\mathcal{F}_{LL}[\rho]$, is defined as

$$
\mathcal{F}_{LL}[\rho] = \min_{\substack{\mathbf{\Psi} \in \mathcal{A}_N \\ \mathbf{\Psi} \mapsto \rho}} \langle \mathbf{\Psi} | T + V_{ee} | \mathbf{\Psi} \rangle
$$

Density Functional Theory

DFT

The ground-state energy can be found through the following minimization

$$E = \min_{\rho \in \mathcal{J}_N} \left\{ \mathcal{F}_{LL}[\rho] + \int \rho(r) V_{ext}(r) \right\} + E_{II}$$

- $\mathcal{F}_{LL}[\rho]$ is hard to calculate
- How to simplify? Recall

$$E^{HF} = \min_{\mathbf{\Psi} \in \mathcal{A}_N^0} \frac{\langle \mathbf{\Psi} | \hat{H} | \mathbf{\Psi} \rangle}{\langle \mathbf{\Psi} | \mathbf{\Psi} \rangle} = \min_{\substack{\mathbf{\Psi} \in \mathcal{A}_N^0 \\ \|\mathbf{\Psi}\|=1}} \langle \mathbf{\Psi} | \hat{H} | \mathbf{\Psi} \rangle$$

optimizes over the set of Slater Determinants $\mathcal{A}_N^0$

Kohn-Sham Density Functional Theory

Kohn-Sham DFT

- Kohn-Sham Idea: Slater Determinant and DFT
- $\forall \rho \in \mathcal{J}_N$, there exists a $\boldsymbol{\Psi} \in \mathcal{A}_N^0$ such that $\boldsymbol{\Psi} \mapsto \rho$

Using Slater Determinants, this becomes

$$\mathcal{F}_{LL}[\rho] = \min_{\substack{\boldsymbol{\Psi} \in \mathcal{A}_N^0 \\ \boldsymbol{\Psi} \mapsto \rho}} \langle \boldsymbol{\Psi} | T | \boldsymbol{\Psi} \rangle + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' + E_{xc}[\rho]$$

- E_{xc} is the **exchange correlation functional**, not known
- E_{xc} contributes little to energy

Kohn-Sham Density Functional Theory

Kohn-Sham DFT Energy

$$\mathcal{F}^{KS} = \langle \mathbf{\Psi} | T | \mathbf{\Psi} \rangle + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' + E_{xc}[\rho]$$
$$+ \int \rho(r) V_{ext}(r) dr + E_{II}$$

and the energy becomes

$$E^{KS} = \min_{\mathbf{\Psi} \in \mathcal{A}_N^0} \mathcal{F}^{KS}[\mathbf{\Psi}]$$

Kohn-Sham Density Functional Theory

Kohn-Sham DFT Energy (Orbitals)

Expressed in terms of Orbitals, we have

$$\mathcal{F}_{orb}^{KS}(\{\psi_i\}_{i=1}^{N}) = \frac{1}{2}\sum_{i=1}^{N}\int |\nabla_r \psi_i(x)|^2 dx + \int \rho(r)V_{ext}(r)dr$$

$$+ \frac{1}{2}\int\int \frac{\rho(r)\rho(r')}{|r-r'|}drdr' + E_{xc}[\rho]$$

And the ground-state energy is

$$E^{KS} = \min_{\substack{\{\psi_i\}_{i=1}^{N} \\ \langle\psi_i|\psi_j\rangle=\delta_{ij}}} \mathcal{F}_{orb}^{KS}(\{\psi_i\}_{i=1}^{N})$$

In principle, exact! Assuming we know E_{xc}

Exchange-Correlation Functionals
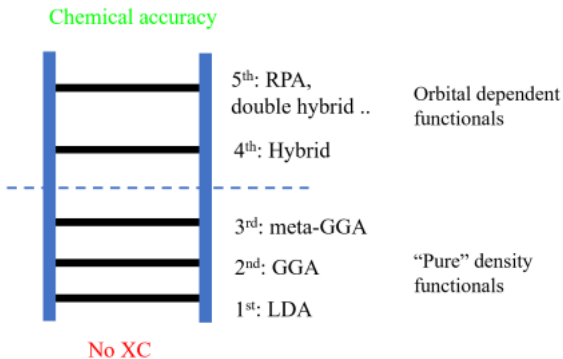
Figure: Source [6]

Kohn-Sham Equations

$$\frac{1}{2}\frac{\delta \mathcal{F}_{orb}^{KS}(\{\psi_i\})}{\delta \psi_i^*(r)} = \left(-\frac{1}{2}\Delta_r + V_{ext}(r) + \int \frac{\rho(r')}{|r - r'|}dr' + \frac{\delta E_{xc}[\rho]}{\delta \rho}\right)\psi_i(r)$$

$$= \sum_j \psi_j(r)\lambda_{ij}$$

And our Euler-Lagrange equation becomes

$$\left(-\frac{1}{2}\Delta_r + V_{ext}(r) + \int \frac{\rho(r')}{|r - r'|}dr' + \frac{\delta E_{xc}[\rho]}{\delta \rho}\right)\psi_i(r) = \epsilon_i\psi_i(r)$$

Kohn-Sham Equations

To Solve: Find Stationary Point of Lagrangian

$$\frac{1}{2}\frac{\delta \mathcal{F}_{orb}^{KS}(\{\psi_i\})}{\delta \psi_i^*(r)} = \left(-\frac{1}{2}\Delta_r + V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|}dr' + \frac{\delta E_{xc}[\rho]}{\delta\rho}\right)\psi_i(r)$$

$$= \sum_j \psi_j(r)\lambda_{ij}$$

And our Euler-Lagrange equation becomes

$$\left(\underbrace{-\frac{1}{2}\Delta_r + V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|}dr' + \frac{\delta E_{xc}[\rho]}{\delta\rho}}_{\text{depends on } \psi_i}\right)\psi_i(r) = \epsilon_i\psi_i(r)$$

Solving a KS-DFT Problem

1. Discretize Hamiltonian onto a basis set using orbitals
2. Solve eigenvalue problem
3. Update orbitals until self-consistency
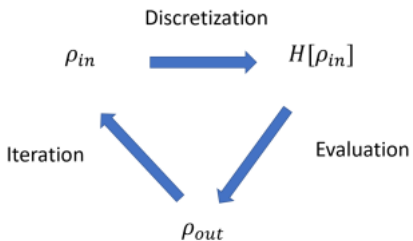
Figure: Source [6]

Questions?

Thanks for coming to the talk!

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