Overview: Monday

- Building the periodic table:
  - Classical mechanics.
  - Electricity.
  - Quantum mechanics: wave function and probability.
  - Hydrogen atom/units.
  - Multi-electron atoms.
  - Periodic table.
- Covalent bonding.
- Adiabatic-decoupling/time scales.
- Ritz variational principle.
- Hartree-Fock: Exchange Interaction.
- Density-Functional-Theory.
- Exchange-correlation energy.
- Examples of DFT applications.

Material Properties

- Crystal Chemistry.
- Ground State Energy.
- Phase Diagrams.
- Vibrational Properties.
- Electronic Density of States.
- Magnetism.
- Solid Solutions. Alloying.
- Elasticity.
- ...

Transport Properties:
- Thermal conductivity.
- Electrical conductivity.
- Viscosity.
- ...

“Minimal” Requirements

- Periodic table.
- Thermodynamics.
- Single theoretical framework for solid, liquid, gas.
- Bulk, surfaces, and molecules.

Requirement

- Description of atoms and interactions.
- Forces.
- Ensembles.
**Scientific Goal**

\[ m \cdot \alpha = F \]
\[ \hat{H} | \psi \rangle = E | \psi \rangle \]

Atoms \rightarrow Interaction \rightarrow "World"

**Classical Mechanics, 18th Century**

\[ m \cdot \ddot{x}_i = m \cdot \ddot{a}_i = \vec{F}_i \]
\[ \vec{F}_i = -\nabla \cdot V(\{r_j\}) \]

**Empirical Potentials**

Born-Meyer potential:
\[ V(r) = \frac{Z_i Z_j}{r} + A \exp(-B \cdot r) + \frac{C}{r^6} \]

Coulomb-Potential \hspace{0.5cm} Non-Coulomb \hspace{0.5cm} Dispersion

Newton’s 2nd law:
\[ m \cdot \alpha_i = \vec{F}_i = \frac{1}{2} \sum_{j \neq i} \nabla V(\{r_j\}) \]

**Assessment**

- Transferability?
- Electronic properties?
- Predictive Power?

⇒ Suggest that electrons should be treated explicitly

**Advantage:**
- Fast.
- Many atoms (> Millions).
- Explicit dispersion forces.

**Disadvantage:**
- Charges (Z); Constants: A, B, C.
- Multiple valance states: 3d, 4d, … Fe^{2+}, Fe^{3+}, …
Electricity, 18th+19th Century

Charles Coulomb (1736 – 1806)

\[ F = -\frac{1}{4\pi \varepsilon_0} \frac{q_1 \cdot q_2}{R^2} \]

James Clerk Maxwell (1831 – 1879)

Electrodynamics

\[ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} - \vec{J} \]

\[ \nabla \cdot \vec{B} = 0 \]

\[ \nabla \cdot \vec{D} = \rho \]

Constituents of Atoms

- Electron (Thomson, 1897): negatively charged particle.
  - need positively charged particle.
- Proton (Thomson + Rutherford, 1907).

Electrodynamics predicts that the electron spirals into the nucleus within \(\sim 10^{-8}\) s.

Classical Physics Predicts that Matter is Unstable?!?

Supposedly Rodin: The Thinker

Solution: Quantum Mechanics

- Max Planck (1899).
- Albert Einstein (1905).
- Niels Bohr (1915).
- Werner Heisenberg (1925).
- Erwin Schroedinger (1925).

\[ E = n\hbar \omega \]

\[ i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \]

\[ E \psi = \hat{H} \psi \]
**Interpretation**

(Time independent) Schroedinger equation:

\[ E \psi = \hat{H} \psi \]

New quantity: Wave function

\[ \hat{H} = \hat{K} + \hat{U} \]

Total energy = Kinetic energy + Potential energy

**What is a Wave Function?**

Interpretation (Max Born, 1927):

- Probability
  \[ = |\psi|^2 dV \]
  \[ = \langle \psi | \psi \rangle dV \]

The square of a wave function describes a probability (density).

Example: Hydrogen Atom

\[ \hat{K} = -\frac{\hbar^2}{2m} \nabla^2; \hat{U} = -\frac{e^2}{r} \]

**Hydrogen Atom**

\[ E_n = -\frac{13.6eV}{n^2} \]

\[ a_n = 0.529 \cdot 10^{-10} m \]

\[ \hat{H} = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{|r|} \]

\[ l = 0, 1, \ldots, n-1 \]

\[ m_l = -l, \ldots, l \]

Degeneracy:

- No spin: \( n^2 \)
- Spin: \( 2 \cdot n^2 \)

\[ 1 \text{ eV} = 1.6022 \cdot 10^{-19} J = 96.4860 \text{ kJ/mol.} \]

\[ 1 \text{ kcal/mol} = 4.184 \text{ kJ/mol} \]

**Thermodynamics**

How to distribute two or more electrons over available states?

Lowest energy that is compatible with constraints

\[ == \]

Ground State
Interactions

Thermodynamics
Finite T : Minimize $F=F(V,T,N)$ or $G=G(P,T,N)$…
T=0 K : Minimize $E=E(V,N)$ or $H=H(P,N)$

Pauli-Exclusion-Principle
Probability $= \left| \psi(r_1, r_2) \right|^2 dV_1 dV_2$
Two Fermions in the same location:
$\psi(r_1, r_2) = -\psi(r_2, r_1)$
$\Rightarrow \psi(r_1, r_1) = 0$
$\Rightarrow$ Probability $= 0$
Slater determinants:
$\psi(r_1, \ldots, r_N) = \frac{1}{N!} \ldots \psi_1(r_1) \ldots \psi_N(r_N)$
Fermions in the exact same quantum state are impossible

Multi-Electron Atoms
Electrons are indistinguishable

Wolfgang Pauli: Pauli exclusion Principle (1925)
In quantum mechanics we have two possibilities:
$\psi(r_1, r_2) = -\psi(r_2, r_1)$  Fermions: electrons, protons, neutrons,…
$\psi(r_1, r_2) = +\psi(r_2, r_1)$  Bosons: photons, phonons, spin-waves,…

Hund’s Rule #1
For a given electron configuration, the term with maximum multiplicity has the lowest energy. Since multiplicity is equal to $2S+1$, this is also the term with maximum $S$.
$\left| \psi \right> = \frac{1}{\sqrt{2}} \left( \left| \uparrow \right> \downarrow + \left| \downarrow \right> \uparrow \right) = \frac{1}{\sqrt{2}} \left( \left| \uparrow \right> \downarrow - \left| \downarrow \right> \uparrow \right)$
“$+$” == symmetric; “$-$” == anti-symmetric.
Consider two electrons:
$S=0$  $\Rightarrow$ anti-symmetric spin state  $\Rightarrow$ symmetric spatial state.
$S=1$  $\Rightarrow$ symmetric spin state  $\Rightarrow$ anti-symmetric spatial state  $\Rightarrow$ zero probability to find electrons at “same” location.  $\Rightarrow$ reduced Coulomb repulsion.
$\Rightarrow S=1$ (triplet) state has a lower energy.
Hund's Rule #1, cont'd

Spatial States

Electrostatic repulsion reduced for anti-symmetric spatial state \( \rightarrow \) lower energy.

Hund's Rule #2

For a given multiplicity, the term with the largest value of \( L \) has the lowest energy. High \( L \) \( \rightarrow \) electrons orbit in the same direction. For low \( L \) some electrons rotate oppositely \( \rightarrow \) must pass \( \rightarrow \) increase in Coulomb repulsion \( \rightarrow \) higher energy.

“Classically” speaking:

- Larger \( L \) \( \rightarrow \) More electrons orbit nucleus in the same sense.
- Reduced Coulomb repulsion.
- Lower energy.

Hund's Rule #3

For a given term, in an atom with outermost subshell half-filled or less, the level with the lowest value of

\[ J = L + S \]

lies lowest in energy. If the outermost shell is more than half-filled, the level with highest value of \( J \) is lowest in energy.

Reason: Spin-orbit coupling \( \sim L \ast S \rightarrow J=L+S \rightarrow \) energy lower if \( L \) and \( S \) are in opposite directions \( \rightarrow \) lower \( J \).
Summary

• Failure of classical mechanics/electrodynamics.
• Quantum mechanics to the rescue.
• New quantity: wave function Probability.
• Building blocks of the periodic table: Pauli exclusion principle. Hund’s rules.

Born-Oppenheimer or Adiabatic Decoupling

Do we need to treat nuclei quantum mechanically as well?

\[ \hat{H} = \hat{K}_{\text{ion}} + \hat{U}_{\text{ion}} + \hat{K}_{\text{el}} + \hat{U}_{\text{el}} + \hat{U}_{\text{el-ion}} \]

\[ m_p/m_e \sim 2000 \Rightarrow \text{motion of electron much faster than nuclei.} \]

Electronic time-scale shortest
\[ \Rightarrow \text{Electrons follow nuclear motion} \text{ \emph{instantaneously}.} \]
(except may be for the lightest element: hydrogen)
**Consequence**

If $T=0 \text{ K} \Rightarrow$ Kinetic energy of the nuclei is zero.

Note: Nuclei are not eliminated from the problem, $U_{\text{nuc-nuc}}$ and $U_{\text{nuc-el}}$.

Static problem.

If $T>0 \text{ K} \Rightarrow$ Nuclei are no longer fixed. Lattice vibrations; thermodynamics.

Electrons: always treated quantum mechanically.

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**Covalent Bonds - I**

\[
\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{|\mathbf{r} - \mathbf{R}/2|} - \frac{e^2}{|\mathbf{r} + \mathbf{R}/2|} + \frac{e^2}{|\mathbf{R}|}
\]

\[
\hat{H}|1\rangle = \lambda|2\rangle \Rightarrow \lambda = \pm 1
\]

\[
|\pm\rangle = \frac{1}{\sqrt{2}} (|1\rangle \pm |2\rangle)
\]

Electron bound to nucleus 1: $|1\rangle$

Electron bound to nucleus 2: $|2\rangle$

\[
\hat{H}_i = \hat{H}_{12}
\]

\[
\hat{H}_0 = \hat{H}_{ii}
\]

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**Covalent Bonds - II**

\[
|\pm\rangle = \frac{1}{\sqrt{2}} (|1\rangle \pm |2\rangle)
\]

\[
E_{\pm} = \frac{1}{1 \pm \langle 1|2 \rangle} (H_{11} \pm H_{12})
\]

\[
\langle 1|2 \rangle \neq 0
\]

\[
\Rightarrow H_{12} = \int \psi_1(r)H\psi_2(r)dV \neq 0
\]

Overlap of electronic wave functions is necessary for covalent bonding.

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**Ritz's Variational Principle**

\[
E_0 \leq \frac{\langle \Psi^*(r_1, \ldots, r_N)|\hat{H}|\Psi(r_1, \ldots, r_N)\rangle}{\langle \Psi^*(r_1, \ldots, r_N)|\Psi(r_1, \ldots, r_N)\rangle}
\]

For a given $H$ the ground state energy can be estimated as the lowest energy found for any possible wave function.

Also reminiscent of Pauli exclusion principle, Hund’s rules, and thermodynamics which all required the minimization of energy.
**Generalization: Hartee-Fock**

Many-electron systems:
Keep:
- Adiabatic decoupling.
- Pauli-principle.

\[ \psi(r_1, ..., r_n) = \frac{1}{N!} \begin{pmatrix} \psi_1(r_1) & \cdots & \psi_1(r_n) \\ \vdots & \ddots & \vdots \\ \psi_n(r_1) & \cdots & \psi_n(r_n) \end{pmatrix} \]

This theory is called Hartree-Fock theory.

**Hartee-Fock: Electrostatics**

Notably the theory contains expressions such as:

\[ \iint \psi_i^2(r_1) \psi_j^2(r_2) dV_1 dV_2 \]

Electrostatic energy

Note:
\[ \psi_i = \psi_j \]  
Electrons at the same location: \( r_{12} = 0 \)  
\( \Rightarrow \) Increase of electrostatic energy.

This is impossible according to the Pauli-exclusion principle.

**Hartee-Fock: Exchange**

But another term appears as well:

\[ -\iint \psi_i(r_1) \psi_j(r_2) \frac{1}{r_{12}} \psi_i(r_1) \psi_j(r_1) dV_1 dV_2 \]

**Exchange energy:**
Origin: Pauli-exclusion principle.
No classical analogue.

\[ \psi_i = \psi_j \]  
Exact compensation of electrostatic term:  
Pauli exclusion principle is fulfilled.

**Exchange: Another Look**

Pauli exclusion principle  
\( \Rightarrow \) Exchange energy  
\( \Rightarrow \) Reduces Coulomb repulsion  
\( \Rightarrow \) Lowers energy of system.
Changing the Point of view

Hartree-Fock:
central quantity: wave functions.

Alternatively: Choose to focus on the charge density.
⇒ Density-Functional-theory.

Density-Functional-Theory (DFT)
Hohenberg-Kohn (1964)

Theorem 1
For any system of interacting particles in an external potential $V_{\text{ext}}(r)$, the potential is determined uniquely by the ground state particle density $n_0(r)$:

$$ E[n,V_{\text{ext}}] = \int n(\vec{r}) \cdot V(\vec{r}) \, d^3r + F[n] $$

⇒ $F[n]$ is unique and depends only on the density, $n$.
⇒ Completely general.

Theorem 2
A universal functional for the energy $E[n,V_{\text{ext}}]$ in terms of the density $n(r)$ exists with a global minimum for the exact ground state density $n_0(r)$.

⇒ Valid for any system (universal): gas, liquid, solid…

Kohn and Sham Ansatz (1965)

Replace correlated many-electron problem by an equivalent single electron independent particle problem in an effective potential.

$$ F[n] = \frac{e^2}{2} \int \frac{n(\vec{r}) \cdot n(\vec{r}^\prime)}{|\vec{r} - \vec{r}^\prime|} \, d^3r \, d^3r^\prime $$

Coulomb interaction

$$ + T_0[n] $$

Kinetic energy

$$ + E_{\text{XC}}[n] $$

Exchange-Correlation-energy
**Kohn and Sham Equations**

Kohn and Sham (1965)

\[
\left[ -\frac{\hbar^2}{2m_{\text{el}}} \nabla^2 + V_{\text{eff}}(r, n(r)) \right] \phi_i(r) = \varepsilon_i \phi_i(r)
\]

\[V_{\text{eff}}(r, n(r)) = V(r) + \sum_{\text{all neighbors}} e^2 \int \frac{n(r')}{|r - r'|} \, dr' \]

\[+ \frac{\delta E_{\text{XC}}(n(r))}{\delta n(r)}\]

Can be generalized to include magnetism:

\[n = n_\uparrow + n_\downarrow\]

**What is the Exchange-Correlation Potential, \(E_{\text{XC}}\)?**

Thermodynamics: ground state == lowest energy state

- Pauli exclusion principle
  - Exchange energy.
- Repulsion of opposite spins
  - Correlation energy.

Both effects lower the energy

Active research field to develop better \(E_{\text{XC}}\) functionals:
- LDA: Ceperley and Alder.
- GGA: PW91, PBE, \(rPBE\), rev\(PBE\),...

**Consequence?**

1 g of Na \(\rightarrow\) \(\sim 3 \times 10^{23}\) electrons.

Need to solve determine for \(10^{23}\) electrons?!?

Recognize that crystals are *periodic* structures.

Sufficient to describe one unit cell. (Bloch’s theorem).

bcc-Na: 22 electrons sufficient.

\[\Rightarrow\text{Our problem has become tractable.}\]

**Periodic Structures: Bloch’s Theorem**

Crystals are 3-d periodic structures:
That is they can be created by periodically repeating a smaller unit.

Crystal == Lattice + Motif
Suitable Electronic Wave Functions

Solutions to Schrödinger equation with constant potential:

Planewaves: $\psi \sim \exp(i \mathbf{k} \cdot \mathbf{r})$

Pseudopotentials

"Problem": Steep potential close to nuclei $\Rightarrow$ plane waves are not well suited.

Idea: Most material/chemical properties rely on valence electrons.

Eliminate core electrons

Optimization: Forces

Hellman-Feynman (force) theorem:

$$\mathbf{F}_i = -\nabla_i E = \langle \psi | \nabla_i \hat{H}_{\text{electronic}} | \psi \rangle - \nabla_i U_{\text{ion-ion}}$$

Summary:

- Periodic Table.
- Pseudopotential $\Rightarrow$ fewer electrons.
- Universal $E_{\text{XC}}$: solid, liquid, gas.
  - Bulk, surface, molecule.
- Optimization.

$\Rightarrow$ Predictive power.

Summary

- Covalent bonding.
- Adiabatic decoupling.
  - $T = 0$ K and finite temperatures.
- Hartree-Fock $\Rightarrow$ Exchange.
- DFT $\Rightarrow$ Exchange and correlation.
- Periodic structures, Bloch's theorem.
- Pseudopotential.
- Forces.
- Predictive power.
Some Applications of DFT

“Fundamentals” of Condensed Matter Physics/Chemistry:
- Sodium at high pressure.
- Octet-rule at high pressure.

Student presentations
- Andrew: Pt\(_{1-x}\)Re\(_x\) solid solutions.
- Eric: Pd on γ-Al\(_2\)O\(_3\).
- Levi: Pd on α-Al\(_2\)O\(_3\).
- Sam: non-Pt based catalysts.

Sodium at High Pressures
(Ma et al., 2009)

**Background:**
- Sodium at ambient conditions is a metal.
- Expected: structures adopt dense packed structures at sufficiently high pressure.

**Experiment**

**Theory**

- Phases: bcc \(\rightarrow\) fcc (close-packed) \(\rightarrow\) non-closed-packed...
- Transparent (non-metallic) high pressure phase.
Octet rule at High Pressures
(Kiefer and Tschauner)

- Octet rule: main group elements tend to achieve a complete outermost shell: eight electrons.

  - CH₄: C: 4e⁻; each hydrogen donates 1e⁻.
  - H₂S: S: 6e⁻; each hydrogen donates 1e⁻.
  - CHOONa: Na-formate.

Experimental Observations

- Sample becomes opaque at ~20 GPa during laser heating to T ~ 1500 K, reverses at T ~ 1300 K.
- H₂ libron observed.

Summary

- DFT versatile tool.
- Exchange and correlation.
- Pseudopotentials.
- Periodic table.
- Applicable to solid, liquid, and gas.
- Bulk, surface, molecule.
- T=0 K, finite temperature.

Outlook

- Review.
- DFT: in's and out's.