Density-Functional-Theory
Lecture I

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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.
- …

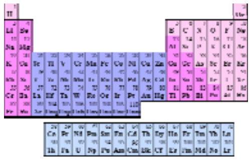
"Minimal" Requirements

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

↓ Requirement

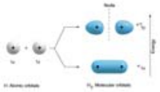
- Description of atoms and interactions.
- Forces.
- Ensembles.

Scientific Goal



$$m \cdot a = F$$

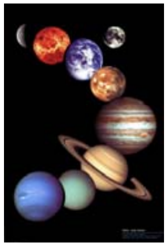
$$\hat{H}|\psi\rangle = E|\psi\rangle$$



Atoms Interaction "World"

Classical Mechanics, 18th Century

Sir Isaac Newton
(1643 – 1727)



$$m \cdot \ddot{\vec{x}}_i = m \cdot \vec{a}_i = \vec{F}_i$$

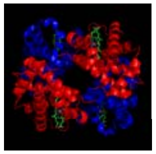
$$\vec{F}_i = -\vec{\nabla}_i V(\{r_j\})$$

Empirical Potentials

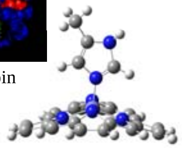
Born-Meyer potential:

$$V(r) = \frac{"Z_1Z_2"}{r} + A\exp(-B \cdot r) + \frac{C}{r^6}$$

Coulomb-Potential Non-Coulomb Dispersion



Hemoglobin



Active site: Fe^{2+}

Newton's 2nd law:

$$m \cdot a_i = \vec{F}_i = \frac{1}{2}\sum_{i \neq j} \nabla_i V(\vec{r}_j)$$

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

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

http://upload.wikimedia.org/wikipedia/commons/3/3d/1GZX_Haemoglobin.png

Assessment

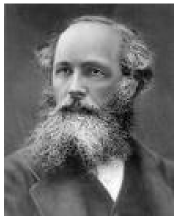
- Transferability?
- Electronic properties?
- Predictive Power?

➔Suggest that electrons
should be treated explicitly

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

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} - \vec{M}$$

$$\nabla \times \vec{H} = -\frac{\partial \vec{D}}{\partial t} + \vec{J}$$

$$\nabla \cdot \vec{D} = \rho$$

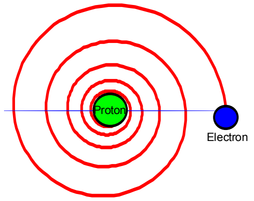
$$\nabla \cdot \vec{B} = 0$$

http://www.microwaves101.com/encyclopedia/images/maxwellsequations/maxwellsequations.jpg
http://upload.wikimedia.org/wikipedia/et/thumb/b/ba/Charles_Coulomb.jpg/250px-Charles_Coulomb.jpg
http://outreach.jach.hawaii.edu/pressroom/2006_jcmbday/Maxwell.jpg

Constituents of Atoms

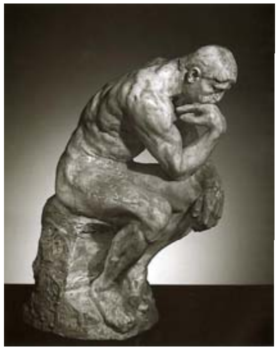
- Electron (Thomson, 1897):
  negatively charged particle.
  ➔ need positively charged particle.

- Proton (Thomson + Rutherford, 1907).



Electrodynamics predicts that the electron spirals into the nucleus within ~10^{-8} s.

Classical Physics Predicts that Matter is Unstable?!?



Auguste Rodin: The Thinker

Solution: Quantum Mechanics

- ➢ Max Planck (1899).

$$E = n\hbar\omega$$

- ➢ Albert Einstein (1905).
- ➢ Niels Bohr (1915).

- ➢ Werner Heisenberg (1925).
- ➢ Erwin Schroedinger (1925).

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

$$E\psi = \hat{H}\psi$$

Interpretation

(Time independent) Schroedinger equation:

Energy eigenvalue

Total energy (operator)

$$E\psi = \hat{H}\psi$$

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):

$$\text{probability} = |\psi^2| dV = \langle \psi | \psi \rangle dV$$

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

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

$$a_n = 0.529 \cdot 10^{-10} m$$

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

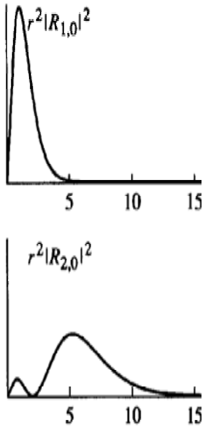
$$l = 0,1,\ldots,n-1$$

$$m_l = -l,\ldots,l$$

$$Degeneracy:$$

$$No-spin:\ n^2$$

$$Spin:\ 2 \cdot n^2$$



1 eV = $1.6022\ 10^{-19}$ J
= 96.4860 kJ/mol.

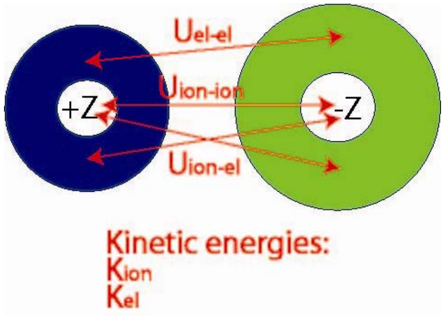
1 kcal/mol = 4.184 kJ/mol

Thermodynamics

How to distribute two or more electrons over available states?

Lowest energy that is compatible with constraints
==
Ground State

Interactions



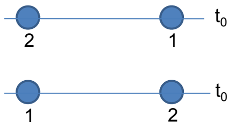
Thermodynamics

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)

Multi-Electron Atoms

Electrons are <u>indistinguishable</u>

Wolfgang Pauli:
Pauli exclusion
Principle (1925)



➔ Physics/Chemistry must be independent of numbering.

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,…

http://www.csub.edu/~mdutton/u61s2s.jpeg

Pauli-Exclusion-Principle

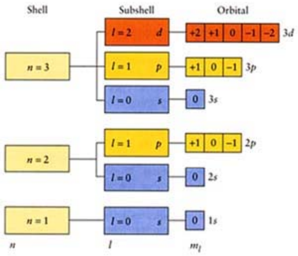
$$\text{Probability} = |\psi(r_1,r_2)|^2\, dV_1 dV_2$$

Two Fermions in the same location:

$$\psi(r_1,r_2)=-\psi(r_2,r_1)$$
$$\Rightarrow \psi(r_1,r_1)=0$$
$$\Rightarrow \text{Probability}=0$$

Slater determinants:

$$\psi(r_1,\ldots,r_n)=\frac{1}{N!}\begin{vmatrix}\psi_1(r_1) & \ldots & \psi_1(r_n)\\ \ldots & & \ldots\\ \psi_n(r_1) & \ldots & \psi_n(r_n)\end{vmatrix}$$



Fermions in the <u>exact</u> same quantum state are impossible

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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*.

$$|1,2\rangle=\frac{1}{\sqrt{2}}\left(|\uparrow\rangle|\downarrow\rangle\mp|\downarrow\rangle|\uparrow\rangle\right) \quad * \quad \frac{1}{\sqrt{2}}\left(|1\rangle|2\rangle\pm|2\rangle|1\rangle\right)$$

"+" == symmetric; "-" == anti-symmetric.

Friedrich Hund

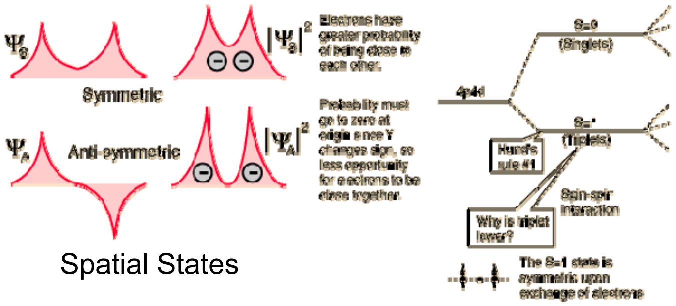
Consider two electrons:
S=0 ➔ anti-symmetric spin state ➔ symmetric spatial state.

S=1 ➔ symmetric spin state ➔ anti-symmetric spatial state
➔ zero probability to find electrons at "same" location.
➔ reduced Coulomb repulsion.

➔ *S=1* (triplet) state has a lower energy.

http://hyperphysics.phy-astr.gsu.edu/Hbase/Atomic/Hund.html#c2

Hund's Rule #1, cont'd

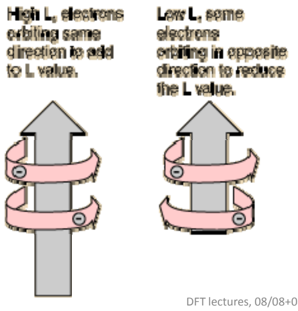


Spatial States

Electrostatic repulsion reduced for anti-symmetric spatial state ➔ lower energy.

Hund's Rule #2

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



"Classically" speaking:
Larger *L*
➔More electrons orbit nucleus in the same sense.
➔ Reduced Coulomb repulsion.
➔ Lower energy.

http://hyperphysics.phy-astr.gsu.edu/Hbase/Atomic/Hund.html#c2

Hund's Rule #3

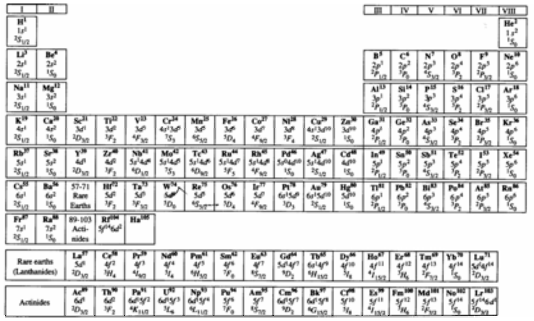
For a given term, in an atom with outermost subshell half-filled or less, the level with the lowest value of

$$J=L+S$$

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 ~ *L* * *S* ➔ *J=L+S* ➔ energy lower if *L* and *S* are in opposite directions ➔ lower *J*.

Periodic Table



N ➔ l-1 ➔ l_z = -l…+l = 2 * l +1; s=±1/2
N=1: l=0, s = ±1/2 ➔ 2 states
N=2: l=0, s = ±1/2 ➔ 2 states
l=1, s = ±1/2 ➔ 6 states
…

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?

$$\hat{H} = \hat{K}_{ion} + \hat{U}_{ion} + \hat{K}_{el} + \hat{U}_{el} + \hat{U}_{el-ion}$$

m_p/m_e ~ 2000 ➔ motion of electron much faster than nuclei.

Born-Oppenheimer or Adiabatic Decoupling

Time scales:

Diffusion	: $D= 10^{-11}$ cm^2/s; d=1 A ➔	$t=d^2/D$	~ 10^{-5} s
Vibrations	: H_2 ~ 4400 cm^{-1}	t=1/(c k)	~ 7.5 10^{-15} s.
Electrons	:	$t= h/c^2\ m_e$ ~ 10^{-20} s.	

Electronic time-scale shortest
➔Electrons follow nuclear motion *instantaneously*.
(except may be for the lightest element: hydrogen)

Consequence

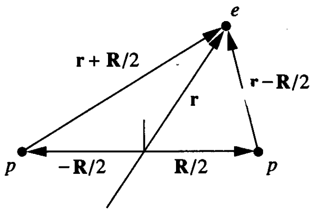
If T=0 K ➔ Kinetic energy of the nuclei is zero.
Note: Nuclei are ***not*** eliminated from the problem, $U_{\text{nuc-nuc}}$ and $U_{\text{nuc-el}}$.
Static problem.

If T>0 K ➔ Nuclei are no longer fixed. Lattice vibrations; thermodynamics.

Electrons: always treated quantum mechanically.

Covalent Bonds- I

$$\hat{H} = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{|\hat{r} - R/2|} - \frac{e^2}{|\hat{r} + R/2|} + \frac{e^2}{|R|}$$



$$\hat{\Pi}|1\rangle = \lambda|2\rangle \Rightarrow \lambda = \pm 1$$

$$|\pm\rangle = \frac{1}{\sqrt{2 \pm 2 \cdot \langle 1|2\rangle}}\left(|1\rangle \pm |2\rangle\right)$$

$$\hat{H}_{ij} = \langle i|H|j\rangle$$

$$\hat{H}_{11} = \hat{H}_{22}$$

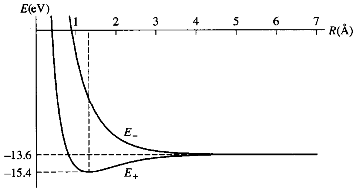
$$\hat{H}_{12} = \hat{H}_{21}$$

Electron bound to nucleus 1: I1>
Electron bound to nucleus 2: I2>

Covalent Bonds- II

$$|\pm\rangle = \frac{1}{\sqrt{2 \pm 2 \cdot \langle 1|2\rangle}}\left(|1\rangle + |2\rangle\right)$$

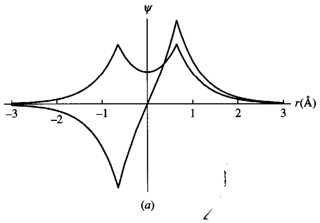
$$E_{\pm} = \frac{1}{1 \pm \langle 1|2\rangle}\left(H_{11} \pm H_{12}\right)$$



$$\langle 1|2\rangle \neq 0$$

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

Overlap of electronic wave functions is necessary for covalent bonding.



Ritz's Variational Principle

$$E_0 \leq \frac{\left\langle \Psi^*(r_1,\ldots,r_N) \middle| \hat{H} \middle| \Psi(r_1,\ldots,r_N) \right\rangle}{\left\langle \Psi^*(r_1,\ldots,r_N) \middle| \Psi(r_1,\ldots,r_N) \right\rangle}$$

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.

$$\psi(r_1,\ldots,r_n)=\frac{1}{N!}\begin{vmatrix}\psi_1(r_1) & \cdots & \psi_1(r_n)\\ \cdots & & \cdots\\ \psi_n(r_1) & \cdots & \psi_n(r_n)\end{vmatrix}$$

This theory is called <u>Hartree-Fock</u> theory.

Hartee-Fock: Electrostatics

Notably the theory contains expressions such as:

$$\iint \psi_i^2(r_1)\frac{1}{r_{12}}\psi_j^2(r_2)\,dV_1 dV_2$$

Electrostatic energy

Note:

$\psi_i = \psi_j$ Electrons at the same location: $r_{12}=0$
➔ Increase of electrostatic energy.

This is <u>*impossible*</u> according to the Pauli-exclusion principle.

Hartee-Fock: Exchange

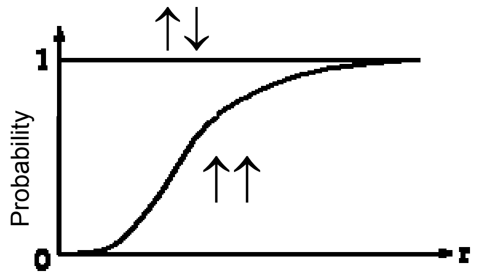
But another term appears as well:

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

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
➔Exchange energy
➔Reduces Coulomb repulsion
➔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 $V_{ext}(r)$, the potential is determined *uniquely* by the ground state particle density $n_0(r)$:

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

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

Theorem 2

A *universal* functional for the energy $E[n,V_{ext}]$ 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…

Iterative Solution

$$\begin{tikzcd}
V_{ext}(r) \arrow[d] & n_0(r)=\langle\Psi_0(\{r\})|\Psi_0(\{r\})\rangle \arrow[l, "HK"'] \\
\Psi_i(\{r\}) \arrow[r] & \Psi_0(\{r\}) \arrow[u]
\end{tikzcd}$$

All States **Ground State**

Kohn and Sham Ansatz (1965)

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

$$\begin{aligned}
F[n]=\frac{e^2}{2}\frac{\int n(\vec{r})\cdot n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r\,d^3r' &\qquad \text{Coulomb interaction}\\
+T_0[n] &\qquad \text{Kinetic energy}\\
+E_{XC}[n] &\qquad \text{Exchange-Correlation-energy}
\end{aligned}$$

Kohn and Sham Equations

Kohn and Sham (1965)

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

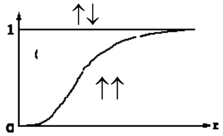
$V_{eff}\left(r,n(r)\right)=V(r)$	External potential.
$+e^2\int\frac{n(r')}{\lvert r-r'\rvert}dr'$	Coulomb interaction.
$+\frac{\delta E_{XC}\left(n(r)\right)}{\delta n(r)}$	Exchange-correlation.

Can be generalized to include magnetism:

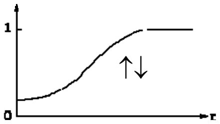
$$n=n_\uparrow+n_\downarrow$$

What is the Exchange-Correlation Potential, E_{XC}?

Thermodynamics: ground state == lowest energy state



Pauli exclusion principle
➔ Exchange energy.



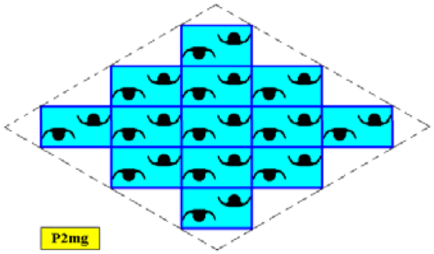
Repulsion of opposite spins
➔ Correlation energy.

Both effects lower the energy

Active research field to develop better E_{XC} functionals:

- LDA : Ceperley and Alder.
- GGA : PW91, PBE, rPBE, revPBE,…

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

http://www.metafysica.nl/ontology/para_10.gif

Consequence?

1 g of Na ➔ ~3 x 10^{23} electrons.

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

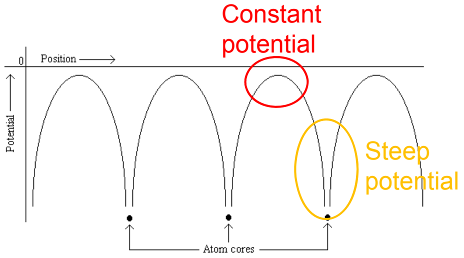
Recognize that crystals are *periodic* structures.

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

bcc-Na: 22 electrons sufficient.

➔ Our problem has become tractable.

Suitable Electronic Wave Functions



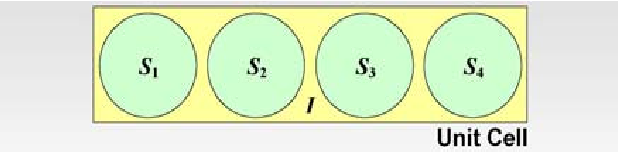
Solutions to Schrödinger equation with constant potential:

Planewaves: ψ~exp(i k r)

http://gauss.sdsmt.edu/~bhemmelm/quantu1.gif

Pseudopotentials

“Problem”: Steep potential close to nuclei
➔ plane waves are not well suited.



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

Eliminate core electrons

Pseudopotential.

Optimization: Forces

Hellman-Feynman (force) theorem:

$$\vec{F}_i = -\nabla_i E$$
$$= \left\langle \psi \middle| \nabla_i \hat{H}_{electronic} \middle| \psi \right\rangle - \nabla_i U_{ion-ion}$$

Summary:
- ✓ Periodic Table.
- ✓ Pseudopotential ➔ fewer electrons.
- ✓ Universal E_{XC}: solid, liquid, gas.
  Bulk, surface, molecule.
- ✓ Optimization.

➔ ***Predictive power.***

Summary

- Covalent bonding.
- Adiabatic decoupling.
  T=0 K and finite temperatures.
- Hartree-Fock ➔ Exchange.
- DFT ➔ 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_2O_3.
Levi:	Pd on α-Al_2O_3.
Sam:	non-Pt based catalysts.

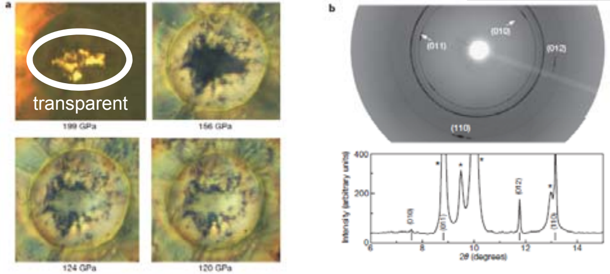
Sodium at High Pressures

(Ma et al., 2009)

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

Experiment

1 GPa ~ 10^4 atm



Theory

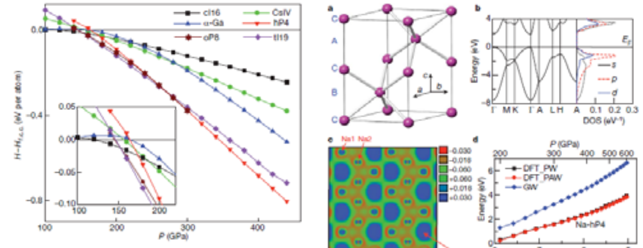


Figure 3 | Enthalpy curves (relative to f.c.c.) as a function of pressure for cI16, CsIV, α-Ga, oP8, tI19 and hP4 structures of Na. The inset shows the transition sequence f.c.c. → cI16 → tI19 (oP8) → hP4 in more detail. Two phase transitions, cI16 → tI19 → hP4, are predicted at 152 and 260 GPa, respectively. The oP8 structure is less stable than the tI19 phase in the pressure range 152–260 GPa, but is energetically very competitive. It is

- Phases: bcc ➔ fcc (close-packed) ➔ non-closed-packed…
- Transparent (non-metallic) high pressure phase.

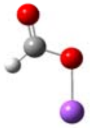
Octet rule at High Pressures

(Kiefer and Tschauner)

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

- CH_4: C: 4e$^-$; each hydrogen donates 1e$^-$.

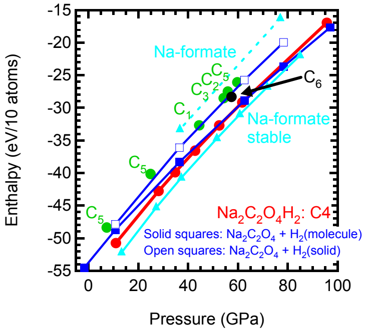
- H_2S: S: 6e$^-$; each hydrogen donates 1e$^-$.

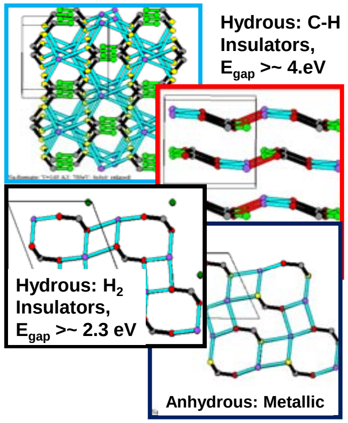


- CHOONa: Na-formate.

Experimental Observations

- Sample becomes opaque at ~20 GPa during laser heating to T ~ 1500 K, reverses at T ~ 1300 K.
- H_2 libron observed.





Hydrous: C-H Insulators, E_{gap} >~ 4.eV

Hydrous: H_2 Insulators, E_{gap} >~ 2.3 eV

Anhydrous: Metallic

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.