# DFT Because We Can

## A Tutorial by Angela Pak and Elif Ertekin

ID4 Seminar Series

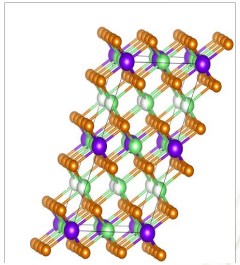
University of Illinois at Urbana-Champaign
16 November 2022

# Outline

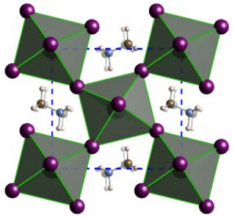
- Schrodinger equation and materials
- Hierarchy of quantum simulation methods
- DFT deep dive
  - Theoretical basis, common formulations
  - Examples - what we use it for, where it struggles
  - TinyDFT demo - atomic
  - Extension to solids - crystalline silicon
  - Basic workflow and common codes
  - Recent methodological developments

# Schrodinger Equation and Materials

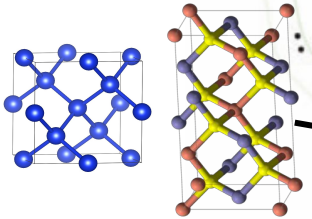
# rich landscape of materials



**Ion conductors**



**Hybrid perovskites**

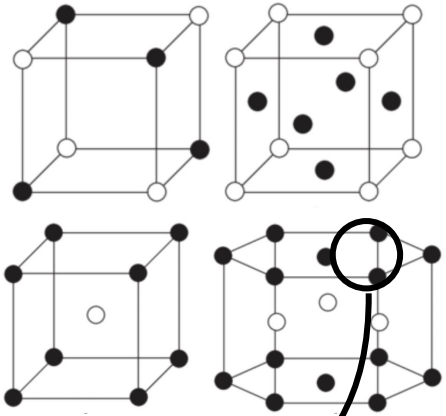


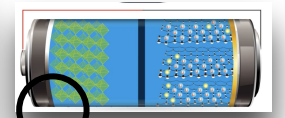
**Photovoltaics**

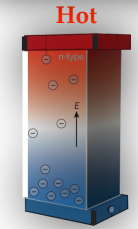
structure property

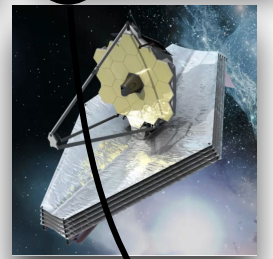
from quantum mechanics

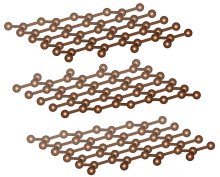
$$\hat{H}\Psi = E\Psi$$



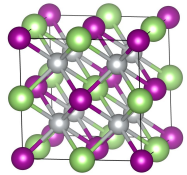




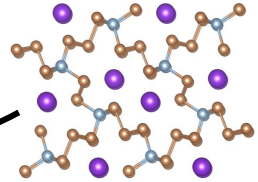





**2D/layered materials**



**Shape memory alloys**



**Thermoelectrics**

*Courtesy*: Taishan Zhu

# Schrödinger Equation

- In quantum mechanics, the Schrödinger equation is the analog to Newton's second law in classical mechanics
- It is applied to atoms, molecules, solids, subatomic systems, etc.
- For a single particle embedded in a potential field: $V(\vec{r}, t)$

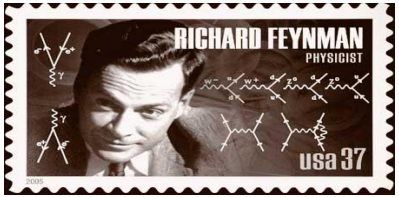
$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right]\psi(\vec{r},t)$$

**Hamiltonian H = T + V**

- The **wave function** $\psi(\vec{r},t)$ describes the quantum state of the system
- S.E. is a linear PDE describing how that quantum state evolves in time (dynamics)

# Schrödinger Equation

"Where did we get that (equation) from? Nowhere. It is not possible to derive it from anything you know. It came out of the mind of Schrödinger." - Feynman




- Think in terms of Einstein and de Broglie's insights into quantization of light – *i.e.*, the idea that light can have a wave and a particle like nature

$$E = h\nu = \hbar\omega \qquad \vec{p} = \hbar\vec{k} \;,\; p = \frac{h}{\lambda}$$

- Schrödinger's insight was to write down the wave function as a plane wave, and note some properties of its spatial and time derivatives:

$$\psi(\vec{r},t) = A\exp\left[i(\vec{k}\cdot\vec{r} - \omega t)\right]$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi = \frac{\vec{p}\cdot\vec{p}}{2m}\psi$$

$$-i\hbar\frac{\partial\psi}{\partial t} = E\psi$$

# Schrödinger Equation is Separable in Time & Position

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right]\psi(\vec{r},t)$$

$$\psi(\vec{r},t) = \Psi(\vec{r})\chi(t) = \Psi(\vec{r})\exp\left[-i\frac{E}{\hbar}t\right]$$

stationary state

$$\langle\hat{H}\rangle = \int \Psi^*(\vec{r})\hat{H}\Psi(\vec{r})d\vec{r} = E$$

$$\langle\hat{H}^2\rangle = \int \Psi^*(\vec{r})\hat{H}^2\Psi(\vec{r})d\vec{r} = E^2$$

$$\sigma_H = \sqrt{\langle\hat{H}^2\rangle - \langle\hat{H}\rangle^2} = 0$$

No spread of energies in a stationary state.
Every measurement gives the same value.
So we call $\Psi(\vec{r})$ an energy eigenstate.

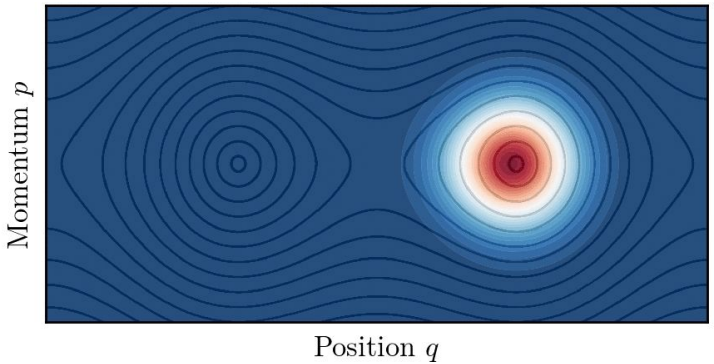
# Schrödinger Equation - Time Evolution Dynamics

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right]\psi(\vec{r},t)$$

Linear combination of stationary states is also a solution:

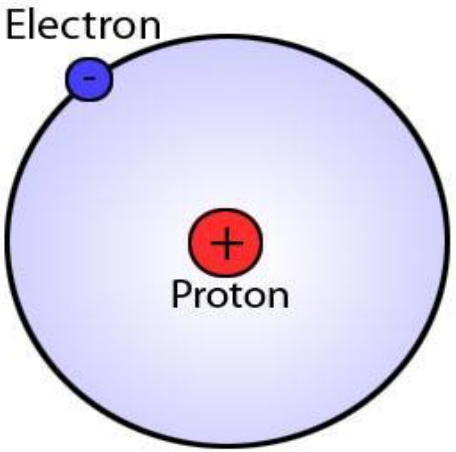
$$\psi(\vec{r},t) = c_1\Psi_1(\vec{r})\exp\left[-\frac{i}{\hbar}E_1 t\right] + c_2\Psi_2(\vec{r})\exp\left[-\frac{i}{\hbar}E_2 t\right]$$

- Oscillating amplitudes on each stationary state gives rise to time dynamics.
- Constructive and destructive interferences between states ⇒ tunneling




Maxime Martinez, From Wikipedia

# Example: Stationary States of the Hydrogen Atom




$$\left[-\frac{\hbar}{2m}\nabla^2 - \frac{1}{r}\right]\Psi(\vec{r}) = E\Psi(\vec{r})$$

Solutions exhibits a separable form (eigenfunctions):

$$\Psi_{nlm} = R_n(r)Y_{lm}(\theta,\varphi)$$

With corresponding energies (eigenvalues) $E_n \sim -1/n^2$

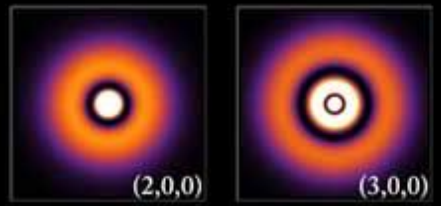
The wavefunctions are commonly referred to as orbitals and are characterized by three quantum numbers *n*, *l*, and *m*.

- *n* is the principle quantum number: 0, 1, 2, …
- *l* is the azimuthal quantum number: 0, 1, … (*n*-1)
- *m* is the magnetic quantum number: -l, -(l-1), …0…,(l-1), l

# Hydrogen Wave Function

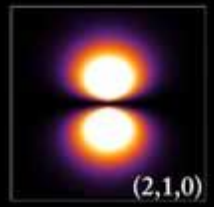
Probability density plots.

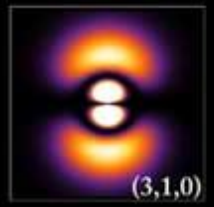
$$\psi_{nlm}(r,\theta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{lm}(\theta,\varphi)$$

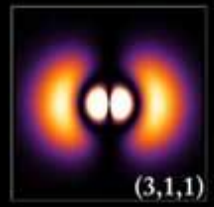


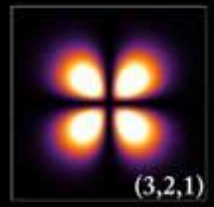


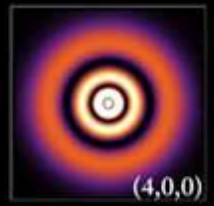


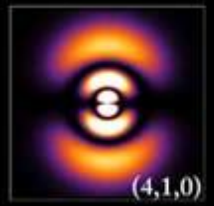


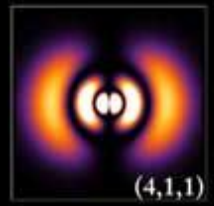



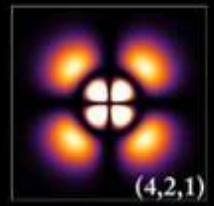



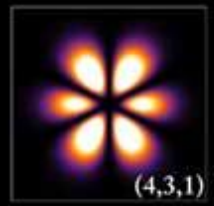


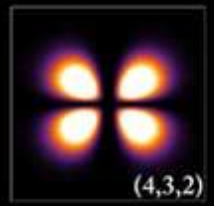






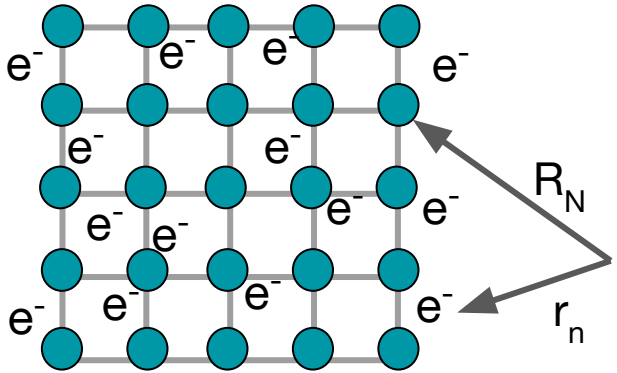
# Multi-Electron Atoms, Molecules, & Solids

Let $R_1$, …., $R_N$ = positions of the N nuclei

$eZ_1$, …., $eZ_N$ = charge of the N nuclei

$M_1$, …, $M_N$ = masses of the nuclei

$r_1$,…, $r_n$ = positions of the n electrons




Usually we assume that the nuclei are fixed with respect to the electrons, and only solve for the electronic degrees of freedom. The electronic S.E. and Hamiltonian looks like this:

$$\hat{H}\Psi(\vec{r}_1,\ldots,\vec{r}_n) = E\Psi(\vec{r}_1,\ldots,\vec{r}_n)$$

$$\hat{H} = \underbrace{\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\frac{Z_i Z_j e^2}{|R_i - R_j|} - \sum_{j=1}^{N}\sum_{i=1}^{n}\frac{Z_j e^2}{|r_i - R_j|}}_{V_{ext}(\vec{r}_i)} + \underbrace{\sum_{j=1}^{n}\left(-\frac{\hbar^2}{2m}\right)\nabla_{r_j}^2}_{T} + \underbrace{\frac{1}{2}\sum_{j=1}^{n}\sum_{i=1}^{n}\frac{e^2}{|r_i - r_j|}}_{V_{int}(\vec{r}_i,\vec{r}_j)}$$

Note how the only part of the Hamiltonian that changes for different material systems is the external potential.

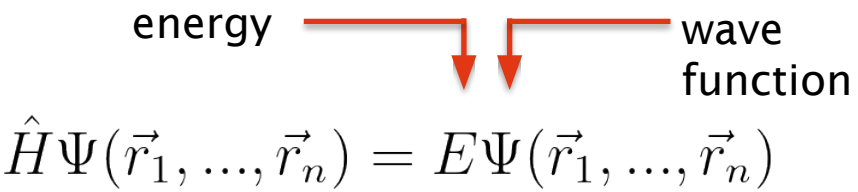
# First-Principles Methods - Overview/Hierarchy

# First-Principles Modeling

“The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.”

- Dirac

# The Schrodinger equation describes all properties of all materials.



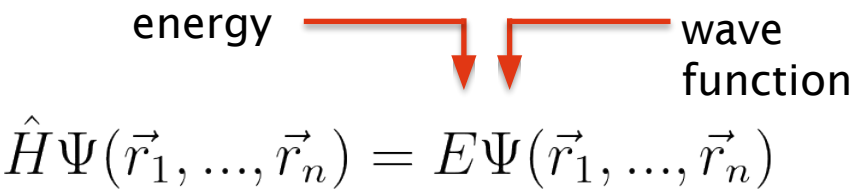

$$\hat{H} = -\frac{1}{2}\nabla^2 - \sum\frac{Z_n}{r_{e-n}} + \sum\frac{1}{r_{e-e}}$$

**Non-interacting part**

**Contains an Electron-Electron Distance!**

- The wave function encodes all information about a system of particles (here the electrons, assuming fixed nuclei)
- Many approximations already: non-relativistic, time-independent, Born-Oppenheimer.
- Eigenvalue/eigenfunction problem: wave functions are eigenfunctions and energies are the eigenvalues

# It is not possible to solve exactly the Schrodinger equation except in the simplest systems.




$$\hat{H} = -\frac{1}{2}\nabla^2 - \sum\frac{Z_n}{r_{e-n}} + \sum\frac{1}{r_{e-e}}$$

**Non-interacting part**

**Contains an Electron-Electron Distance!**

- Electron-electron term makes the solution non-separable

  $$\Psi(\vec{r}_1,\ldots,\vec{r}_n) = \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2)\ldots\Psi_n(\vec{r}_n)$$

  (Hartree, Hartree-Fock)

- For an n electron system, wave function is a function of 3n variables

- Quickly becomes unmanageable, e.g. storing a wave function on a 2x2x2 real space grid requires storing
  - 1 electron : 8 values
  - 10 electrons : $10^9$ values
  - 100 electrons : $10^{90}$ values
  - 1000 electrons : $10^{900}$ values

# First Principles - Approaches to Solving

**This problem is generally not solvable analytically. Typical approaches to approximating the solution are:**

- Perturbation Theory
- Variational Method
- WKB Approximation
- Hartree-Fock & post Hartree-Fock Methods
- Density Functional Theory
- Quantum Monte Carlo
- Some methods are combinations of these approaches: GW, DMFT

first prin·ci·ples

/fərst ˈprinsəpəlz/

*noun*

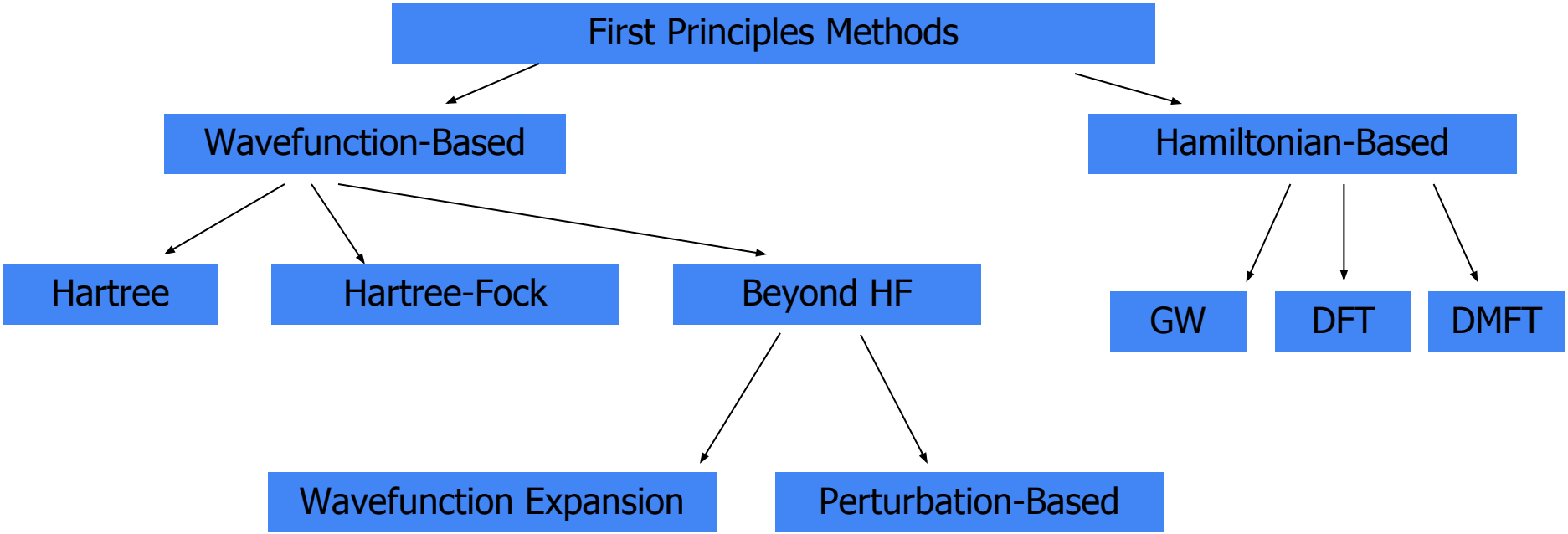
the fundamental concepts or assumptions on which a theory, system, or method is based.
"I think we have to start again and go right back to first principles"

https://en.wikipedia.org › wiki › First_principle

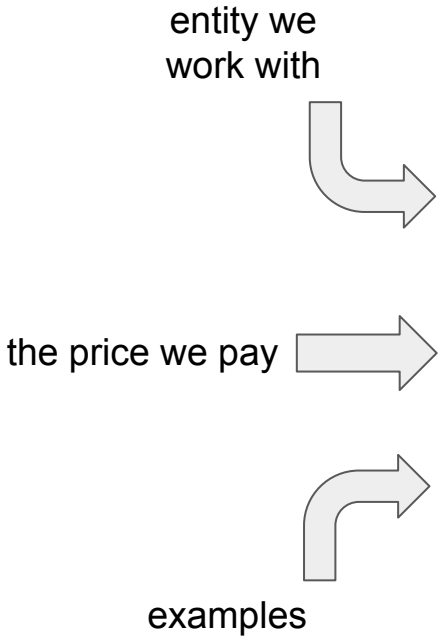
First principle - Wikipedia

In philosophy and science, a first principle is **a basic proposition or assumption that cannot be deduced from any other proposition or assumption**.

# Approaches to solving



# approaches to solving




| **Many Body Wave Function** | **Charge Density** | **Single Particle Green Function** |
|---|---|---|
| Dimensionality | Approximate exchange/correlation functional | Approximate the Green function |
| QMC, CI, CCSD | DFT | GW, DMFT |

# Methodology: DFT & QMC

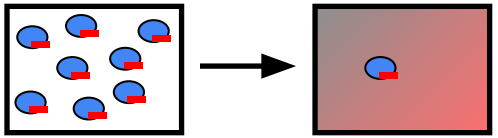
## Density Functional Theory

Energy ⟷ Electron density

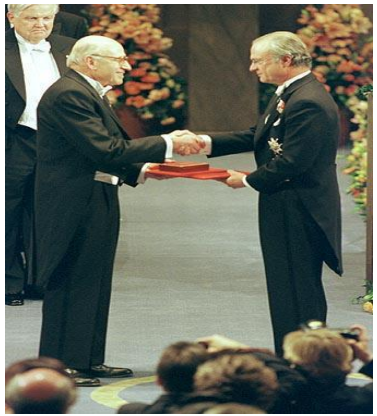
$$E_0 = E[n_0]$$

Hohenberg & Kohn, 1964

Interacting → Non-interacting



Kohn & Sham, 1965

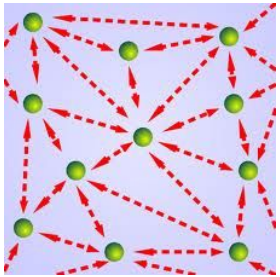


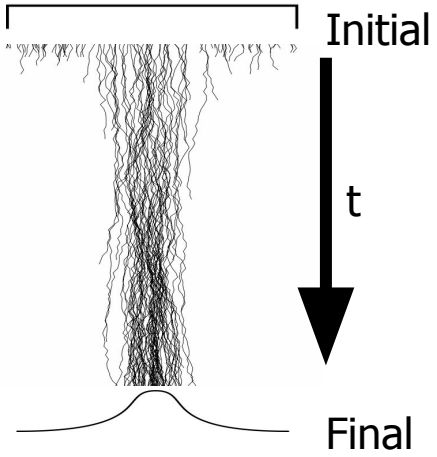
Walter Kohn (left), receiving the Nobel prize in chemistry in 1998.

## Quantum Monte Carlo

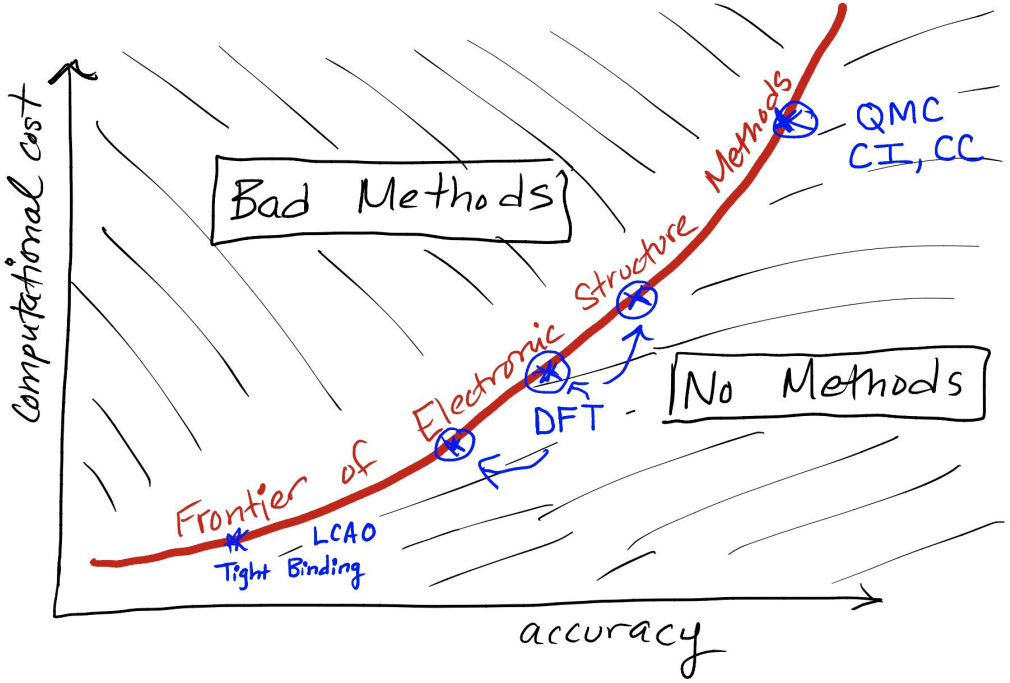
Stochastic Approach to Solving the Interacting, Many Body Problem

$$H\psi(r_1, r_2, r_3 r_4 \ldots) = E\psi(r_1, r_2, r_3 r_4 \ldots)$$





# Tradeoffs: Today DFT represents the best available compromise between accuracy and computational efficiency.




Really why we use DFT:

it's surprisingly good and pretty fast

# The first ‘first-principles’ calculation

MAY 15, 1933 PHYSICAL REVIEW VOLUME 43

## On the Constitution of Metallic Sodium

E. WIGNER AND F. SEITZ, *Department of Physics, Princeton University*

(Received March 18, 1933)

Previous developments in the theory of metals may be divided clearly into two parts: that based principally upon the hypothesis of free electrons and dealing with conductivity properties, and that based upon calculations of valence forces and dealing with the chemical properties. In the present article an intermediate point of view is adopted and the free-electron picture is employed in an investigation of chemical properties of metallic sodium. The assumption is made that in the metal the $K$ and $L$ shells of an atom are not altered from their form in the free atom. The properties of the wave functions of the electrons are discussed qualitatively, first of all, and it is concluded that the binding energy will be positive even when the Pauli principle is taken account of. This is followed by a quantitative investigation of the energy to be associated with the lowest state. First of all it is shown to what extent the present picture takes account of the interactions of electrons with both parallel and antiparallel spins, and to what extent remaining effects may be neglected. Next a Schroedinger equation is solved in order to determine the lowest energy level for various values of the lattice constant. To this a correction is made to account for the Pauli principle and from the result the lattice constant, binding energy and compressibility are calculated with favorable results.

# DFT Deep Dive

# prelude: Hartree and Hartree-Fock

Hartree and Hartree-Fock begin with a guess at a complex wavefunction, based on a product of single-particle “orbitals”:

$$\Psi(\vec{r}_1,\ldots,\vec{r}_n) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\ldots\phi_n(\vec{r}_n) \qquad \text{Hartree ansatz}$$

$$\Psi(\vec{r}_1,\vec{r}_2) = \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_1(\vec{r}_2) \\ \phi_2(\vec{r}_1) & \phi_2(\vec{r}_2) \end{vmatrix} = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) \qquad \text{Hartree-Fock ansatz}$$

If the Hamiltonian is the usual kinetic and potential terms,

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i} + \sum_i V_{ion}(\mathbf{r}_i) + \frac{e^2}{2}\sum_{ij(j\neq i)}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Then by applying the variational argument, one can obtain the single-particle Hartree-Fock equations:

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i} + V_{ion}(\mathbf{r}_i) + e^2\sum_{j\neq i}\left\langle\varphi_j\left|\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right|\varphi_j\right\rangle\right]\varphi_i(\mathbf{r}_i) - e^2\sum_{j\neq i}\left\langle\varphi_j\left|\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right|\varphi_i\right\rangle\varphi_j(\mathbf{r}_i) = \varepsilon_i\varphi_i(\mathbf{r}_i)$$

# Hartree and Hartree-Fock - Self Consistent Field

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i} + V_{ion}(\mathbf{r}_i) + e^2\sum_{j\neq i}\left\langle\varphi_j\left|\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right|\varphi_j\right\rangle\right]\varphi_i(\mathbf{r}_i) - e^2\sum_{j\neq i}\left\langle\varphi_j\left|\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right|\varphi_i\right\rangle\varphi_j(\mathbf{r}_i) = \varepsilon_i\varphi_i(\mathbf{r}_i)$$

The single-particle picture (or “mean-field” picture) comes from the fact that the Hartree product is a product of single-particle states.

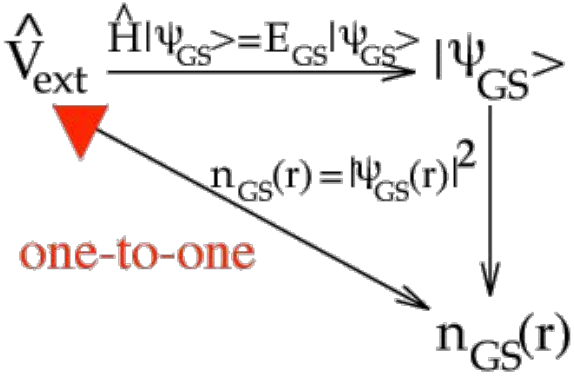
Each orbital can be determined by solving these single-particle Schrödinger equations, if all the other orbitals are known.

However, this is not the case, and instead what we do is simply to guess at some set of initial orbitals.

Then, the Hamiltonian can be “constructed” from these orbitals, and the single-particle equations can be solved for a “new” set of orbitals.

This process is repeated until the new and old orbitals don’t change (by much). This process is known as Self Consistency, or the Self Consistent Field approach.

# DFT works by mapping the interacting Schrodinger equation onto an effective non-interacting equation.




$$E[\rho(\mathbf{r})] = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho(\mathbf{r})]$$

**UNIVERSAL**
but unknown

Hohenberg and Kohn, 1964

- Founded on the two Hohenberg-Kohn theorems
- Hohenberg-Kohn I: one to one mapping between the external potential of the nuclei, ground state wave function, and ground state charge density
- Hohenberg-Kohn II: there exists a universal functional of the density F[ρ(r)] such that the ground state energy E is minimized at the true ground state density
- Typically formulated as an Euler-Lagrange system of equations

# The Kohn-Sham approach is most widely used in practice.

Comparison to Hartree-Fock:

$$E = \int \Psi^* (V_{ext} + T + V_{\text{int}}) \Psi d^{3n} r$$

$$E[\rho(\mathbf{r})] = \int V_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + F[\rho(\mathbf{r})]$$

**UNIVERSAL**

By inspection:

$$F[\rho(\mathbf{r})] = E_{KE}[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})]$$

- Formulates a expression for the unknown universal functional
- The assumed form defines the exchange-correlation functional (which itself is still unknown)

# The Kohn-Sham approach is most widely used in practice.

Kohn and Sham said:

$$F[\rho(\mathbf{r})] = E_{KE}[\rho(\mathbf{r})] + E_{H}[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})]$$

where we have a separation of kinetic, Coulomb, and exchange/correlation terms.

Importantly, the kinetic part is defined as the kinetic energy of the system of non-interacting electrons at the same density.

The Coulomb term is simply the Hartree electrostatic energy - namely, a classical interaction between two charges summed over all possible pairwise interactions.

The equation above, in a sense, acts to define the last term, the exchange-correlation part, as simply everything else that should be there to make this approximation to *F* exact.

# The Kohn-Sham approach is most widely used in practice.

The next step to solving for the energy is to introduce a set of one-electron orthonormal orbitals.

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

Now the variational condition can be applied, and one obtains the one-electron Kohn-Sham equations.

$$\left\{ -\frac{\nabla_1^A}{2} - \left( \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} dr_2 + V_{XC}\left[\rho(\mathbf{r}_1)\right] \right\} \varphi_i(\mathbf{r}_1) = \varepsilon_i \varphi_i(\mathbf{r}_1)$$

- set of coupled, non-linear equations that can be solved for the orbitals
- two common approaches: self-consistency loop and direct diagonalization

where $V_{XC}$ is the exchange correlation functional, related to the xc energy as:

$$V_{XC}[\mathbf{r}] = \left( \frac{\delta E_{XC}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \right)$$

# The Kohn-Sham approach is most widely used in practice.

To solve the Kohn-Sham equations, a number of different methods exist.

These tend to differ first and foremost in the choice of basis set for expanding the Kohn-Sham orbitals.

For molecular systems a typical choice is some type of atom-centered basis such as sums of Gaussians.

In extended (e.g., solid, liquid) systems, plane waves are more suitable.

One important difference between DFT and Hartree-Fock, in general, is that the Kohn-Sham orbitals used in DFT are a set of non-interacting orbitals designed to give the correct density and have no physical meaning beyond that.

This is in contrast to the orbitals in Hartree-Fock theory, which directly represent electrons and are designed to give the correct wavefunction as opposed to just the density.

# DFT - the Kohn-Sham Equations

real Schrodinger Equation:

$$H\psi(r_1,\ldots,r_n) = E\psi(r_1,\ldots,r_n)$$

- electron-electron interactions explicitly present
- need to solve an interacting differential equation for a multi-dimensional function
- at least its a linear equation

instead, in Kohn-Sham DFT:

$$\hat{H}_{ks}\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$$

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

$$\left\{-\frac{\nabla_1^A}{2} - \left(\sum_{A=1}^{M}\frac{Z_A}{r_{1A}}\right) + \int\frac{\rho(\mathbf{r}_2)}{r_{12}} + V_{XC}[\mathbf{r}_1]\right\}\varphi_i(\mathbf{r}_1) = \varepsilon_i\varphi_i(\mathbf{r}_1)$$

electron kinetic energy

electron-ion Coulomb interaction

Hartree term. The electron-electron interaction expressed as the Coulomb interaction of a charge density interacting with itself

exchange and correlation. our best guess at fixing everything that is wrong with the prior terms.

# Since the exact form of the exchange correlation functional not known, it needs to be approximated.

The local density approximation (LDA) assumes that at each point in real space, the exchange -correlation energy at that point is equal to the exchange-correlation energy of a homogeneous electron gas of equivalent density.

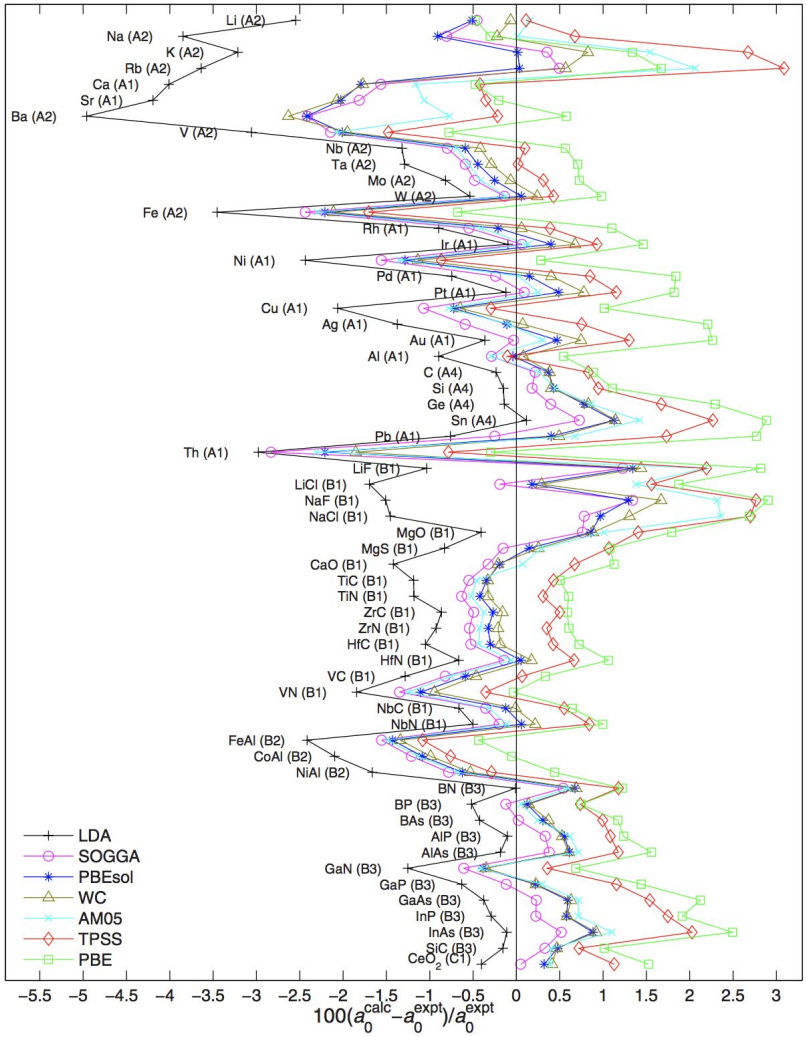
The generalized gradient approximations (GGAs) describes the exchange-correlation energy at a point in terms of the total density at that point and its gradient.

Meta-GGAs use even higher order derivatives of the density at a point. e.g. SCAN

Hybrid functionals - incorporation of exact exchange, to eliminate some of the self-interaction in LDA, GGA.

van der Waals functionals - for weak interactions, layered materials, 2D material heterostructures.

~*~*~*




**DFT is typically very useful for the prediction of ground state properties such as lattice constants, elastic moduli, and equation of state.**

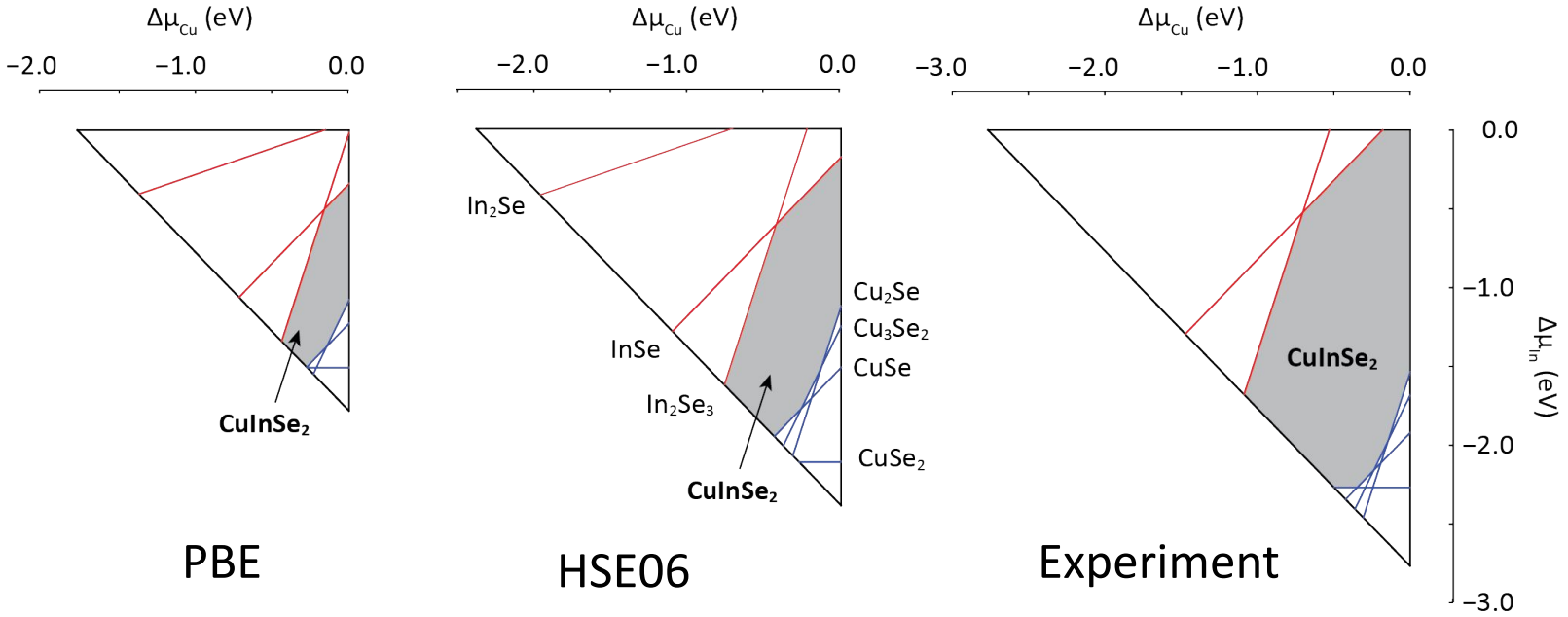
Haas, Tran, and Blaha.
Phys. Rev. B 79, 085104
2009

~*~*~*~

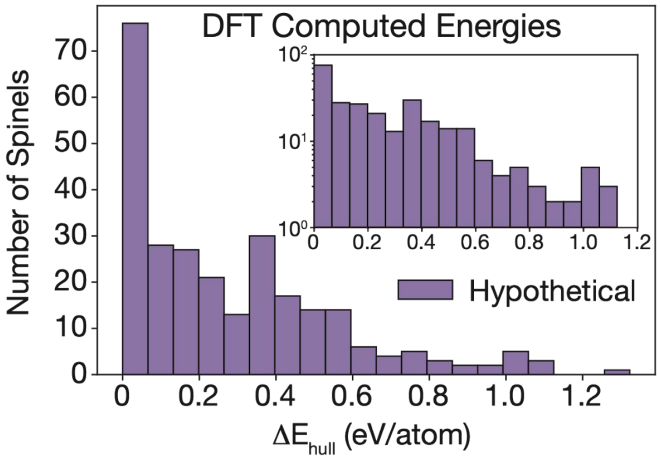
Can you find any systematic trends?

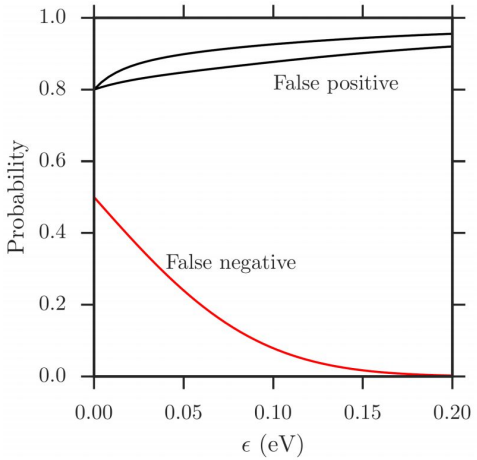
# phase stability example

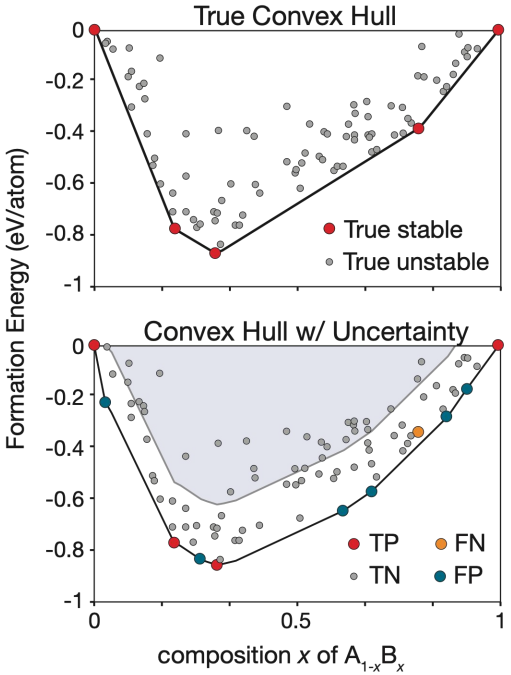
*Case study of chalcopyrite material $CuInSe_2$*



# why it is hard to predict stability with DFT: … a bayesian explanation



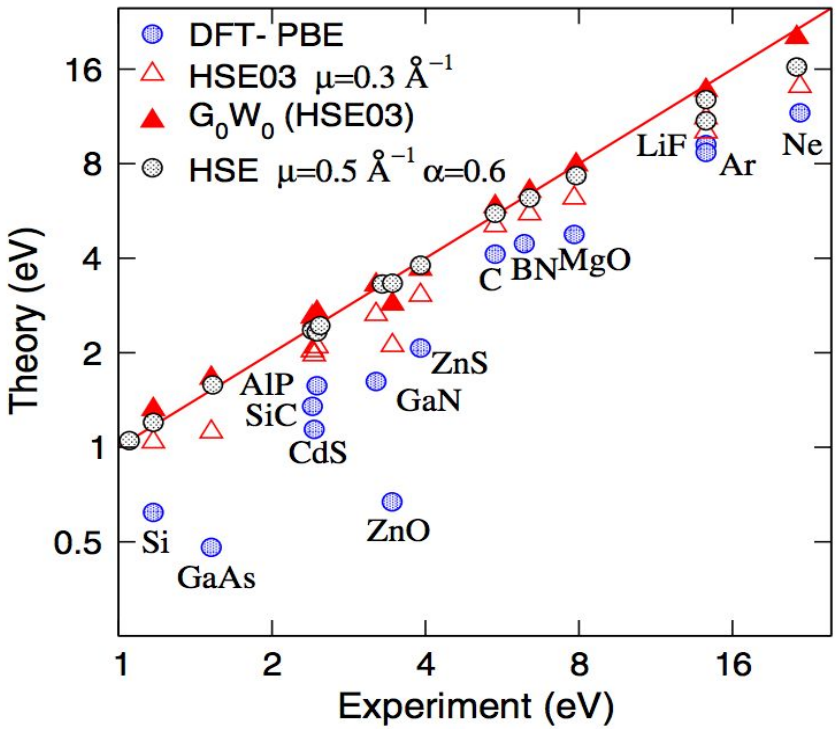



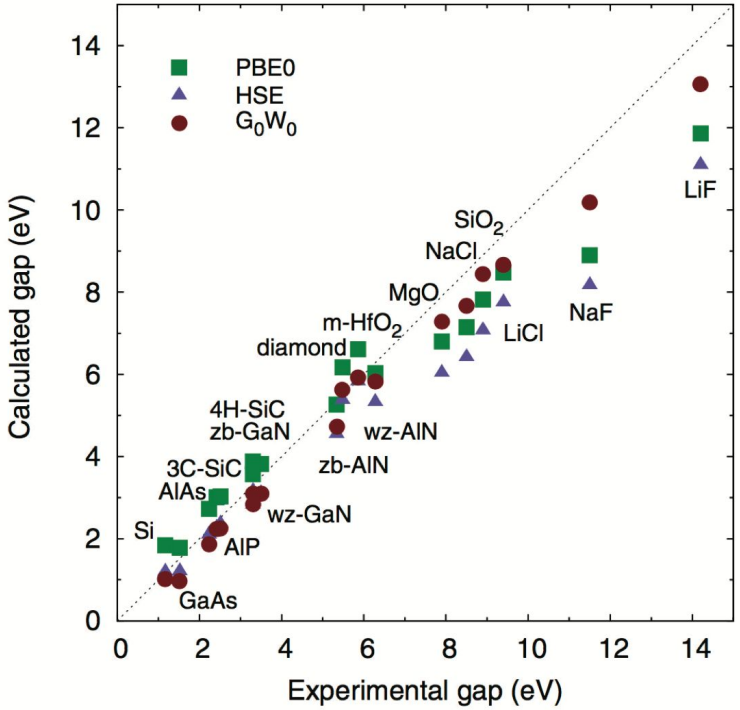




$$p\left(S\middle|\Delta H<\varepsilon\right)=\frac{p\left(\Delta H<\varepsilon\middle|S\right)p\left(S\right)}{p\left(\Delta H<\varepsilon\right)}$$

inherent uncertainties in DFT energies results in a large false positive rate
(and a non-negligible false negative rate)

# Band Gaps




Chen W, Pasquarello A. Phys. Rev. B. 2012; 86:035134

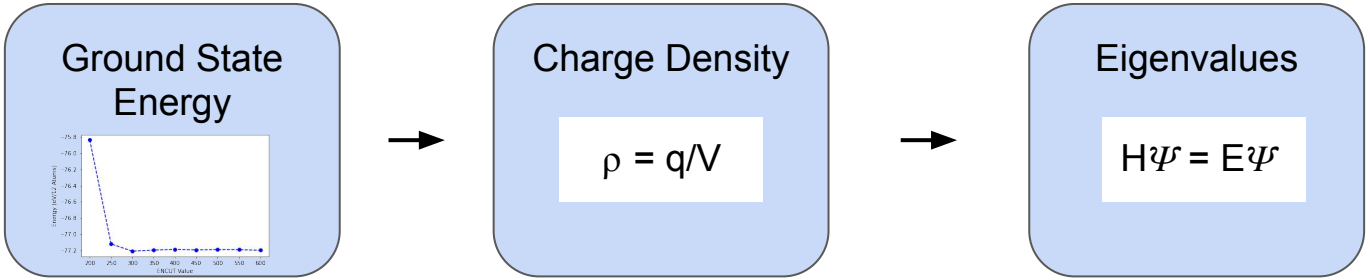
# TinyDFT Demo

- The following mini tutorial uses https://github.com/theochem/tinydft but with a modified main script, program_mendelejev.py
- Necessary programs/packages: Python 3, numpy >=1.4.0, scipy >=1.0.0, matplotlib >= 2.2.4, autograd >=1.2
- Changes to the main script include:
    - Selecting elements: Na, Ti, Si (by atomic number)
    - Reducing the density plots
    - Create tinyEIGENVAL files with each orbital's energy eigenvalue
  - To start from the modifications, use the files in: https://github.com/angelapak/HDR_tinyDFT_demo

- To run:
    - CD to your tinyDFT directory
    - "Python program_mendelejev.py
    - Primary outputs of interest are "rho_…" and "tinyEIGENVAL_…"

# TinyDFT Demo

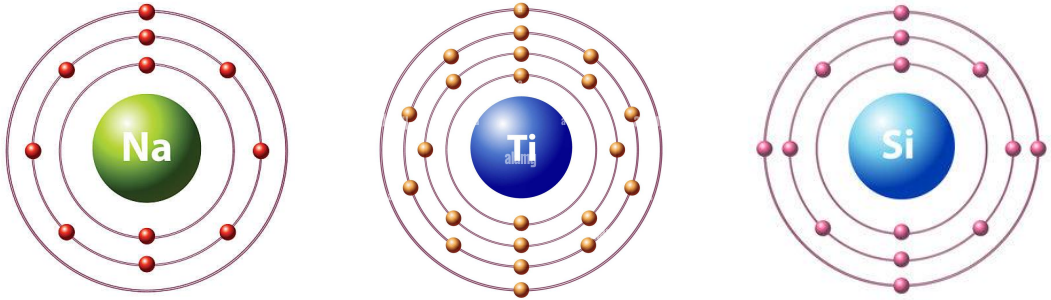
- What aspects of DFT does this demo conserve?
  - Self-consistent field (SCF) method




- What simplified aspects should we be mindful of in this demo?
  - Single atom calculations
  - Simplified exchange correlation functions

# TinyDFT Demo

- Change into your tinyDFT (or HDR_tinyDFT_demo) directory



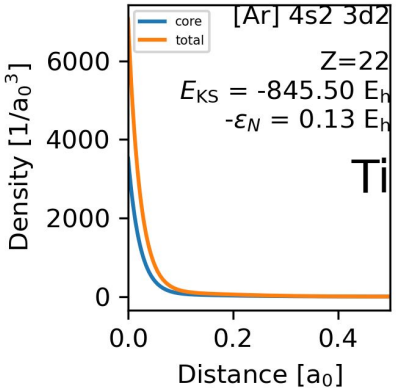

- Entering atomic numbers 11,14, 22
- Output:
  - Charge density figures “rho_….png”
  - Eigenvalue files “tinyEIGENVAL…”

“python program_mendelejev.py”

# TinyDFT Demo

| It | Total |
|---|---|
| 0 | -751.604737 |
| 1 | -828.044626 |
| 2 | -843.550666 |
| 3 | -845.321129 |
| 4 | -845.464509 |
| 5 | -845.491360 |
| 6 | -845.496816 |
| 7 | -845.497748 |
| 8 | -845.497897 |
| 9 | -845.497921 |
| 10 | -845.497925 |
| 11 | -845.497926 |
| 12 | -845.497926 |
| 13 | -845.497926 |
| 14 | -845.497926 |
| 15 | -845.497926 |
| 16 | -845.497926 |
| 17 | -845.497926 |
| 18 | -845.497926 |
| 19 | -845.497926 |
| 20 | -845.497926 |
| 21 | -845.497926 |
| 22 | -845.497926 |
| 23 | -845.497926 |
| 24 | -845.497926 |

energy convergence




density component R(r)

s : [-1.77194465e+02 -1.93984067e+01 -2.21070030e+00 -1.35167170e-01]
p :[-16.22419885 -1.376303 ]
d : [-0.12742141]

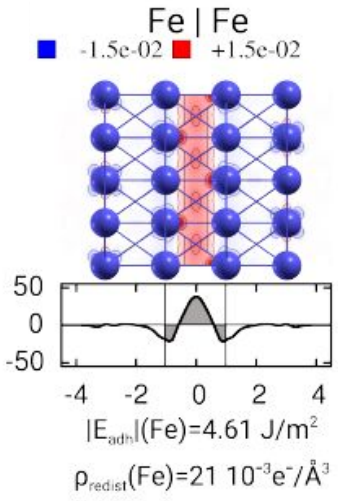
$$\hat{H}_{ks}\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$$

eigenvalues

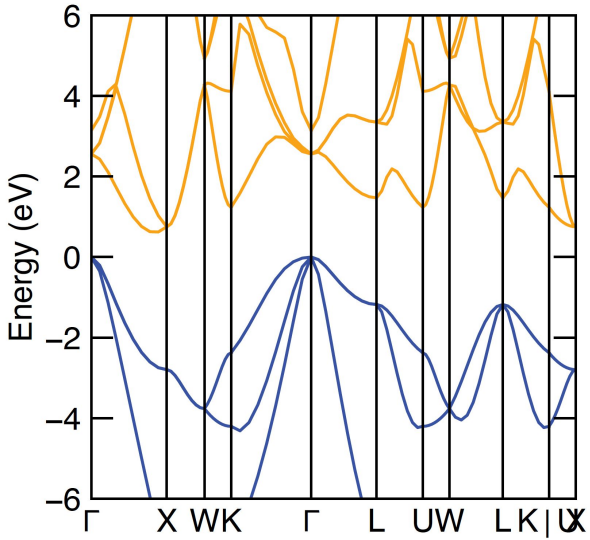
# Extension to Solids - Crystalline Silicon

```
  free energy    TOTEN  =        57.56716033 eV
  free energy    TOTEN  =       -40.17787643 eV
  free energy    TOTEN  =       -43.28833798 eV
  free energy    TOTEN  =       -43.32076464 eV
  free energy    TOTEN  =       -43.32142901 eV
  free energy    TOTEN  =       -43.56745630 eV
  free energy    TOTEN  =       -43.39302712 eV
  free energy    TOTEN  =       -43.38067845 eV
  free energy    TOTEN  =       -43.38988976 eV
  free energy    TOTEN  =       -43.39115720 eV
  free energy    TOTEN  =       -43.39176668 eV
  free energy    TOTEN  =       -43.39189169 eV
  free  energy   TOTEN  =       -43.39189169 eV
```

energy convergence

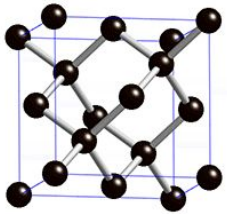



charge density




eigenvalues

# Extension to Solids - Crystalline Silicon

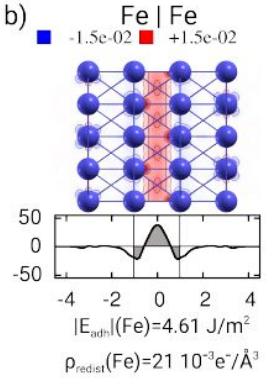


```
Si8
1.0
5.468728 0.000000 0.000000
0.000000 5.468728 0.000000
0.000000 0.000000 5.468728
Si
8
direct
0.250000 0.750000 0.250000 Si
0.000000 0.000000 0.500000 Si
0.250000 0.250000 0.750000 Si
0.000000 0.500000 0.000000 Si
0.750000 0.750000 0.750000 Si
0.500000 0.000000 0.000000 Si
0.750000 0.250000 0.250000 Si
0.500000 0.500000 0.500000 Si
```

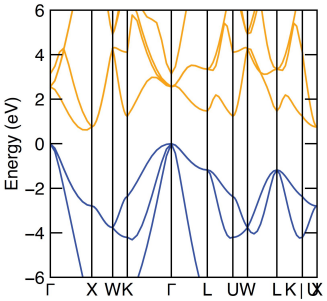
lattice

```
 free energy    TOTEN  =        57.56716033 eV
 free energy    TOTEN  =       -40.17787643 eV
 free energy    TOTEN  =       -43.28833798 eV
 free energy    TOTEN  =       -43.32076464 eV
 free energy    TOTEN  =       -43.32142901 eV
 free energy    TOTEN  =       -43.56745630 eV
 free energy    TOTEN  =       -43.39302712 eV
 free energy    TOTEN  =       -43.38067845 eV
 free energy    TOTEN  =       -43.38988976 eV
 free energy    TOTEN  =       -43.39115720 eV
 free energy    TOTEN  =       -43.39176668 eV
 free energy    TOTEN  =       -43.39189169 eV
 free  energy   TOTEN  =       -43.39189169 eV
```

energy convergence



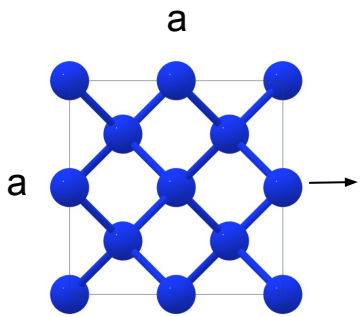

charge density




eigenvalues

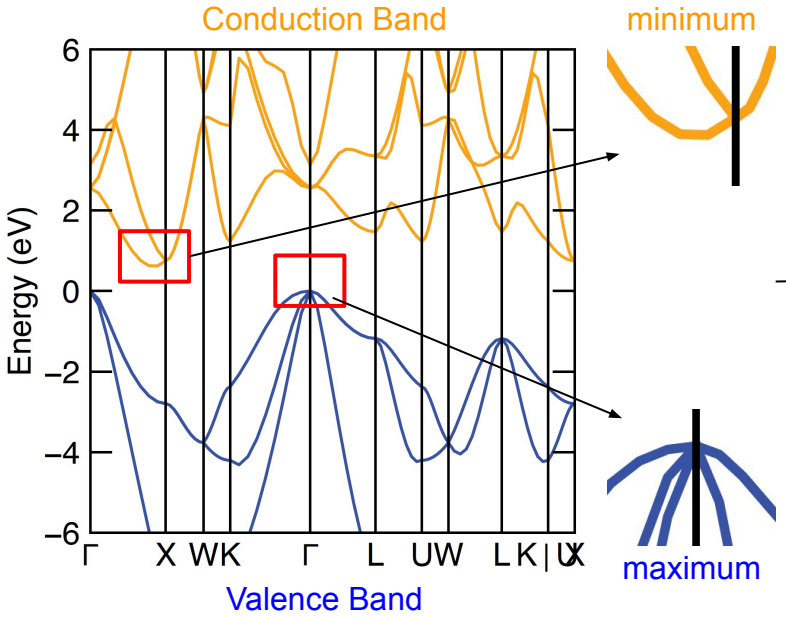
- We now have to initialize a lattice rather than an atom

# Extension to Solids - Crystalline Silicon




lattice constants

bulk modulus




conductivity

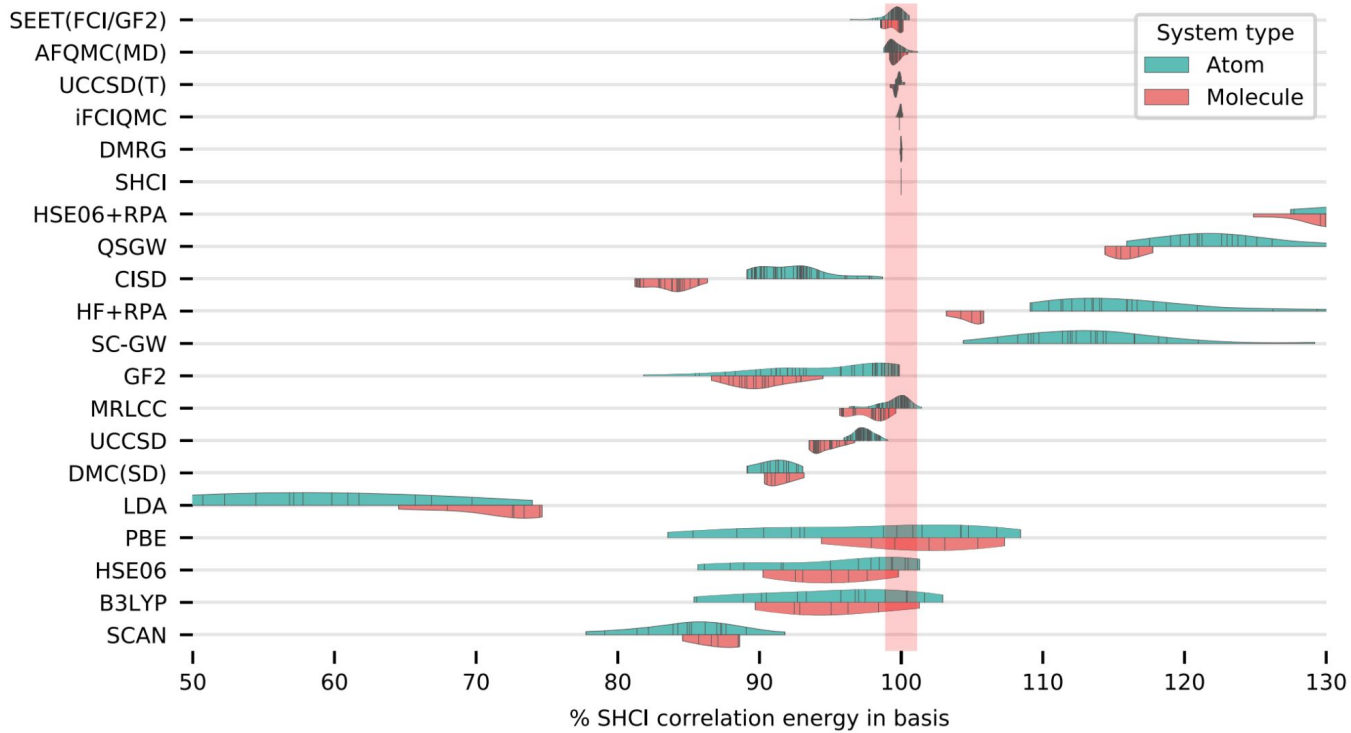
mobility

$m_{DOS}$

- Evaluation of basic DFT calculations gives us bulk and electronic properties

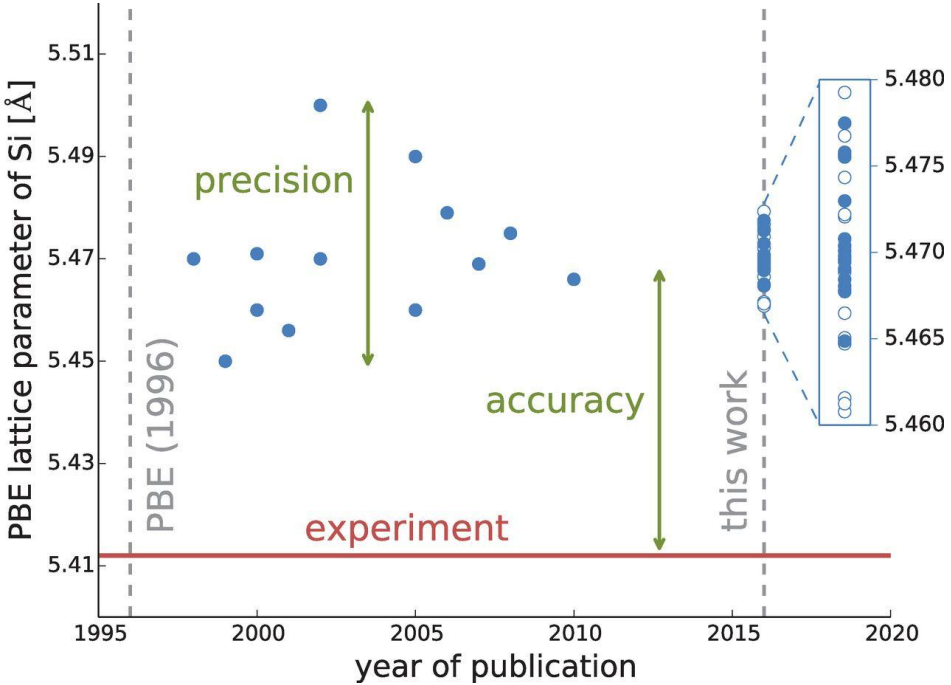
# Recent Developments in DFT

# benchmarking




Williams et al., “Direct Comparison of Many-Body Methods for Realistic Electronic Hamiltonians”, Phys Rev X 10, 011041 (2020). (Simons collaboration on Many-Electron problem)

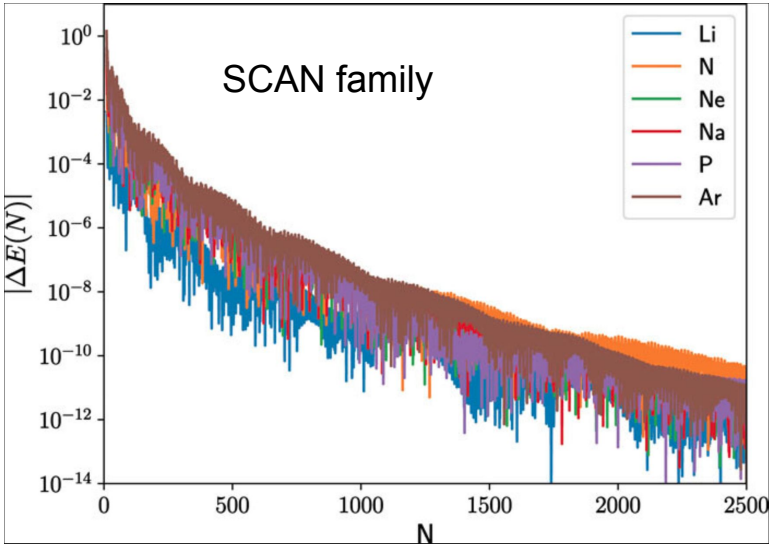
# benchmarking




"Density functional theory (DFT) is now routinely used for simulating material properties. Many software packages are available, which makes it challenging to know which are the best to use for a specific calculation. Lejaeghere *et al.* compared the calculated values for the equation of states for 71 elemental crystals from 15 different widely used DFT codes employing 40 different potentials . Although there were variations in the calculated values, most recent codes and methods converged toward a single value, with errors comparable to those of experiment."

Lejaeghere et al., "Reproducibility in density functional theory calculations of solids", Science 351 6280 (2016)

# Challenges with newer functionals

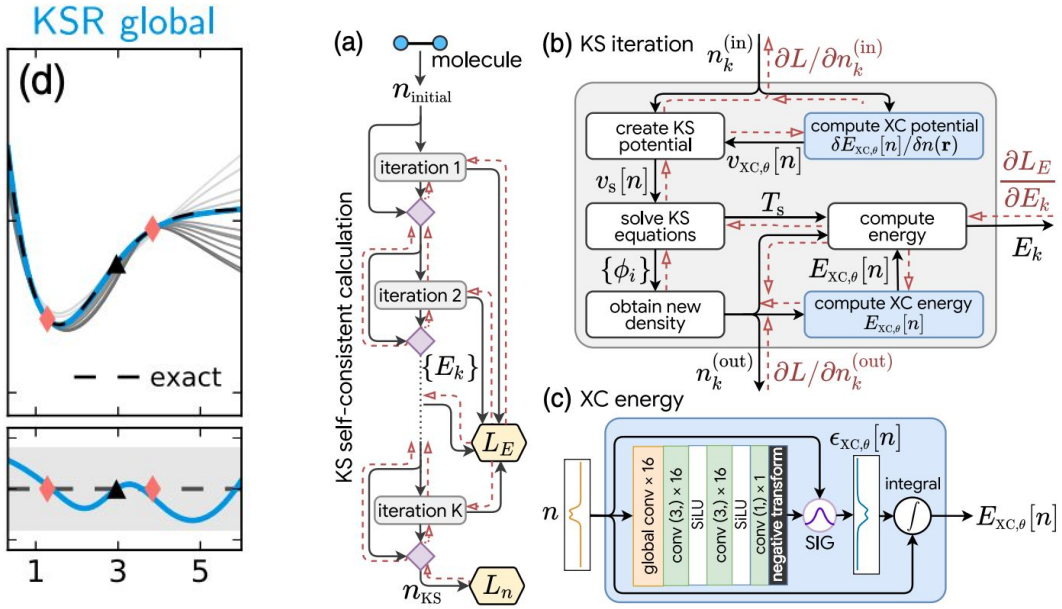



- As the form of the exchange correlation functional gets more complex, numerical evaluations become more and more tricky
- Analysis of the number of quadrature points needed to converge the total energy (for a single electronic scf step!) grows out of control

$$E_{\mathrm{xc}}[n] = \int n\epsilon_{\mathrm{xc}}\left(n_\uparrow, n_\downarrow, \gamma_{\uparrow\uparrow}, \gamma_{\uparrow\downarrow}, \gamma_{\downarrow\downarrow}, \nabla^2 n_\uparrow, \nabla^2 n_\downarrow, \tau_\uparrow, \tau_\downarrow\right) \mathrm{d}^3 r,$$

Lehtola and Marques, “Many recent density functionals are numerically ill-behaved”, J. Chem. Phys. **157**, 174114 (2022)

# Machine learned functionals




- *Approach*: Deep neural networks with differentiable programming used to construct accurate density functionals using the Kohn−Sham equations as a regularizer …
- *Generalizability as a challenge:* *"*However, such ML-designed functionals have not been implemented in standard codes because of one last great challenge: generalization. We discuss how effortlessly human-designed functionals can be applied to a wide range of situations, and how difficult that is for ML."

Kieron Burke and others:

- "Kohn−Sham equations as regularizer: building prior knowledge into machine-learned physics." Phys. Rev. Lett. 126, 036401 (2021).
- "Learning to approximate density functionals", Acc. Chem. Res. 54, 818−826 (2021).

# Good references

- R. M. Martin, “Electronic Structure: Basic Theory and Practical Methods”. (“the book”, very physics-y)
- Kieron Burke, “The ABC of DFT”
  - https://dft.uci.edu/doc/g1.pdf
- R. O. Jones, “Density functional theory: its origins, rise to prominence, and future”, Rev Mod Phys 87 (2015).
- Kieron Burke and others, “Learning to approximate density functionals”, Acc. Chem. Res. 54, 818−826 (2021).