Cornell University

"I would found an institution where any person can find instruction in any study." – Ezra Cornell, 1868

PARADIM
AN NSF MATERIALS INNOVATION PLATFORM

First-principles simulations I

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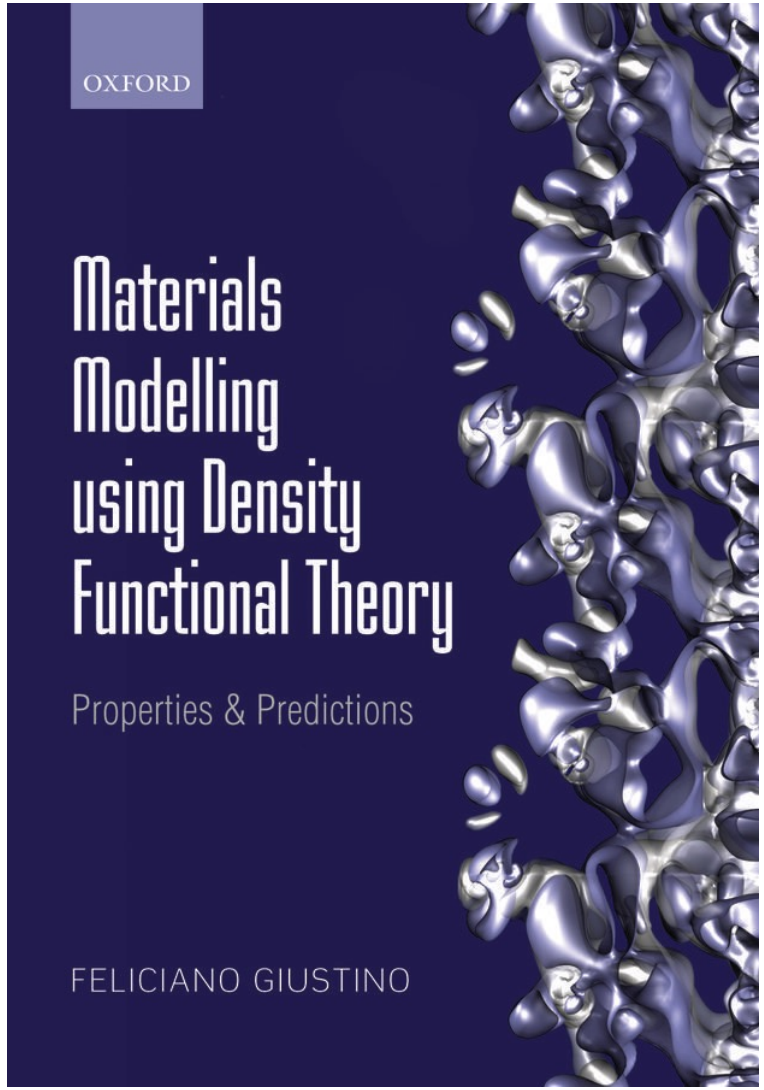
Short-term School:
Magnetic Properties from First Principles

24 November 2021

Resources for further reading



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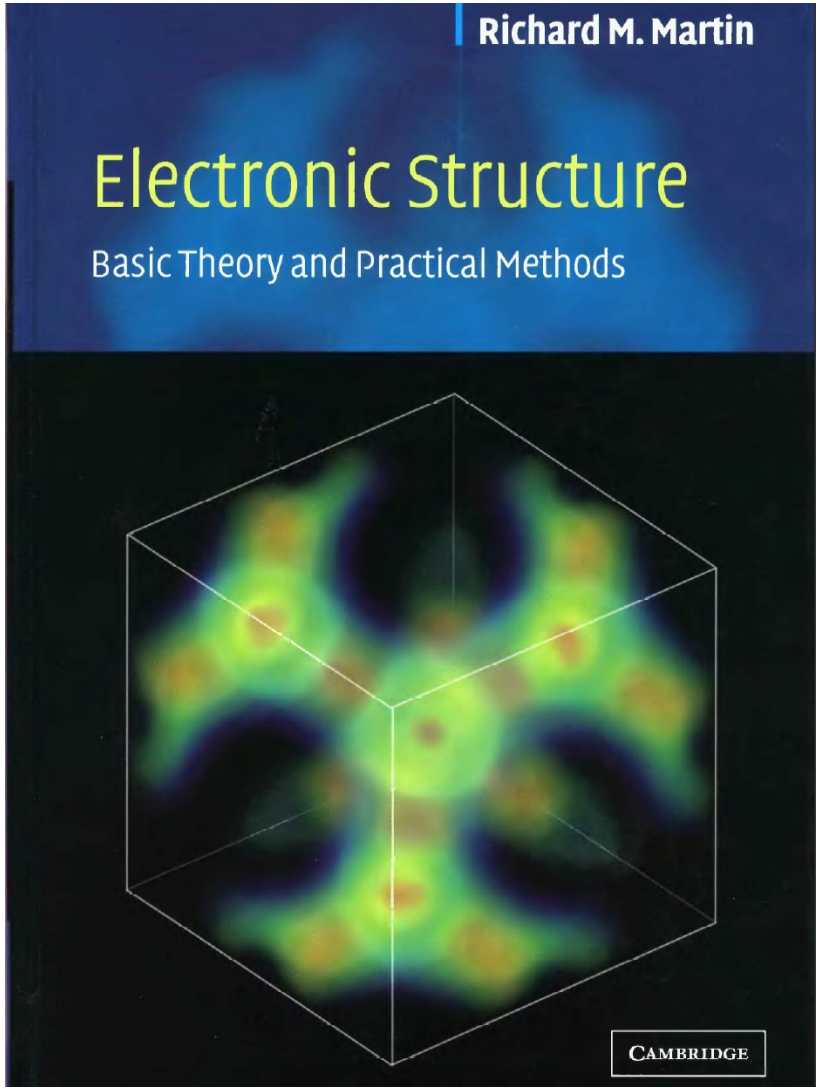
PARADIM
PLATFORM FOR THE ACCELERATED REALIZATION, ANALYSIS & DISCOVERY OF INTERFACE MATERIALS

An Introduction to Density Functional Theory for Experimentalists

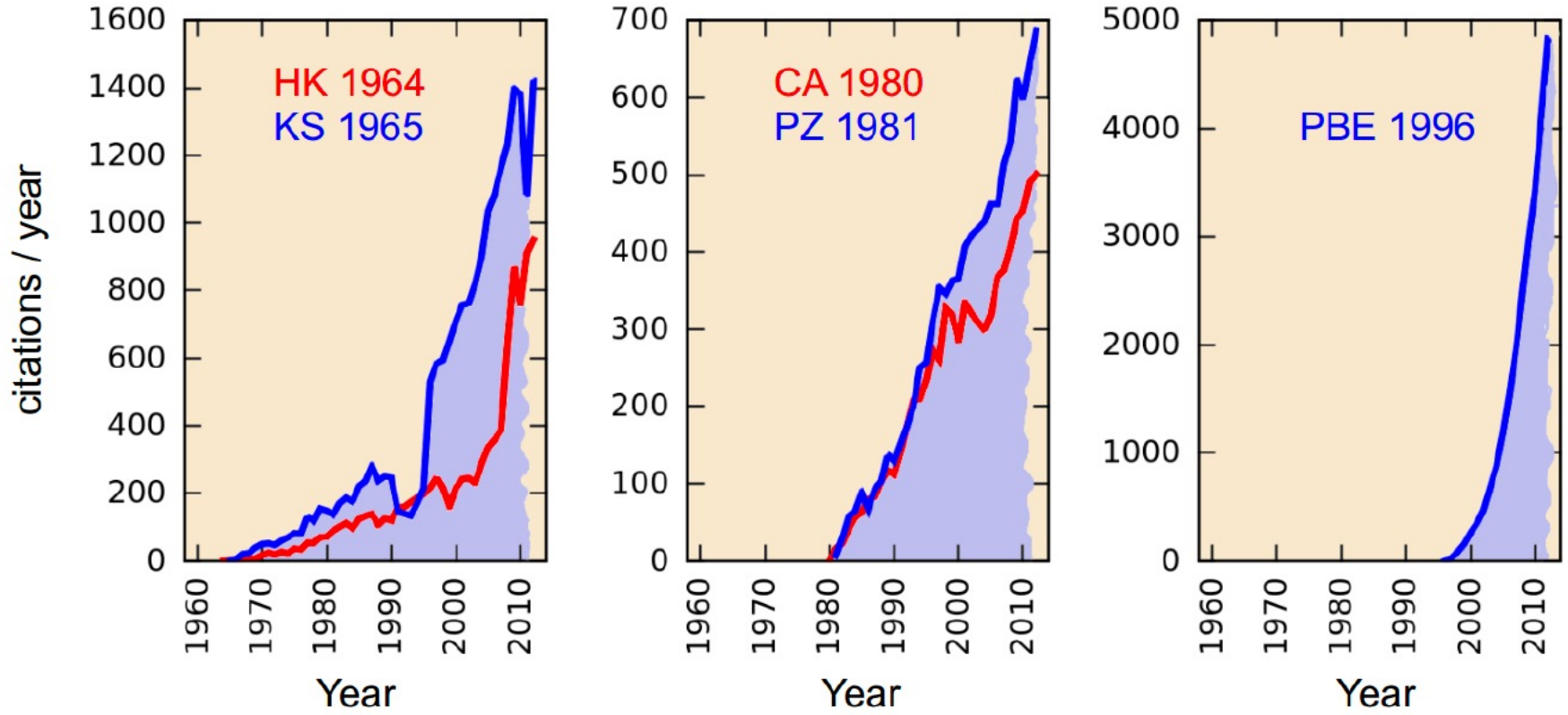
Feliciano Giustino

The University of Texas at Austin

Ithaca, 11-18 July 2021



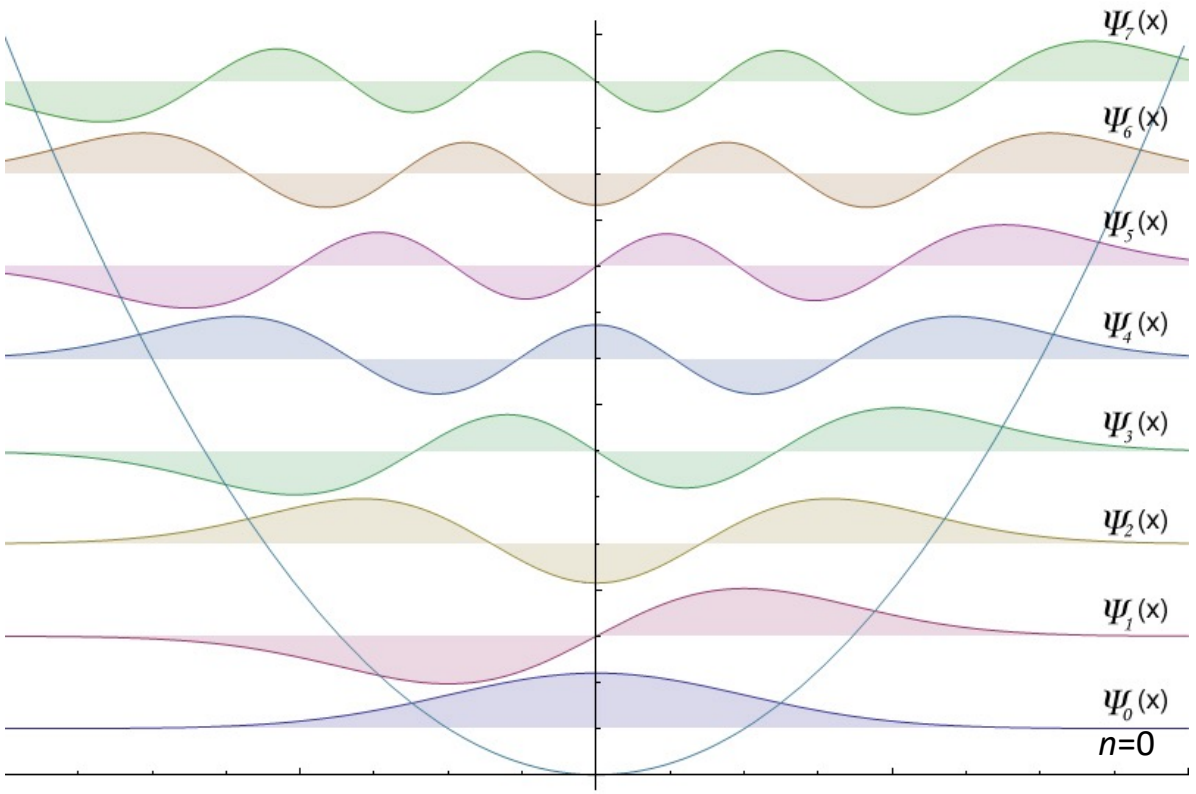
First-principles simulations are highly cited



HK 1964	Hohenberg, Kohn, Phys. Rev. 136, B864 (1964)
KS 1965	Kohn, Sham, Phys. Rev. 140, A1133 (1965)
CA 1980	Ceperley, Alder, Phys. Rev. Lett. 45, 566 (1980)
PZ 1981	Perdew, Zunger, Phys. Rev. B 23, 5048 (1981)
PBE 1996	Perdew, Burke, Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)

In quantum mechanics, the energy is quantized

Quantum Harmonic Oscillator



Electrons in a potential
with discrete energy levels

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

https://en.wikipedia.org/wiki/Quantum_harmonic_oscillator

What are the interactions?

Material = electrons + nuclei

Coulomb interaction between

electrons $E_{ee} = \frac{e^2}{4\pi\epsilon_0 d_{ee}}$ repulsive

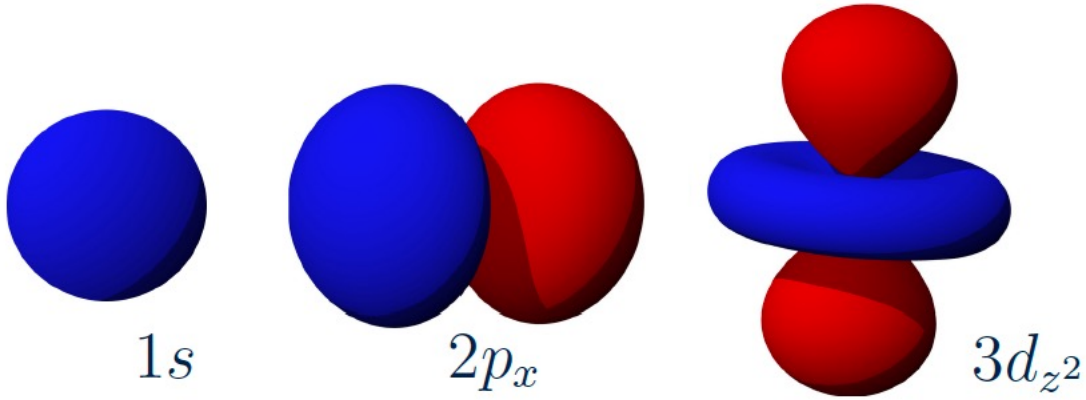
nuclei $E_{nn} = \frac{Z^2 e^2}{4\pi\epsilon_0 d_{nn}}$ repulsive

electrons and the nuclei $E_{en} = -\frac{Z e^2}{4\pi\epsilon_0 d_{en}}$ attractive

What is the simplest material?

We can solve the Schrödinger equation for the H atom

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}|}\psi(\mathbf{r}) = E_{\text{tot}}\psi(\mathbf{r})$$



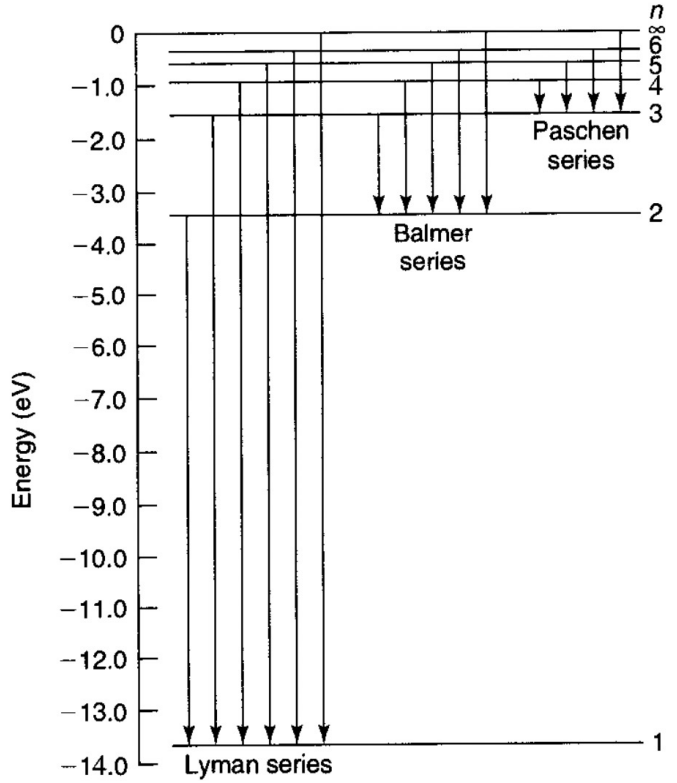


Figure 4.5: Energy levels and transitions in the spectrum of hydrogen.

What about more than 1 electron?

Time-independent Schrödinger equation

$$\left[\frac{\mathbf{p}^2}{2m_e} + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\,\psi(\mathbf{r})$$

$$\mathbf{p} = -i\hbar\nabla, \qquad \nabla = \mathbf{u}_x\frac{\partial}{\partial x} + \mathbf{u}_y\frac{\partial}{\partial y} + \mathbf{u}_z\frac{\partial}{\partial z}$$

Ground state wavefunction: ψ_0

Ground state electron charge distribution $|\psi_0(\mathbf{r})|^2$

Probability of finding an electron at $\boldsymbol{r}$

What about more than 1 electron?

Many-body wavefunction: N electrons and M nuclei $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_M)$

$$P(\mathbf{r}_1 = \mathbf{r}) = \int |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N; \mathbf{R}_1, \ldots, \mathbf{R}_M)|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N d\mathbf{R}_1 \ldots d\mathbf{R}_M$$

Charge density: Probability of finding any electron at $\boldsymbol{r}$

$$n(\mathbf{r}) = P(\mathbf{r}_1 = \mathbf{r}) + P(\mathbf{r}_2 = \mathbf{r}) + \cdots + P(\mathbf{r}_N = \mathbf{r})$$

Indistinguishability: $n(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N; \mathbf{R}_1, \ldots, \mathbf{R}_M)|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N d\mathbf{R}_1 \ldots d\mathbf{R}_M$

Normalization $\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N; \mathbf{R}_1, \ldots, \mathbf{R}_M)|^2 d\mathbf{r}_1 \ldots d\mathbf{r}_N d\mathbf{R}_1 \ldots d\mathbf{R}_M = 1$

for N electrons $\int n(\mathbf{r}) d\mathbf{r} = N.$

Many-body Schrödinger equation

Kinetic energy of N electrons $-\sum_{i=1}^{N} \frac{\hbar^2}{2m_e} \nabla_i^2$ M nuclei $-\sum_{I=1}^{M} \frac{\hbar^2}{2M_I} \nabla_I^2$

Coulomb interaction

Electron-electron $\frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$ Nuclei-nuclei $\frac{1}{2} \sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$

Electron-nuclei $-\sum_{i,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$

Many-body Schrödinger equation

Kinetic energy of N electrons $-\sum_{i=1}^{N} \frac{\hbar^2}{2m_e} \nabla_i^2$ M nuclei $-\sum_{I=1}^{M} \frac{\hbar^2}{2M_I} \nabla_I^2$

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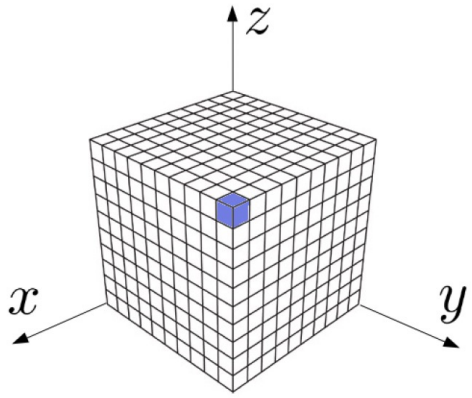
Electron-electron $\frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$ Nuclei-nuclei $\frac{1}{2} \sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$

Electron-nuclei $-\sum_{i,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$

$$\left[-\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right] \Psi = E_{\text{tot}} \Psi$$

Many-body Schrödinger equation hits the "exponential wall"

$$\left[-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J}\frac{e^2}{4\pi\epsilon_0}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} - \sum_{i,I}\frac{e^2}{4\pi\epsilon_0}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}\right]\Psi = E_{\text{tot}}\Psi$$



Unit cell of Si in diamond structure: $a^3/4$ lattice parameter: $a{=}5.43$ Å

Discretization size: $\Delta x \sim 0.1$ Å

Number of points: $N_{\text{p}} = (a^3/4)/(\Delta x)^3 \sim 40{,}000$

$N = 4$ valence electrons $M = 2$ nuclei in the unit cell → 10 particles

Many-body wavefunction: $\Psi_{\text{Si}}(\mathbf{r}_1, \ldots, \mathbf{r}_8; \mathbf{R}_1, \mathbf{R}_2)$

You need complex numbers of $N_{\text{p}}^{N+M} \sim 10^{46}$

How can we simplify this complex problem? Atomic units

$$\left[-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J}\frac{e^2}{4\pi\epsilon_0}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} - \sum_{i,I}\frac{e^2}{4\pi\epsilon_0}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}\right]\Psi = E_{\text{tot}}\Psi$$

masses in m_e length in a_0 energy in $\frac{e^2}{4\pi\epsilon_0 a_0}$

$$\left[-\sum_i \frac{\nabla_i^2}{2} - \sum_I \frac{\nabla_I^2}{2M_I} - \sum_{i,I}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}\right]\Psi = E_{\text{tot}}\Psi$$

Clamped nuclei approximation

$$\left[-\sum_i \frac{\nabla_i^2}{2} - \sum_I \frac{\nabla_I^2}{2M_I} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}\right] \Psi = E_{\text{tot}} \Psi$$

Nuclear mass $M_I = \infty$

Clamped nuclei approximation

$$\left[-\sum_i \frac{\nabla_i^2}{2} - \sum_I \frac{\nabla_I^2}{2M_I} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}\right]\Psi = E_{\text{tot}}\Psi$$

Nuclear mass $M_I = \infty$

$$V_{\text{n}}(\mathbf{r}) = -\sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

$$\Psi = \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

Clamped nuclei approximation

$$\left[-\sum_i \frac{\nabla_i^2}{2} - \cancel{\sum_I \frac{\nabla_I^2}{2M_I}} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \cancel{\frac{1}{2}\sum_{I\neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}}\right] \Psi = E_{\text{tot}} \Psi$$

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$$\Psi = \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

$$\left[-\sum_i \frac{\nabla_i^2}{2} + \sum_i V_{\text{n}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right] \Psi = E \Psi$$

Electronic structure theory

Independent electron approximation

Many electron Hamiltonian $\hat{H}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_i \hat{H}_0(\mathbf{r}_i) + \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$

Single electron $\hat{H}_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{\mathrm{n}}(\mathbf{r})$

Probability for independent electrons: $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1) \cdots \phi_N(\mathbf{r}_N)$

Single electron Schrödinger equation: $\hat{H}_0(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$

Filling the lowest energy eigenstates of the single-particle equation gives the lowest energy configuration of the system

$E = \varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_N$

Independent electron approximation

Many electron Hamiltonian $\hat{H}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_i \hat{H}_0(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$

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Single electron $\hat{H}_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{\mathrm{n}}(\mathbf{r})$

Probability for independent electrons: $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1) \cdots \phi_N(\mathbf{r}_N)$

Single electron Schrödinger equation: $\hat{H}_0(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$

Filling the lowest energy eigenstates of the single-particle equation gives the lowest energy configuration of the system

$E = \varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_N$

X Exclusion principle
X Coulomb interaction

Pauli's exclusion principle

Electron density of 2 independent electrons

$$n(\mathbf{r}) = 2\int |\Psi(\mathbf{r},\mathbf{r}_2)|^2\, d\mathbf{r}_2 = 2\int |\phi_1(\mathbf{r})|^2 |\phi_2(\mathbf{r}_2)|^2\, d\mathbf{r}_2 = 2\,|\phi_1(\mathbf{r})|^2$$

Fermions have an antisymmetric wavefunction $\Psi(\mathbf{r}_2,\mathbf{r}_1) = -\Psi(\mathbf{r}_1,\mathbf{r}_2)$

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) \end{vmatrix}$$

Slater determinant

$$n(\mathbf{r}) = 2\int |\Psi(\mathbf{r},\mathbf{r}_2)|^2\, d\mathbf{r}_2 = |\phi_1(\mathbf{r})|^2 + |\phi_2(\mathbf{r})|^2$$

For *N* electrons: $n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$

Charge density is "OR" probability of finding electrons at the same point

Mean-field approximation – Hartree Potential

Electronic charge $n(\mathbf{r})$ generates an electrostatic potential $\varphi(\mathbf{r})$

Poisson's equation: $\nabla^2\varphi(\mathbf{r}) = 4\pi\, n(\mathbf{r})$

Potential energy of the electrons is $V_{\mathrm{H}}(\mathbf{r}) = -\varphi(\mathbf{r})$

$\nabla^2 V_{\mathrm{H}}(\mathbf{r}) = -4\pi\, n(\mathbf{r})$ Hartree Potential: $V_{\mathrm{H}}(\mathbf{r}) = \int d\mathbf{r}'\, \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{n}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\,\phi_i(\mathbf{r}),$$

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2,$$

$$\nabla^2 V_{\mathrm{H}}(\mathbf{r}) = -4\pi n(\mathbf{r}).$$

Average potential experienced by each electron

Self-consistent field solution to the mean-field approximation

$$\hat{H}_0(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

$$V_{\mathrm{H}}(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{n}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r})\right] \phi_i'(\mathbf{r}) = \varepsilon_i\, \phi_i'(\mathbf{r})$$

scf approximation

Hartree Potential (1928)

Solves for independent electrons iteratively

Fock Exchange Potential

Fermions have an antisymmetric wavefunction $\Psi(\mathbf{r}_2, \mathbf{r}_1) = -\Psi(\mathbf{r}_1, \mathbf{r}_2)$

Hartree approximation by itself does not impose this constraint on the many-body wavefunction

Hartree-Fock Equations (1930):

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{n}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r})\right]\phi_i(\mathbf{r}) + \int d\mathbf{r}'\, V_{\mathrm{X}}(\mathbf{r}, \mathbf{r}')\,\phi_i(\mathbf{r}') = \varepsilon_i\,\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2,$$

$$\nabla^2 V_{\mathrm{H}}(\mathbf{r}) = -4\pi n(\mathbf{r}).$$

$$V_{\mathrm{X}}(\mathbf{r}, \mathbf{r}') = -\sum_j \frac{\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$

Fock exchange potential is non-local

Correlation Potential

Probability of finding an electron decreases due to Coulomb repulsion, if there is another electron nearby.

Constraint to the many-body wavefunction: $|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 \quad < \quad |\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)|^2$

Slater determinant as the many-body wavefunction fails to incorporate correlations

$V_c(\mathbf{r})$ Add a potential to the Hamiltonian that incorporates the correlations

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{n}} + V_{\mathrm{H}} + V_{\mathrm{X}} + V_{\mathrm{c}}\right]\phi_i = \varepsilon_i\,\phi_i$$

Kohn-Sham Equations

Simplify it to have local exchange $V_x(\mathbf{r})$ and correlation $V_c(\mathbf{r})$ potentials

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{n}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_x(\mathbf{r}) + V_c(\mathbf{r})\right] \phi_i(\mathbf{r}) = \varepsilon_i \, \phi_i(\mathbf{r})$$

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{n}} + V_{\mathrm{H}} + V_{xc}\right] \phi_i = \varepsilon_i \, \phi_i$$

V_{xc} eXchange and Correlation potential

Cornell University

"I would found an institution where any person can find instruction in any study." – Ezra Cornell, 1868

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First-principles simulations II

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Short-term School:
Magnetic Properties from First Principles

24 November 2021

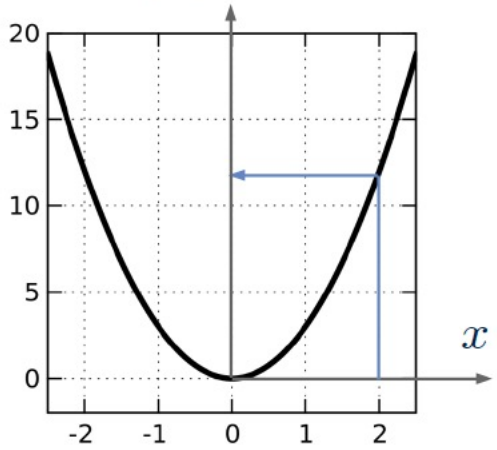
Density Functional Theory

What is a functional?

function

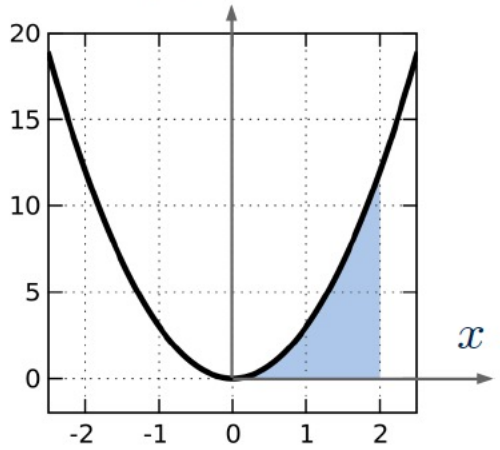
functional

$g(x) = 3x^2$



$g(2) = 12$

$g(x) = 3x^2$



$F[g] = \int_0^2 dx\, g(x) = 8$

Density Functional Theory

Ground state *energy* is the *functional* of the electron *density*

Total energy of the electronic ground state

Many body ground state energy

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \int d\mathbf{r}_1 \dots d\mathbf{r}_N \, \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \, \hat{H} \, \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = -\sum_i \frac{1}{2}\nabla_i^2 + \sum_i V_{\mathrm{n}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$E = \mathcal{F}[\Psi]$ Energy of any state is a *functional* of the wavefunction

$E = F[n]$ Ground state energy is the *functional* of the electron *density*
Density Functional Theory, Hohenberg and Kohn (1964)

Hohenberg-Kohn Theorem

$n \rightarrow V_{\mathrm{n}}$ Ground state density uniquely determines the external potential

$V_{\mathrm{n}} \rightarrow \Psi$ External potential uniquely determines the many-body wavefunction

$\Psi \rightarrow E$ Energy is a functional of the many-body wavefunction

$$n \rightarrow V_{\mathrm{n}} \rightarrow \Psi \rightarrow E$$

Ground state density uniquely determines the total energy

$$E = F[n]$$

Total energy is a functional of the ground state density

Hohenberg-Kohn Theorem

$n \rightarrow V_{\mathrm{n}}$ Ground state density uniquely determines the external potential

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = -\sum_i \frac{1}{2}\nabla_i^2 + \sum_i V_{\mathrm{n}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{T} = -\sum_i \frac{1}{2}\nabla_i^2, \quad \hat{W} = \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$E = \langle \Psi | \sum_i V_{\mathrm{n}}(\mathbf{r}_i) | \Psi \rangle + \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle$$

$$n(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N; \mathbf{R}_1, \ldots, \mathbf{R}_M)|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N d\mathbf{R}_1 \ldots d\mathbf{R}_M$$

$$E = \int d\mathbf{r}\, n(\mathbf{r}) V_{\mathrm{n}}(\mathbf{r}) + \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle$$

Hohenberg-Kohn Theorem

$$n \rightarrow V_{\mathrm{n}} \rightarrow \Psi \rightarrow E$$

Ψ is ground state many-body wavefunction for potential V_{n} with energy E and density n.

$$E = \int d\mathbf{r}\, n(\mathbf{r}) V_{\mathrm{n}}(\mathbf{r}) + \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle$$

Assume there exists another potential $V'_{\mathrm{n}} \neq V_{\mathrm{n}}$ with same density n leading to Ψ' and E'

Ψ is *not* ground state many-body wavefunction for potential $V'_{\mathrm{n}} \neq V_{\mathrm{n}}$

$$E' < \int d\mathbf{r}\, n(\mathbf{r}) V'_{\mathrm{n}}(\mathbf{r}) + \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle$$

$$E - E' > \int d\mathbf{r}\, n(\mathbf{r}) [V_{\mathrm{n}}(\mathbf{r}) - V'_{\mathrm{n}}(\mathbf{r})]$$

Repeat the same argument: Ψ' is not the ground state many-body wfcn for potential V_{n}

$$E' - E > \int d\mathbf{r}\, n(\mathbf{r}) [V'_{\mathrm{n}}(\mathbf{r}) - V_{\mathrm{n}}(\mathbf{r})]$$

$0 > 0$ Contradiction

Energy functional

$$E = F[n] = \int d\mathbf{r}\, n(\mathbf{r}) V_{\mathrm{n}}(\mathbf{r}) + \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle$$

explicitly implicitly depends on n

Kohn-Sham ansatz (1965) split it into the kinetic and Coulomb energy of *independent electrons*

$$E = F[n]$$

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$$= \overbrace{\underbrace{\int d\mathbf{r}\, n(\mathbf{r}) V_{\mathrm{n}}(\mathbf{r})}_{\text{External potential}} - \underbrace{\sum_i \int d\mathbf{r}\, \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r})}_{\text{Kinetic energy}} + \underbrace{\frac{1}{2} \iint d\mathbf{r}\, d\mathbf{r}'\, \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{\text{Hartree energy}}}^{\text{Total energy in the independent electrons approximation}} + \underbrace{E_{xc}[n]}_{\text{XC energy}}.$$

Hohenberg-Kohn variational principle

If we know $E_{xc}[n]$, we can determine ground state energy $E = F[n]$ using density n.

$$\left.\frac{\delta F[n]}{\delta n}\right|_{n_0} = 0$$

Hohenberg-Kohn variational principle (1964)
Ground state density n_0 is the function that minimizes total energy

Solve for a set of $\phi_i(\mathbf{r})$ that also needs to be $\int d\mathbf{r}\phi_i^*(\mathbf{r})\phi_j(\mathbf{r}) = \delta_{ij}$ to get the density n.

Kohn-Sham Equation

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Kohn-Sham equation (1965)

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{n}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$V_{xc}(\mathbf{r}) = \left.\frac{\delta E_{xc}[n]}{\delta n}\right|_{n(\mathbf{r})}$$

eXchange and Correlation potential

What is the eXchange and Correlation functional?

Nobel Prize Lecture by Kohn (1999):

'The Kohn–Sham theory may be regarded as the formal exactification of Hartree theory. With the exact E_{xc} and V_{xc} all many-body effects are in principle included. Clearly this directs attention to the functional $E_{xc}[n]$. The practical usefulness of ground-state DFT depends entirely on whether approximations for the functional $E_{xc}[n]$ could be found, which are at the same time sufficiently simple and sufficiently accurate.'

Local Density Approximation (LDA)

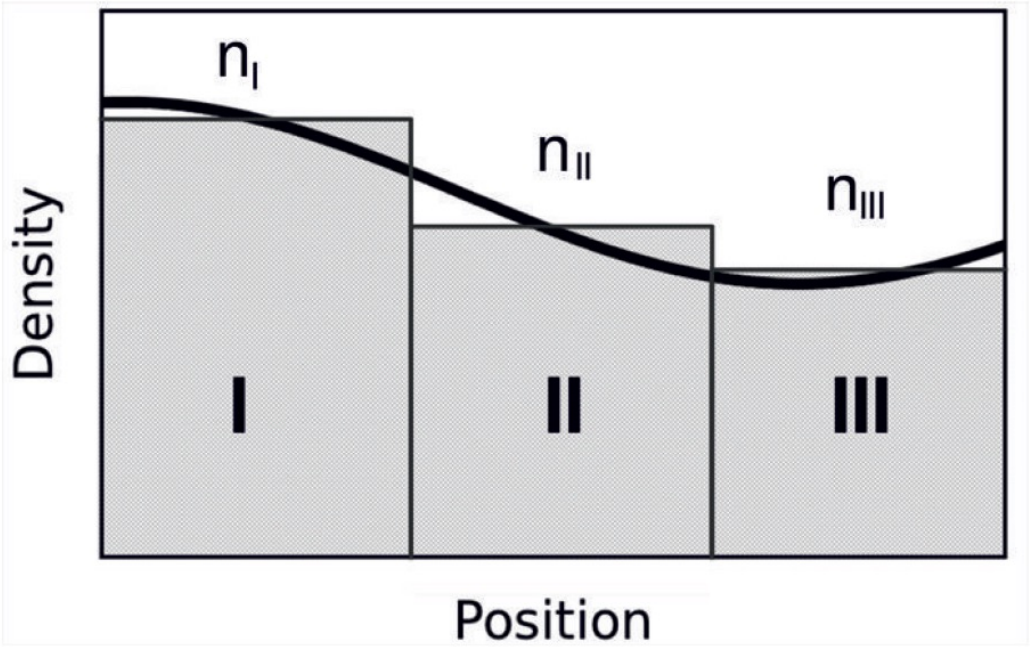
Homogenous electron gas

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp(i\mathbf{k}\cdot\mathbf{r}) \text{ and } \varepsilon_{\mathbf{k}} = \frac{|\mathbf{k}|^2}{2}$$

Ceperley, Alder (1980)
Perdew, Zunger (1981)

Exchange energy

$$E_{\mathrm{X}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} n^{\frac{4}{3}} V.$$

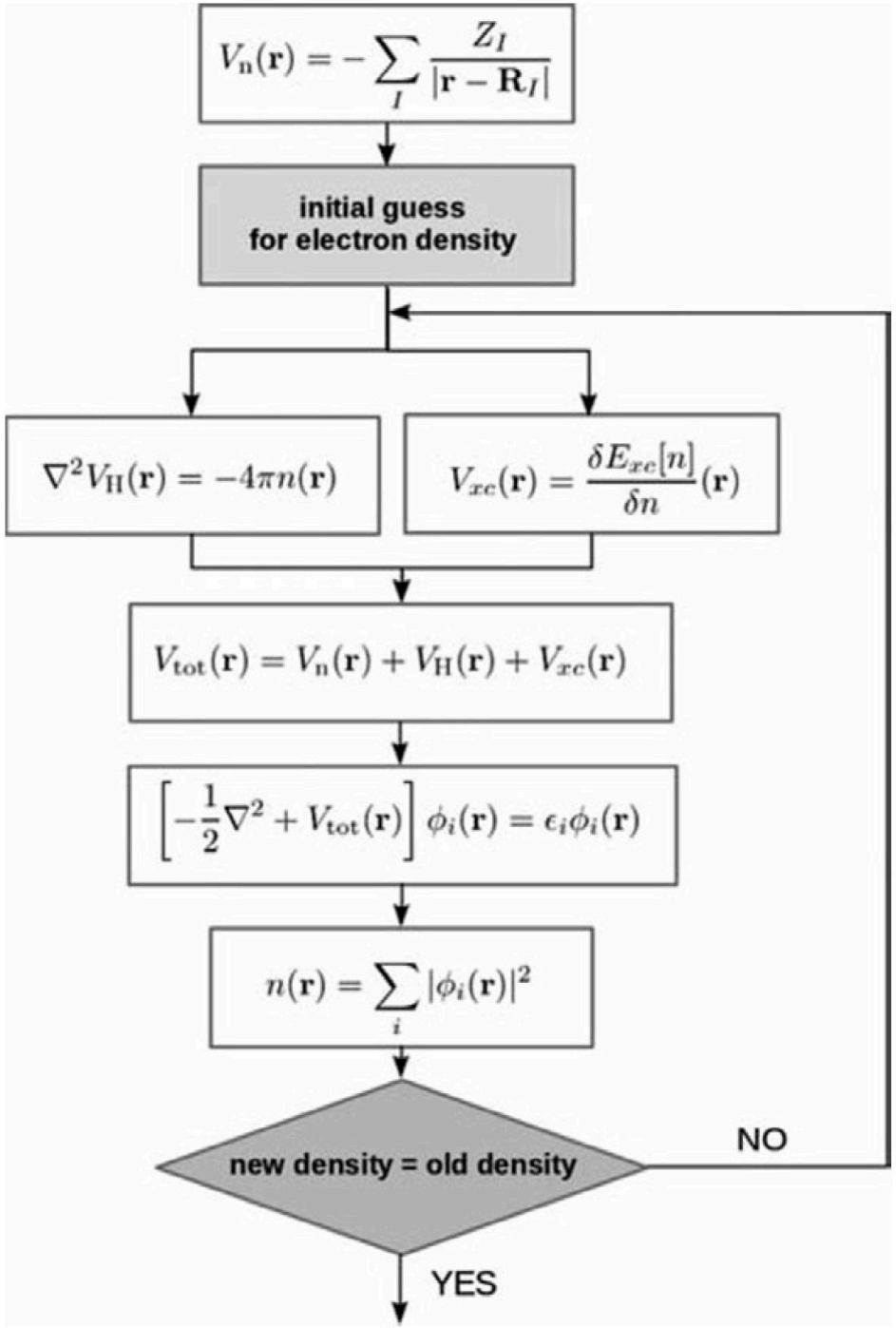


$$E_{xc}^{\mathrm{LDA}} = \int_V dE_{xc}^{\mathrm{LDA}} = \int_V \frac{E_{xc}^{\mathrm{HEG}}[n(\mathbf{r})]}{V}\, d\mathbf{r}$$

$$E_x^{\mathrm{LDA}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int_V n^{4/3}(\mathbf{r})\, d\mathbf{r}$$

$$V_x^{\mathrm{LDA}} = \frac{\delta E_x^{\mathrm{LDA}}}{\delta n} = -\left(\frac{3}{\pi}\right)^{\frac{1}{3}} n^{\frac{1}{3}}(\mathbf{r})$$

Self-consistent field (SCF) calculations

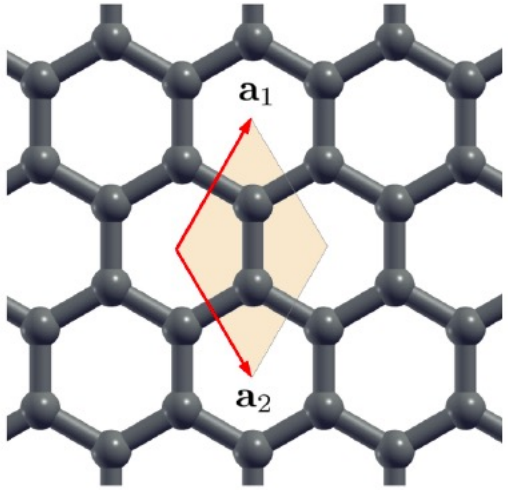


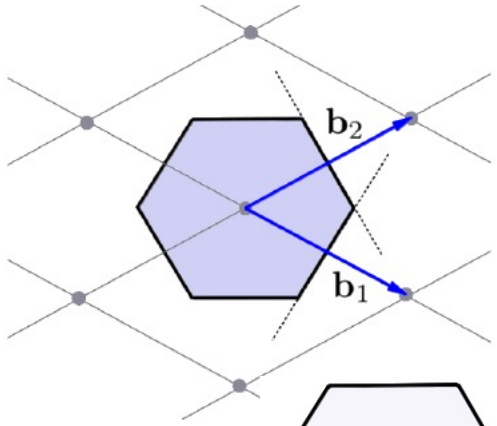
What can we calculate using DFT?

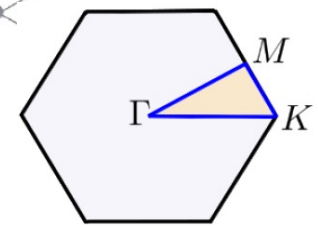
Electronic band structure

Bloch theorem $\phi_i(\mathbf{r}) \rightarrow \phi_{i\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} u_{i\mathbf{k}}(\mathbf{r})$

$$\left[-\frac{1}{2}(\nabla + i\mathbf{k})^2 + V_{\mathrm{tot}}(\mathbf{r})\right] u_{i\mathbf{k}}(\mathbf{r}) = \varepsilon_{i\mathbf{k}} u_{i\mathbf{k}}(\mathbf{r})$$



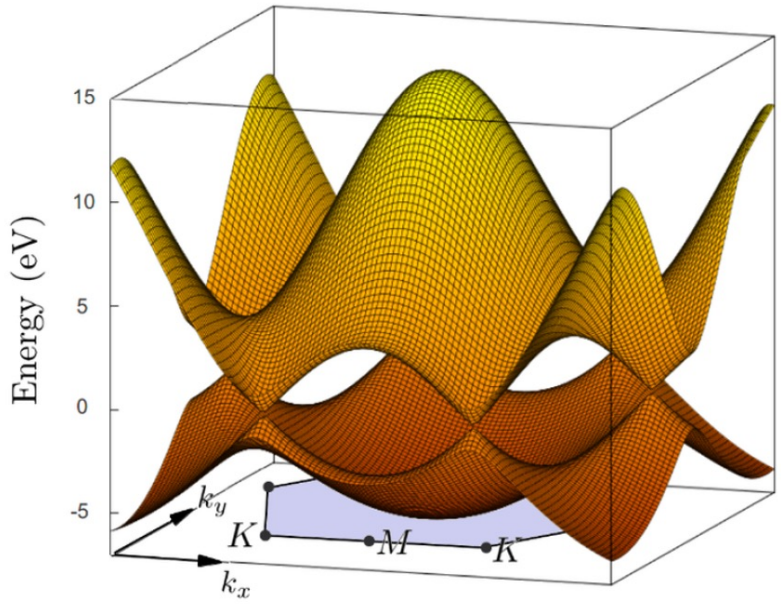


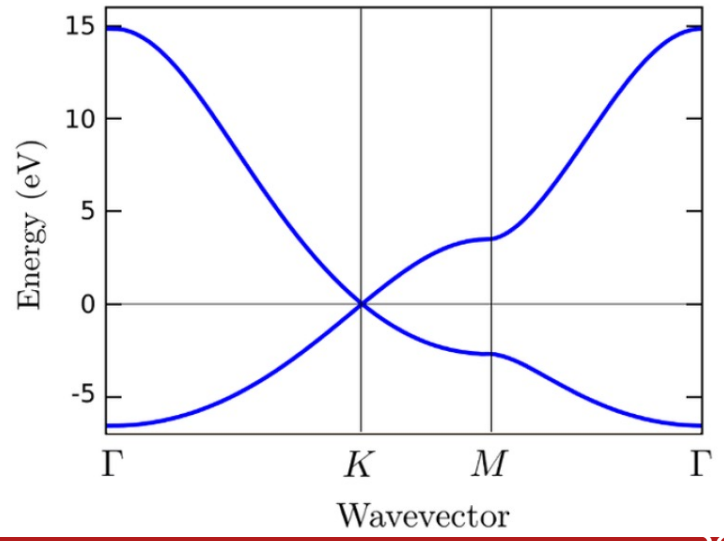


Born-von Kármán (Periodic) Boundary Conditions

$$\phi_i(x + a, y, z) = \phi_i(x, y, z)$$

$$\nabla\phi_i(x + a, y, z) = \nabla\phi_i(x, y, z)$$





What can we calculate using DFT?

- Electronic band structure
- Atomic forces
- Equilibrium structures
- Elastic properties
- Phonons, vibrational properties
- Dielectric function, optical spectra
- Magnetic properties
- Defects
- Molecular dynamics
- …

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What can we not calculate?

- Band gaps of semiconductors and insulators
- Mott-Hubbard insulators
  - Correlated materials
- Matter with long-range correlations
  - van der Waals interactions

DFT beyond LDA

- Generalized Gradient Approximation (GGA) $E_{xc}^{\mathrm{GGA}} = \int d\mathbf{r}\, f[n(\mathbf{r}), \nabla n(\mathbf{r})]$

  The PBE functional: Perdew, Burke, Ernzerhof (1996)

- DFT+U for transition metals (3*d*) and rare earth (4*f*) electrons in strongly-correlated materials

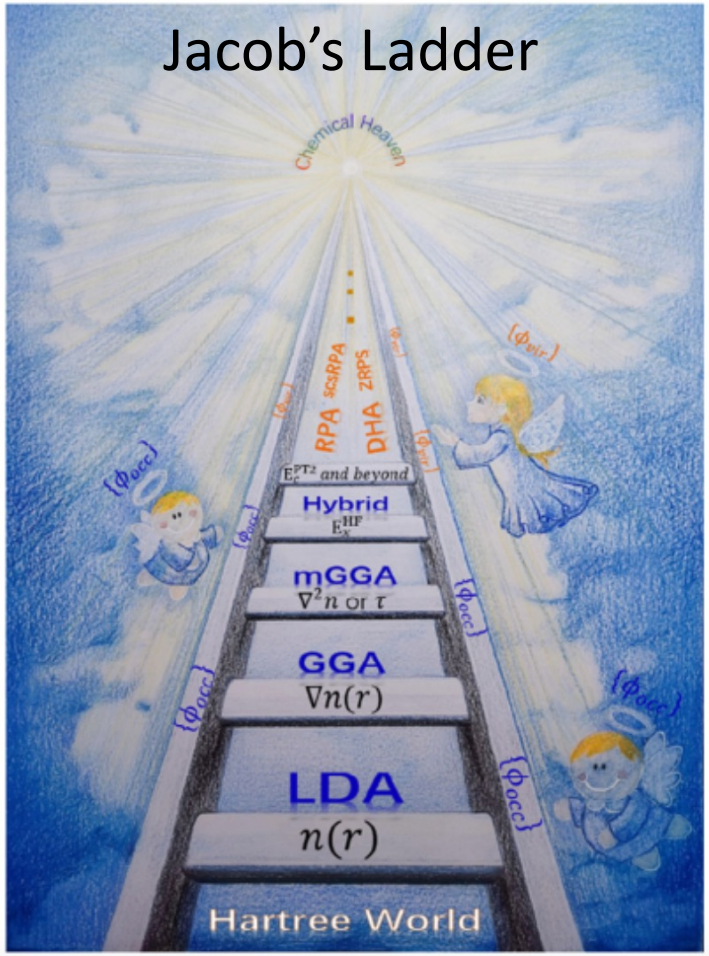
  Hubbard-like correction to the underestimated on-site Coulomb energy of LDA/PBE

- Hybrid functionals: B3LYP, PBE0, HSE06, …

  Add a fraction of the non-local exchange interaction

- van der Waals corrections: long-range dipole fluctuations $U = -\frac{C}{d^6}$

  Grimme, Langreth & Lundqvist, Tkatchenko & Scheffler



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Acknowledgements and Resources

Magnetic Properties from First Principles

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