



Welcome to CHE 384T: Computational Methods in Materials Science

Approximations to the Many-Body Problem: Intro to Quantum Chemistry and DFT

LeSar Ch. 4; App. F

Course Feedback

- Be specific and objective
- Be civil and professional
- Provide an explanation of “why”
- Include aspects of the course that were helpful and good, too!



CHE 384T - COMP
METHODS IN
MATERIALS SCI (15755)

Students

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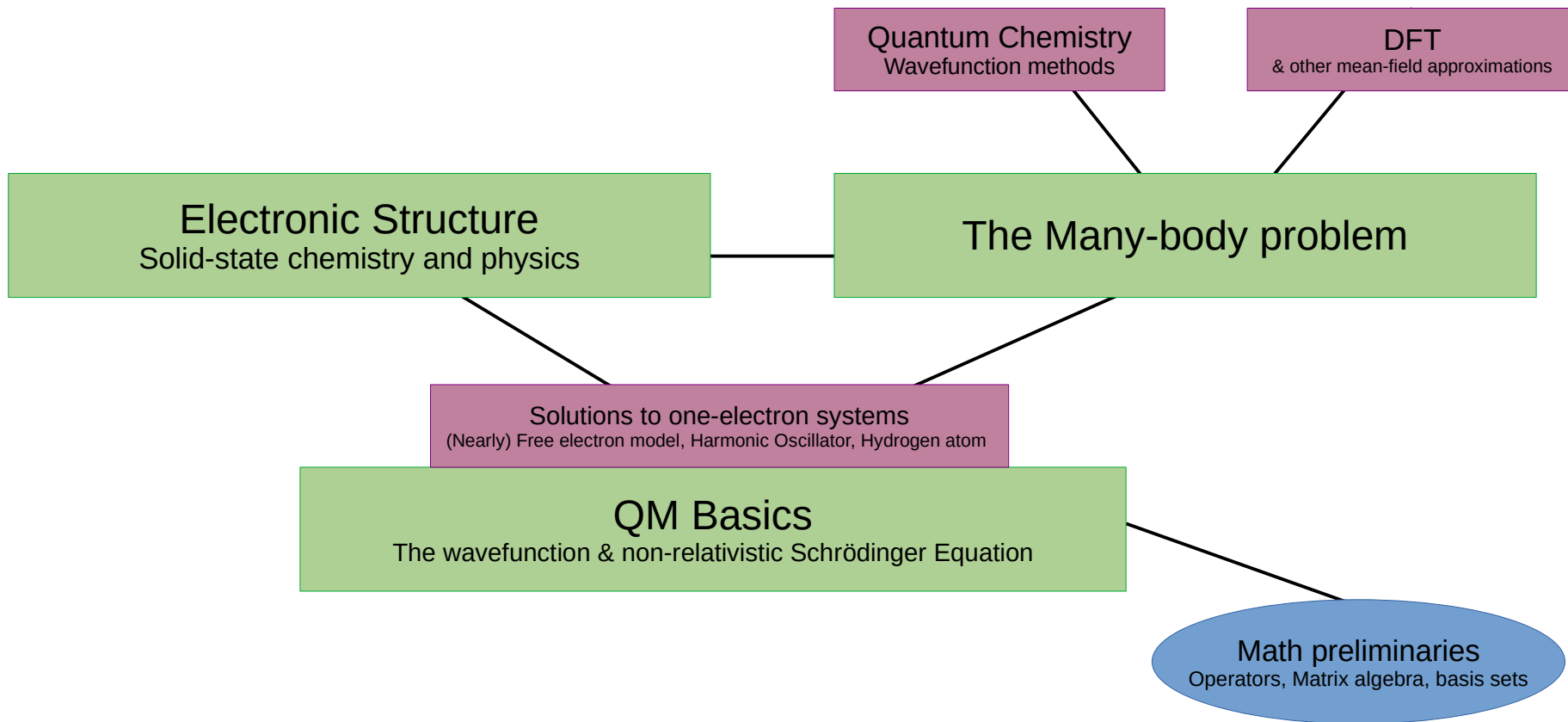
<https://go.blueja.io/H3hPINxz2EmE2v7NoAiKtA>

<https://testingservices.utexas.edu/cis/students>

<https://www.youtube.com/watch?v=EakEuc-XHIA&feature=youtu.be>



Road map



Lecture Outline

The Many-body problem

2-electron system

Correlation and Exchange
Spin statistics of fermions

Basic Approximations:

- Born-Oppenheimer approximation
- Non-relativistic
- Single-electron picture

Precursors to DFT:

- Reminder of variational principle
- Hartree-Fock theory
- Slater determinants
- Open v closed shell systems
- Practical aspects of HF theory

Reaching a self-consistent solution

Beyond Hartree-Fock

DFT formalism

Motivations for DFT

The rise of DFT

Development of DFT:

- Thomas-Fermi
- Local density approximation

Basis of DFT:

- Hohenberg-Kohn theorem
- Kohn-Sham framework
- Interpretation of the KS states:
 - Slater-Janak theorem
- Reaching self-consistency

Exchange correlation functionals:

- LDA, GGA, meta-GGA, hybrids
- Jacob's ladder
- self-interaction and error cancellation

The many-body problem

The many-electron system

The full many-body interacting Hamiltonian

$$\hat{H} = -\sum_I^N \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2 + \frac{1}{2} \sum_{I \neq J}^N \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{\hbar^2}{2m} \sum_i^n \nabla_{\mathbf{r}_i}^2 - \sum_I^N \sum_j^n \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_j|} + \frac{1}{2} \sum_{i \neq j}^n \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{H} = \hat{T}_e + \hat{V}_{ext} + \hat{V}_{int} + E_{II}$$

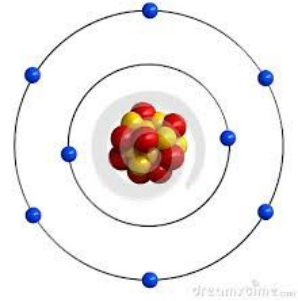
The many-electron system

Consider sampling the system with G grid points

e.g., Oxygen atom with $G = 10$ grid points

$10^{3 \times 8}$ Numbers to store

Assume 1 number/byte



“Oxygen atom”

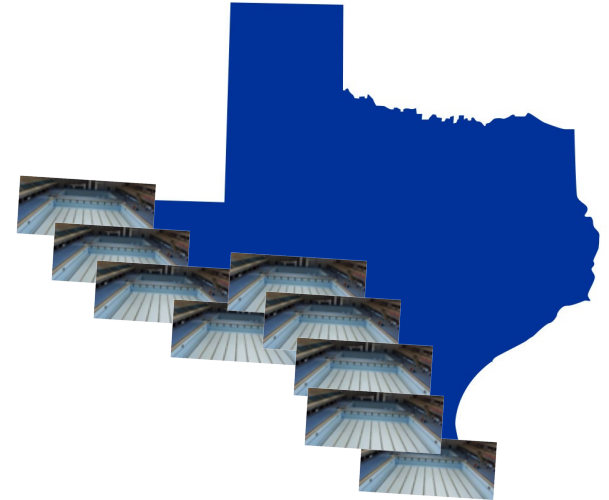
How much memory is a yottabyte?



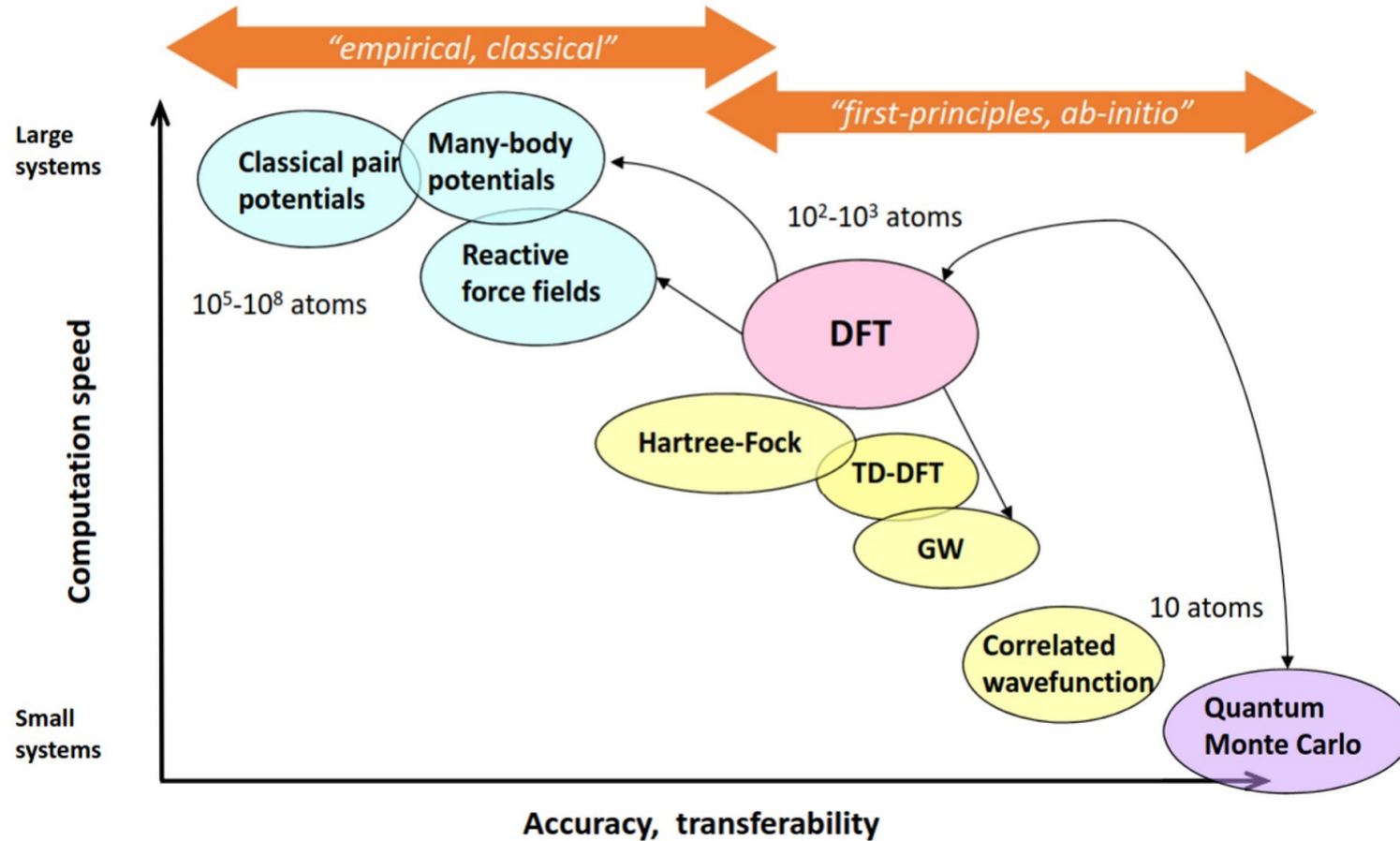
1 TB hard drive



Olympic Pool



How do we approximate the atomic properties of materials?



Single-electron approximation: Hartree Approach

Approximate the many-body wavefunction as simple product of single-particle wavefunctions

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_n(\mathbf{r}_n)$$

This approximation leads to a set of N single-particle equations:

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}_i) + V_{int}(\mathbf{r}_i) \right] \psi_i(\mathbf{r}_i) = \varepsilon_i \psi_i(\mathbf{r}_i)$$

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}_i) + \sum_{j \neq i}^n \int d\mathbf{r} \frac{|\psi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_j - \mathbf{r}_i|} \right] \psi_i(\mathbf{r}_i) = \varepsilon_i \psi_i(\mathbf{r}_i)$$

“Mean-field approximation”

3N coupled Schrodinger-like equations

Electrons interact electrostatically with charge density due to all other electrons

Individual electrons move independently from the mean field (i.e., effective potential)
from all other electrons and nuclei

Exchange and Correlation: QM many-body effects

Problem: Hartree's approach does not properly account for the **exchange** or **correlation**

Correlation:

A single electron only sees the average density of the other electrons
In reality, the instantaneous position defines the true e-e interaction

On average, leads to too much electrostatic repulsion

Exchange interaction: states of indistinguishable particles

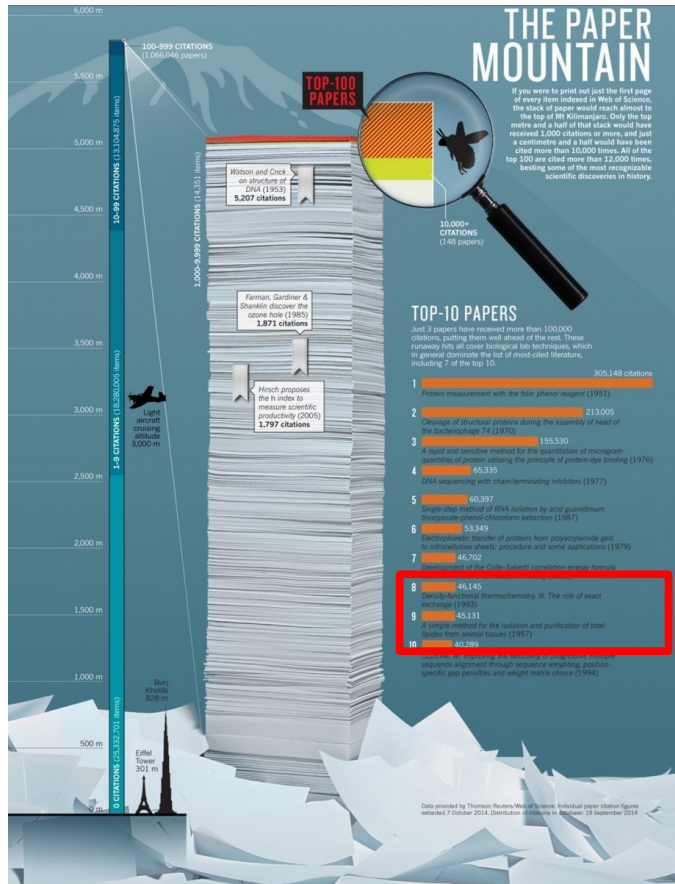
electrons are indistinguishable fermions

i.e., Electron wavefunction is anti-symmetric to exchange of electrons

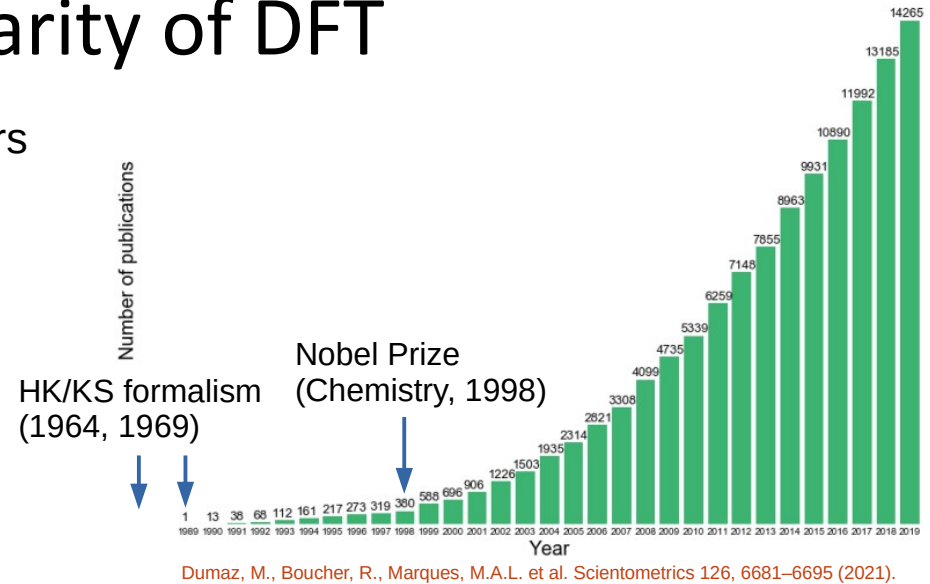
$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$$

Introduction to DFT: Formalism

Rise and popularity of DFT



The top 100 papers
Nature (2014)



Coincided with the rise of computing:

1940s: 10^2 FLOPS

1950s: 10^3 FLOPS (kiloscale)

1960s-1980s: 10^6 FLOPS (megascale)

1990s: 10^9 FLOPS (gigascale)

2000s: 10^{12} FLOPS (terascale)

2010s: 10^{15} FLOPS (petascale)

2020s: 10^{18} FLOPS (exascale)

~12 related to DFT methods
2 in the top 10 papers

Human time in DFT v other electronic structure methods

Method	E_{coh} % error	Scaling with # electrons	Time for 1 atom	Total time for 100 atoms
HF	50%	N^3 - N^4	0.1 sec	3.8 months
MP2	25%	N^5	0.1 sec	32 years
CCSD(T)	10%	N^7	0.1 sec	320,000 years
DFT-LDA	15-25%	N^2 - N^3	0.1 sec	27 hrs

DFT formalism: Hohenberg-Kohn Theorem

Why can we use a functional of the electron density in the first place?

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†

École Normale Supérieure, Paris, France

AND

W. KOHN‡

École Normale Supérieure, Paris, France and Faculté des Sciences, Orsay, France

and

University of California at San Diego, La Jolla, California

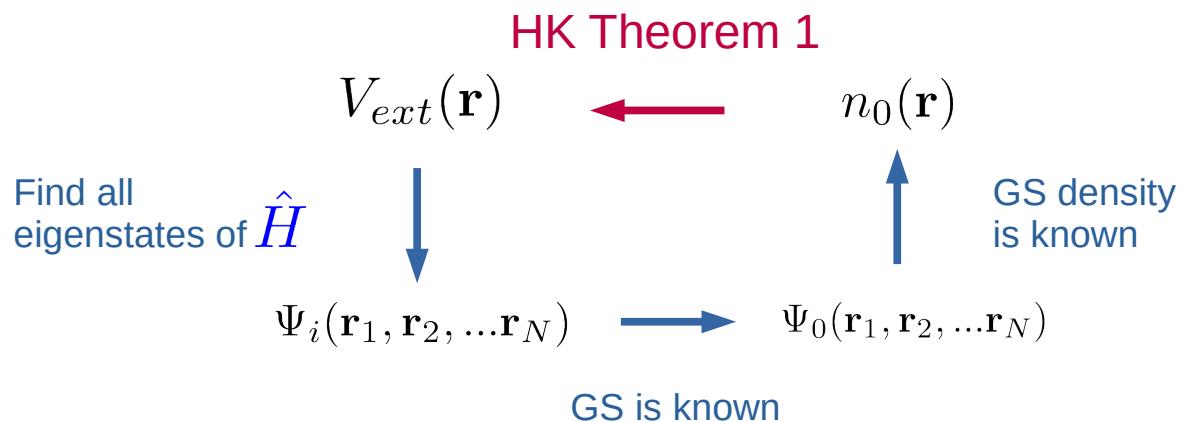
(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 \ll 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \rightarrow \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

DFT formalism: Hohenberg-Kohn Theorem #1

Proof of Existence:

For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, there exists a ground-state particle density $n_0(\mathbf{r})$ that uniquely determines the potential $V_{ext}(\mathbf{r})$ (to within a constant)



All properties of the system are completely known given with knowledge of $n_0(\mathbf{r})$
But the form of a universal external potential is not known

DFT formalism: Hohenberg-Kohn Theorem #1

Proof of Existence (*reductio ad absurdum*)

Supposed we had two different external potentials
that give the same ground state density

 V_{ext} V'_{ext}

DFT formalism: Hohenberg-Kohn Theorem #1

Total energy of the system

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

A Universal Functional

$$F[n(\mathbf{r})] = \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

This universal functional contains the exact many-body interaction for any system and does not depend on the form of the external potential

If we knew what F was or how to evaluate it, we could solve all quantum many-body problems exactly!

No free lunch: The form of the universal function is not exactly known

DFT formalism: Hohenberg-Kohn Theorem #2

Variational Theorem

There exists a universal functional $F[n(\mathbf{r})]$.
For any potential $V_{\text{ext}}(\mathbf{r})$, the exact ground state energy is the global minimum of $E[n(\mathbf{r})]$ and the density that minimizes $E[n(\mathbf{r})]$ is the exact ground state density $n_0(\mathbf{r})$

The density is now the fundamental descriptor of the system

Reformulates quantum mechanics into new Schrodinger-like equations expressed in terms of the charge density

$$E[n'(\mathbf{r})] = F[n'(\mathbf{r})] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})n'(\mathbf{r}) \geq E_0$$

The exact solution may be found by minimizing this functional with respect to n

DFT formalism: Kohn-Sham Framework

How do we actually go about solving these new Schrodinger-like functionals?

PHYSICAL REVIEW

VOLUME 140, NUMBER 4A

15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM

University of California, San Diego, La Jolla, California

(Received 21 June 1965)

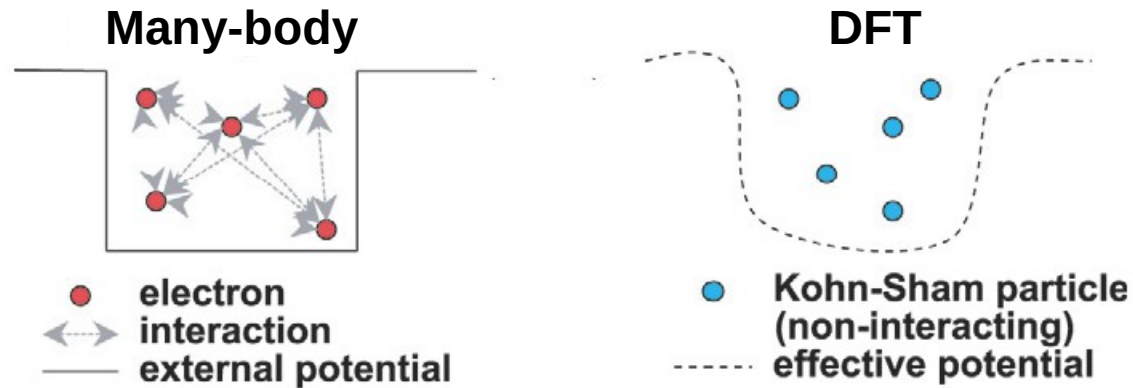
From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

Recapitulates some ideas from Hartree-Fock and Thomas Fermi theory

DFT formalism: Kohn-Sham Framework

Idea: map the many-body, fully interacting system onto a reference system of non-interacting particles in an external potential (K-S potential)

Ansatz: the ground-state charge density of the non-interacting system is identical to the ground-state charge density of the many-body, fully interacting system



NB: for a system of non-interacting electrons, the Slater determinant is the exact many-body wavefunction

DFT formalism: Kohn-Sham Framework

Kohn-Sham energy functional

$$\begin{aligned} E[n(\mathbf{r})] &= F[n(\mathbf{r})] + \int d\mathbf{r} V_{ext}(\mathbf{r})n(\mathbf{r}) \\ &= T[n(\mathbf{r})] + E_{Hartree}[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})] + \int d\mathbf{r} V_{ext}(\mathbf{r})n(\mathbf{r}) \end{aligned}$$

Kinetic energy of the
fictitious non-interacting system
at the **same** density

$$\begin{aligned} T[n(\mathbf{r})] &= \sum_i^N -\frac{1}{2} \int d\mathbf{r} \phi_i(\mathbf{r})^* \nabla^2 \phi_i(\mathbf{r}) \\ n(\mathbf{r}) &= \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \end{aligned}$$

Coulomb-like interaction

$$E_{Hartree}[n(\mathbf{r})] = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

We define $E_{xc}[n(\mathbf{r})]$, the **exchange-correlation** energy, which describes all the many-body interactions and represents everything else that should be approximated to make $F[n(\mathbf{r})]$ as accurate as possible.

DFT formalism: Kohn-Sham Framework

We had rewritten the *many-body, interacting* problem in terms of a fictitious, non-interacting system in an *effective* potential, leading to a set of *N independent single-particle Schrodinger-like equations*

$$\left(-\frac{1}{2}\nabla^2 + V_{eff} \right) \phi_i = \epsilon_i \phi_i \qquad n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

Kohn-sham *eigenfunction* and *eigenvalue*

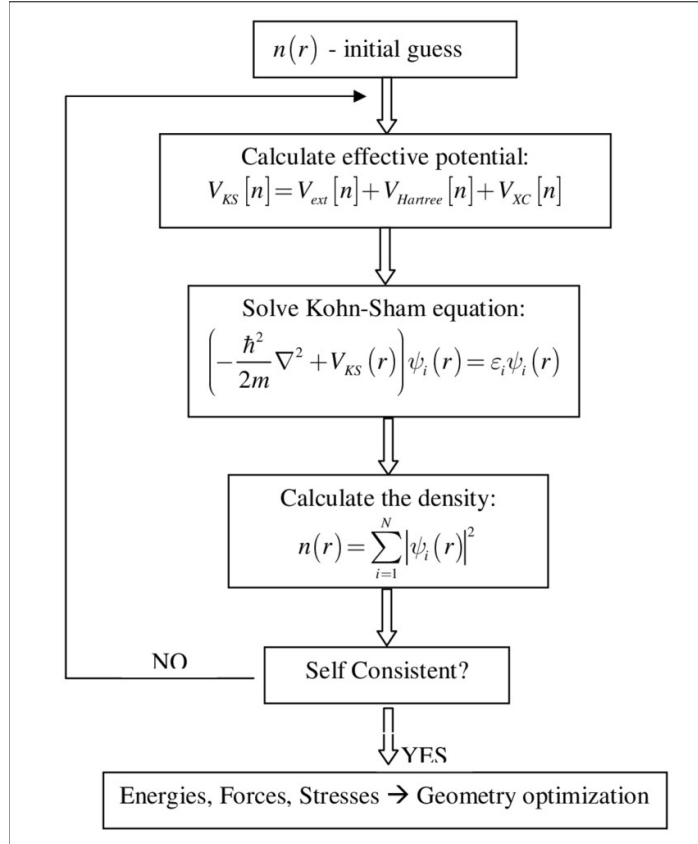
Kohn-Sham potential is an effective single-particle local potential

$$\begin{aligned} V_{eff} &= V_{ext} + V_{Hartree} + V_{XC} \\ &= V_{ext} + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{XC}[n]}{\delta n} \end{aligned}$$

We do not know the form of E_{XC} (and consequently V_{XC}) and are left to approximate it

DFT formalism: Self-consistency in KS

Like in Hartree-Fock, the KS equations are coupled to the density and solved self-consistently



- Pick a basis to numerically represent the orbitals and density
 - Localized orbitals: molecules, clusters
 - Plane waves: periodic solids, metals, liquids
- Solve the eigenvalue system (matrix diagonalization)
 - Usually the density is mixed with those of previous steps to improve convergence

DFT formalism: Interpretation of KS states

In principle, the orbitals are meaningless
(i.e., there is no mathematical proof that they have physical meaning)
“Helper” functions to represent the true density

Total energy is not the sum of the K-S eigenvalues

K-S eigenvalues have a mathematical interpretation, but do not represent the energy to add or subtract electrons (which would include rigorously many-body interactions)

e.g., Slater-Janak theorem $\frac{\partial E[n]}{\partial n_i} = \epsilon_i$

Empirically, there is some ad-hoc justification that the
K-S orbitals approximate quasiparticle distributions (qualitatively)
and the K-S eigenvalues approximate the electronic spectrum

Introduction to DFT: Applications and Practice

XC Functionals: Local Density Approximation (LDA)

Idea: Approximate the XC energy as the homogeneous electron gas
(in a similar spirit to Thomas-Fermi for quantum kinetic energy)

Assumes the density is slowly varying in space (Kohn & Sham, 1965)

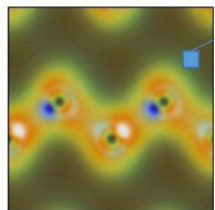
$$E_{xc}^{LDA}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \underline{\varepsilon_{xc}[n(\mathbf{r})]}$$

XC energy per
particle in uniform
electron gas

Ceperley and Alder:
Computed accurately with QMC
Phys Rev Lett 45, 566 (1980)

Perdew and Zunger:
Parametrized to get an analytic form
Phys. Rev. B 23, 5048 (1981)

$$\varepsilon_{xc}[n] = \varepsilon_x[n] + \varepsilon_c[x]$$



$$\varepsilon_x[n] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} n^{4/3}$$
$$\varepsilon_c[n]$$

Exchange energy known for HEG

Correlation energy known in the limit of high- and low-density regimes

Various parametrizations for intermediate regimes → different flavors of LDA
e.g., “PW91”, “Perdew-Zunger”, “VWN”

XC Functionals: Local Density Approximation (LDA)

Performance of LDA example:

lattice parameters across multiple types of materials;

also does pretty well for conventional metals

Material	Expt	Theory	Delta	Type
LaBi	6.57	6.648	1.2%	alloy
CaF ₂	5.4626	5.496	0.6%	halide
Ag	4.086	4.112	0.6%	metal
V	3.028	3.019	-0.3%	metal
ZrN	4.62	4.634	0.3%	misc
NbO	4.2103	4.2344	0.6%	oxide
GaAs	5.653	5.663	0.2%	semiconductor
CoSi ₂	5.36	5.3	-1.1%	silicide

LDA is still widely used

XC Functionals: Local Density Approximation (LDA)

Why does LDA do ok (for e.g., lattice constants, bulk moduli, phonon frequencies)?

The many-body effects (XC) are relatively small compared to the total energy

Example: Contributions to the total valence energy of Mn atom

- Kinetic energy (valence; $T_{0,V}$)
- Electrostatics b/t core and valence (E_{cv} , E_{VV})
- Exchange energy (E_x)
- Correlation energy ($E_c \ll E_x$)

Also understood to come from cancellation of errors in the approximation of exchange and correlation energies

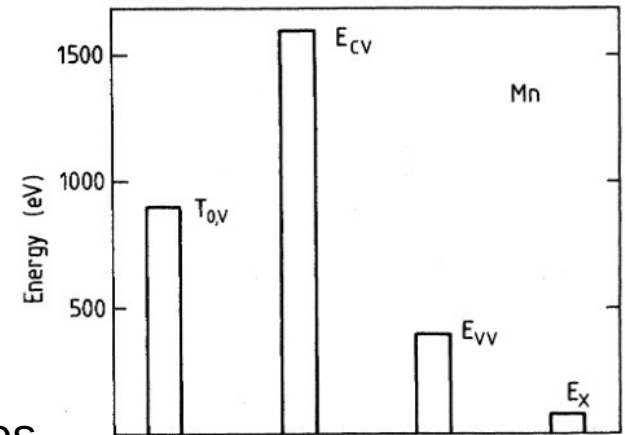


FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

XC Functional: General Gradient Approximation

In general, the electron density is not uniform and can vary rapidly

To improve upon the LDA functional, add gradient corrected “non-local functionals”

$$E_{xc}^{GGA}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})]$$

Also generalized to meet certain physical constraints, such as the sum rule for XC hole

PW91: parameter-free GGA

PBE (popular for solids): simplified from PW91

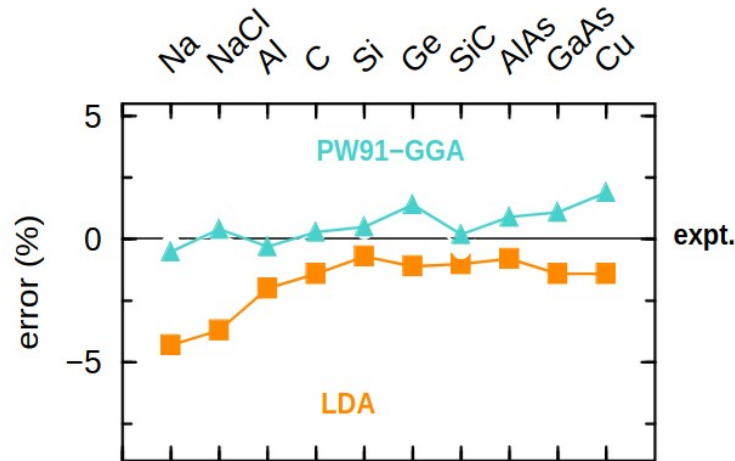
BLYP (popular for molecules): analytic model + empirical parameters

Usually not much more computationally expensive than LDA

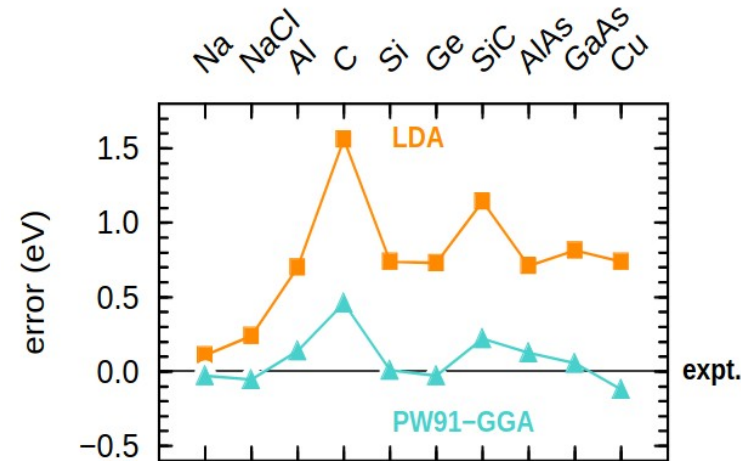
Performance of LDA and GGA

	LDA	GGA
Structural, elastic, vibrational properties	Bulk lattice: within ~3% error (often underestimated) → overly stiff phonons	Bulk lattice: within ~2% error (often overestimated) → Softer phonons
Cohesive energies	Tends to overbind (too negative, up to several eV) Formation enthalpies often ok	Tends to overbind a bit (a few 100s meV) but performs better than LDA

Bulk Lattice Constants



Cohesive energies



Performance of LDA and GGA

	LDA	GGA
Structural, elastic, vibrational properties	Bulk lattice: within ~3% error (often underestimated) → overly stiff phonons	Bulk lattice: within ~2% error (often overestimated) → Softer phonons
Cohesive energies	Tends to overbind (too negative, up to several eV) Formation enthalpies often ok	Tends to overbind a bit (a few 100s meV) but performs better than LDA
Activation energies	Too small or absent	Also can be low, but still improved over LDA
Prediction of relative phase stability	Can be uncertain or incorrect	Improves over LDA
Magnetic states	Can stabilize incorrect state (e.g., Fe is paramagnetic)	Better description of stable magnetic states

GGA favors lower coordination environments (gradients play a larger role)

GGA has improved electron affinities (negative ions are more stable)

GGA better describes hydrogen bonds (important for organic chemistry, catalysis, solution chemistry)

Neither have long-range van der Waals interactions!
Band gaps are generally still underestimated for both.

XC functionals: Jacob's ladder

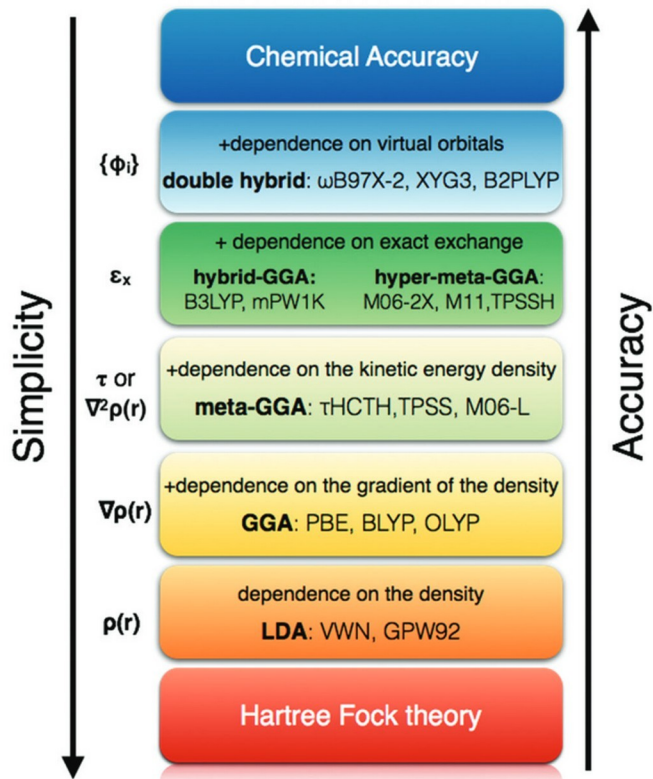


Fig. 5 The hierarchy of exchange–correlation functionals is often represented by the rungs of Jacob’s ladder, according to the number and kind of local ingredients.



Informal poll of popular functionals
(like, neutral, hate)

1. PBE
2. PBE0
3. PBE-D
4. PBE-sol
5. SCAN

Primera Divisió 2023

Segona Divisió 2023

Summary of Assumptions in DFT

- **Born-Oppenheimer approximation:** nuclei decoupled from electrons
- **Mean-field approximation:** all many-body interactions stuffed in XC functional comprising of an effective potential
- **XC functional:** level of theory to represent approximation of many-body interactions
- **Atomic structure:** periodic boundary conditions, convergence wrt cell size
- **Representation of wavefunctions:** plane-wave basis set versus localized basis set
- **Brillouin zone integrals:** integrals are computed as sums over k -points
need to check convergence wrt number of k -points
- **Pseudopotentials:** core electrons are frozen;
only valence electrons are explicitly modeled

Choosing the XC functional

Over 600+ XC functionals; currently available with the LibXC library, which interfaces with many electronic structure codes

LDA Exchange	NCG.DA_X	LDA exchange	6.02 [40, 41]	NCG.GA_XAM06	Amendte & Mattsson 05 exchange	61.39 [78, 79]	NCG.GA_XPBEHYPW	PBEHYPW (functional fitted for water)	79.12 [115]
	NCG.DA_XD	State exchange in 2D	9.86	NCG.GA_XPBFA	Madsen 97	30.98 [98]	NCG.GA_XQCCT2	Kohn and Toyer, version 2	31.78 [98]
	NCG.DA_XD	State exchange in 2D	8.36	NCG.GA_XPWF0	MPW0 of Adamo & Barone	17.49 [95]	NCG.GA_XTHLFC	Toner and Handy v. FC0	54.64 [116]
	NCG.DA_XD	State exchange in 2D	3.82 [42]	NCG.GA_XD2D38JGJC	Becke 86 with modified gradient correction for 2D	33.19 [95]	NCG.GA_XTHLFC	Toner and Handy v. FC1	24.75 [116]
LDA Correlation	NCG.DA_XWNER	Wigner parameterization	6.55 [43]	NCG.GA_XJAYSIAN	Requiesc best fit for the enhancement factor	18.91 [98]	NCG.GA_XTHLFC0	Toner and Handy v. FC0	35.05 [116]
	NCG.DA_XPFA	Hopfer Phase Approximation	11.94 [44]	NCG.GA_XPBE-SR	Reparametrized PBE by Pederson, Silva & Capelle	38.71 [98]	NCG.GA_XTH2	Toner and Handy v. 2	35.64 [117]
	NCG.DA_XL	Bedin & Lundqvist	9.86 [45]	NCG.GA_XOPTB86_VDW	opt-B86 for cVW	25.24 [95]	NCG.GA_XTH3	Toner and Handy v. 3	35.64 [117]
	NCG.DA_XL	Gumunova & Lundqvist	12.19 [46]	NCG.GA_XPBEHYP_VDW	Reparametrized PBE for vDW	18.72 [95]	NCG.GA_XTH3	Toner and Handy v. 3	35.64 [117]
NCG.DA_XALPFA	NCG.DA_XALPFA	Slater's Xc (X-alpha)	9.33	NCG.GA_XOPTB86_VDW	Reparametrized PBE for vDW	14.49 [95]	GGA Kinetic Energy		
	NCG.DA_XWNS	Viola, Wilk & Nusser	24.14 [27]	NCG.GA_XJGJ2	Reparametrized PBE	40.61 [95]			
	NCG.DA_XWNS	Viola, Wilk & Nusser (RFA)	18.21 [47]	NCG.GA_XBPW86	Revised Perdew & Wang 86	30.82 [95]			
	NCG.DA_XZ	Perdew & Zunger	8.80 [48]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]			
NCG.DA_XBPZ	NCG.DA_XBPZ	Carter & Balduke (PZ parameterization)	12.06 [8, 48, 49]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]	Meta-GGA		
	NCG.DA_XW	Perdew & Wang	17.63 [50]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]			
	NCG.DA_XW	Perdew & Wang fit to the RFA energy	17.63 [50]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]			
	NCG.DA_XW	Carter & Balduke (PW parameterization)	12.33 [8, 49, 50]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]			
NCG.DA_XDAMB3	NCG.DA_XDAMB3	Atkinson, Moroni, Gori-Giorgi, and Giuliani (LDA fit to 2D systems)	10.44 [51]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]	Meta-GGA		
	NCG.DA_XDAMB3	Atkinson, Moroni, Gori-Giorgi, and Giuliani (LDA fit to 2D systems)	10.44 [51]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]			
	NCG.DA_XDAMB3	Atkinson, Moroni, Gori-Giorgi, and Giuliani (LDA fit to 2D systems)	10.44 [51]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]			
	NCG.DA_XDAMB3	Atkinson, Moroni, Gori-Giorgi, and Giuliani (LDA fit to 2D systems)	10.44 [51]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]			
NCG.DA_XDAMB3	NCG.DA_XDAMB3	Atkinson, Moroni, Gori-Giorgi, and Giuliani (LDA fit to 2D systems)	10.44 [51]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]	Meta-GGA		
	NCG.DA_XDAMB3	Atkinson, Moroni, Gori-Giorgi, and Giuliani (LDA fit to 2D systems)	10.44 [51]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]			
	NCG.DA_XDAMB3	Atkinson, Moroni, Gori-Giorgi, and Giuliani (LDA fit to 2D systems)	10.44 [51]	NCG.GA_XL	Ross and Taylor, version 1	23.96 [98]			
	N								

LDA Exchange-Correlation	NCG.DA_XLTERMIN	Lee 1993	9.22 [37]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.DA_XLTERMIN	Lee 1993	9.22 [37]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.DA_XLTERMIN	Lee 1993	9.22 [37]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.DA_XLTERMIN	Lee 1993	9.22 [37]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
LDA Kinetic Energy	NCG.DA_XL	Thomas-Fermi kinetic energy	6.74 [11, 12]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.DA_XL	Thomas-Fermi kinetic energy	6.74 [11, 12]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.DA_XL	Thomas-Fermi kinetic energy	6.74 [11, 12]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.DA_XL	Thomas-Fermi kinetic energy	6.74 [11, 12]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
GGA Functionals	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
GGA Exchange	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
GGA Exchange-Correlation	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
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	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
GGA Exchange-Correlation	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
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	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
GGA Exchange-Correlation	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
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	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
GGA Exchange-Correlation	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
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	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
GGA Exchange-Correlation	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
GGA Exchange-Correlation	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
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	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XLTERMIN	Local tan approximation	24.67 [142]
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GGA Exchange-Correlation	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG.GA_XL	van Leeuwen & Baerends	29.97 [109]	NCG		

Things you can compute with DFT

Solving the KS equations gives you KS eigenenergies and wavefunctions



Limitations of (conventional) DFT

- **Strong correlations:** strongly correlated systems are poorly described in DFT
typical for *d*- and *f*-electron systems (localized orbitals)
e.g., transition metal oxides, rare-earth materials
- **Van der Waals interactions:** often included ad-hoc with empirical parameters
important for layered materials
- **Self-interaction error:** band gap underestimation, spurious charge delocalization
see also DFT+U for methods with comparable computational cost
as LDA and GGA
- **Excited States:** DFT is a ground-state method,
typically does not perform well for open shell systems (spin contamination)

Final thoughts on CHE384T

I hope you enjoyed this foray into atomistic methods
in computational materials science

*Using simple models to
understand essential
physics:*

Random Walk Diffusion

Lennard-Jonesium

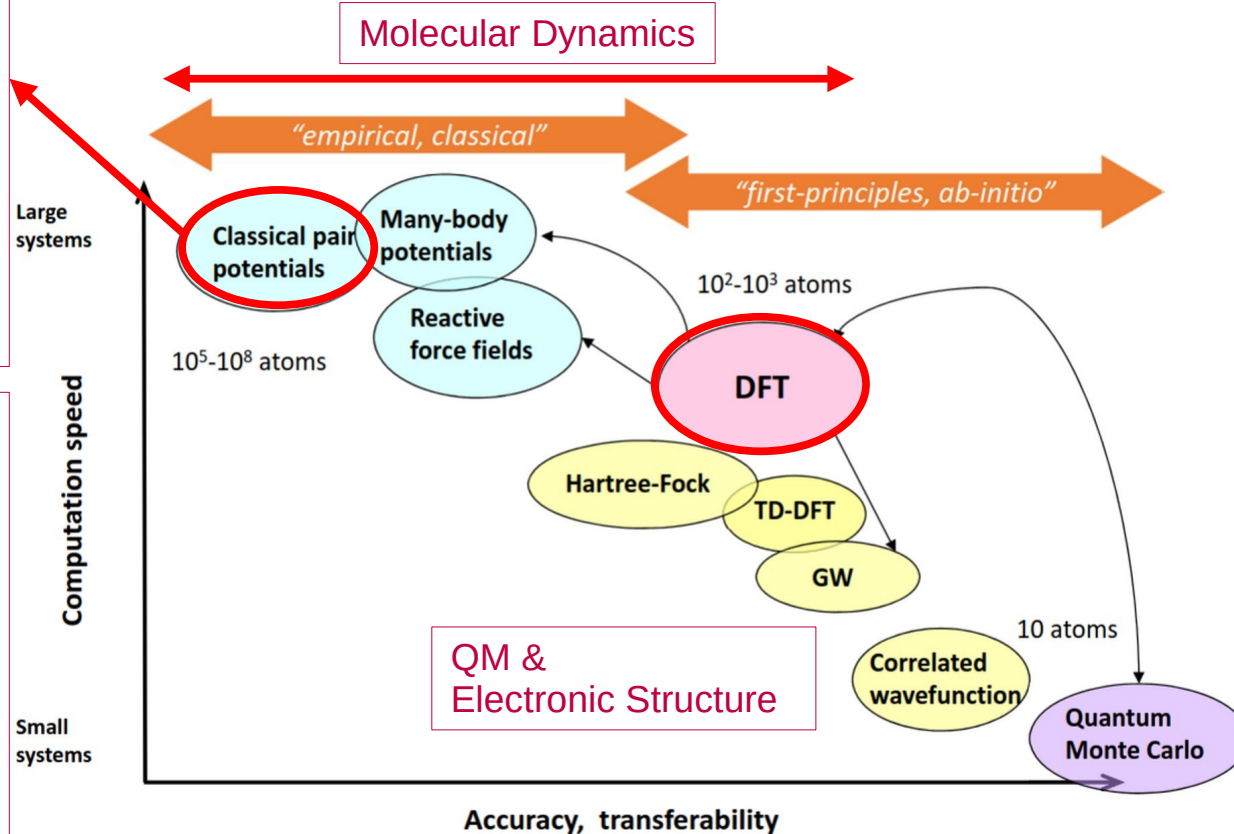
Lattice Sums and defects

*Research practices with
Python:*

Data visualization

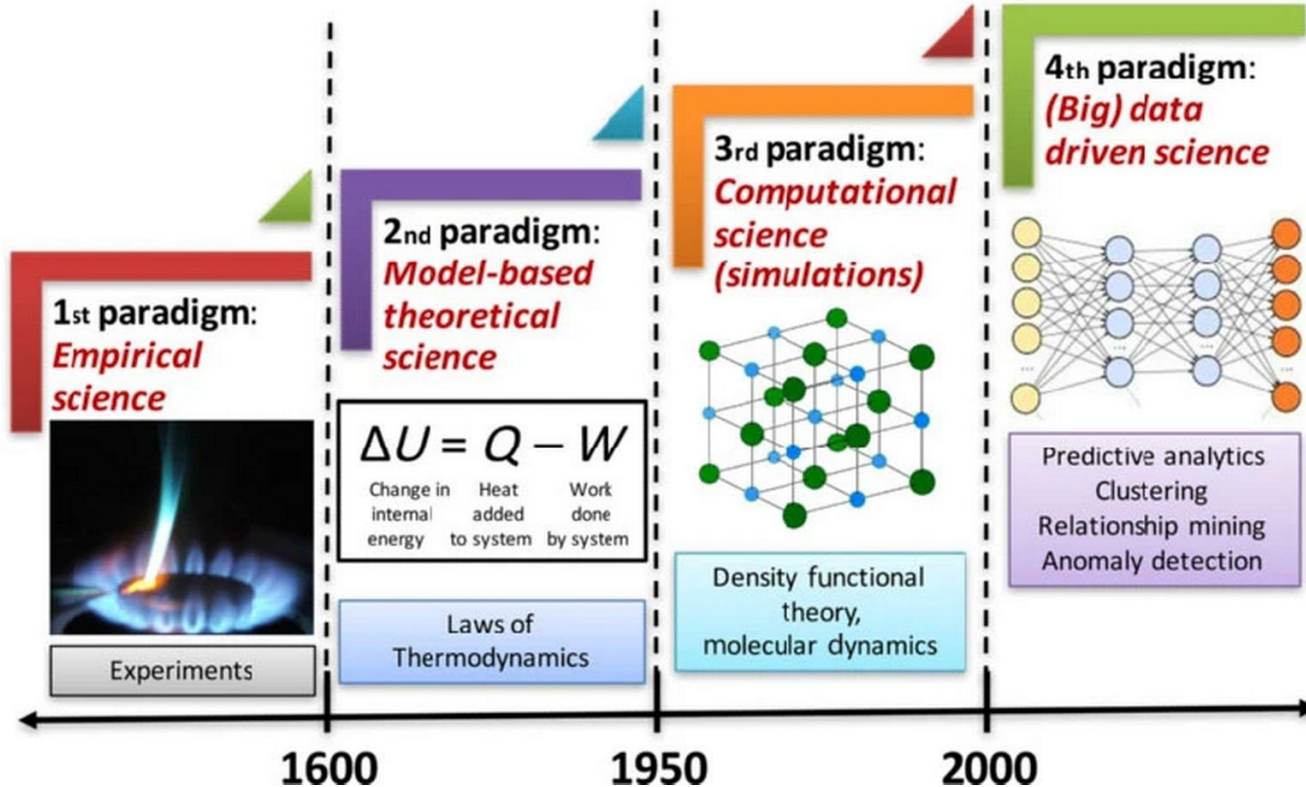
Coding
environment/conventions

Writing and Analysis,
Peer Review



Future directions in computational materials science

Integration of Machine Learning and AI: Materials Genome



High-throughput computation

High-throughput synthesis

High-throughput analysis,
image processing

Materials Discovery

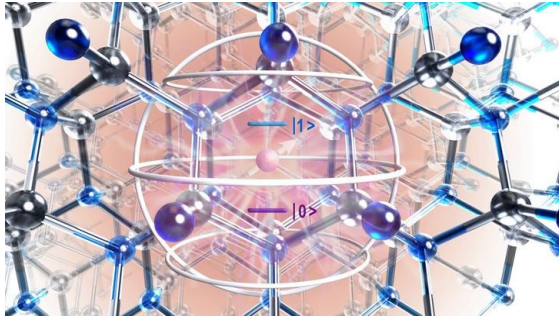
Crystal structure Prediction

Active learning for interatomic
potentials

Bayesian inference for
experimental decision making

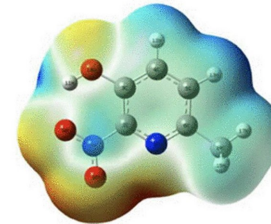
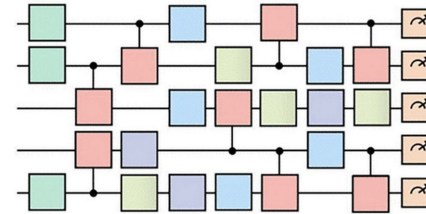
Future directions in computational materials science

Quantum computers for the electronic structure problem



Engineering solid-state qubits

Implementing and running
simulations of materials on
quantum computers



Guest Lecturer:
Dr. Roozbeh Anvari

Chem. Rev. 2020, 120, 22, 12685–12717

npj Comput Mater 6, 85 (2020).

Course Feedback

- Be specific and objective
- Be civil and professional
- Provide an explanation of “why”
- Include aspects of the course that were helpful and good, too!



CHE 384T - COMP
METHODS IN
MATERIALS SCI (15755)

Students

<https://go.blueja.io/H3hPINxz2EmE2v7NoAiKtA>

<https://go.blueja.io/H3hPINxz2EmE2v7NoAiKtA>

<https://testingservices.utexas.edu/cis/students>

<https://www.youtube.com/watch?v=EakEuc-XHIA&feature=youtu.be>

