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!



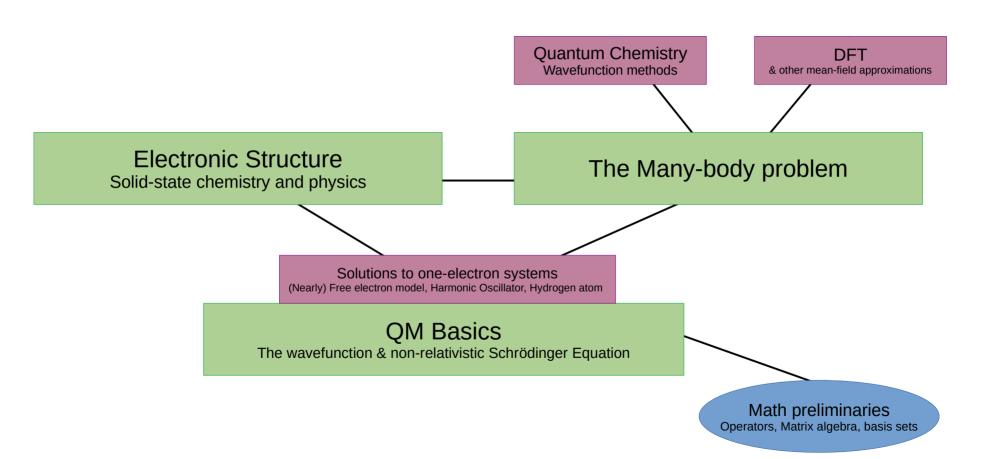
https://go.bl ueja.io/H3h PINxz2EmE 2v7NoAiKtA



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

$$\hat{H} = -\sum_{I}^{N} \frac{\hbar^{2}}{2M_{I}} \nabla_{\mathbf{R}_{I}}^{2} + \frac{1}{2} \sum_{I \neq J}^{N} \frac{Z_{I} Z_{J} e^{2}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|} - \frac{\hbar^{2}}{2m} \sum_{i}^{n} \nabla_{\mathbf{r}_{i}}^{2} - \sum_{I}^{N} \sum_{j}^{n} \frac{Z_{I} e^{2}}{|\mathbf{R}_{I} - \mathbf{r}_{j}|} + \frac{1}{2} \sum_{i \neq j}^{n} \frac{e^{2}}{|\mathbf{r}_{i} - \mathbf{r}_{j}|}$$

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

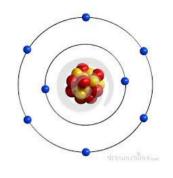
The many-electron system

Consider sampling the system with G grid points

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

 $10^{3 imes8}$ Numbers to store

Assume 1 number/byte



"Oxygen atom"

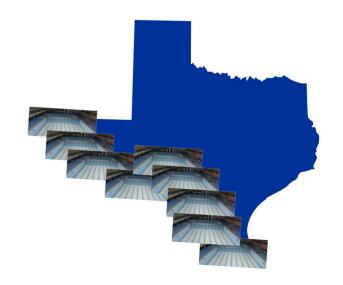
How much memory is a yottabyte?



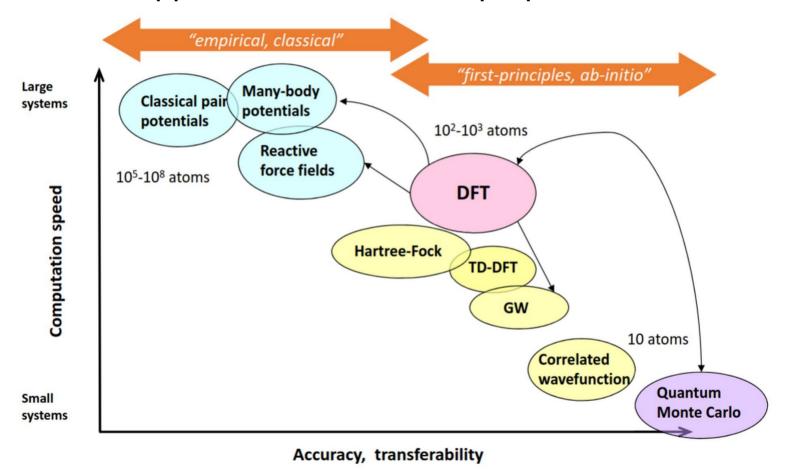
1 TB hard drive



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

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

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 <u>other</u> 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:

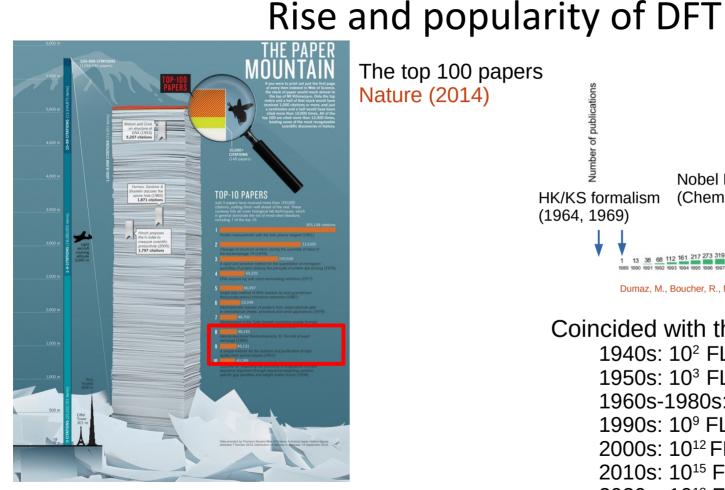
A single electron only sees the <u>average</u> density of the other electrons In reality, the instantaneous position defines the true e-e interaction

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

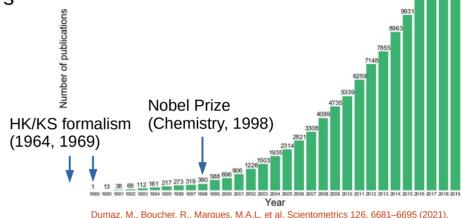
$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$$

Introduction to DFT: Formalism



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

The top 100 papers Nature (2014)



Coincided with the rise of computing:

1940s: 10² FLOPS

1950s: 10³ FLOPS (kiloscale)

1960s-1980s: 10⁶ FLOPS (megascale)

1990s: 109 FLOPS (gigascale) 2000s: 10¹² FLOPS (terascale) 2010s: 10¹⁵ FLOPS (petascale) 2020s: 10¹⁸ FLOPS (exascale)

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

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

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

P. Hohenberg† École Normale Superieure, Paris, France

AND

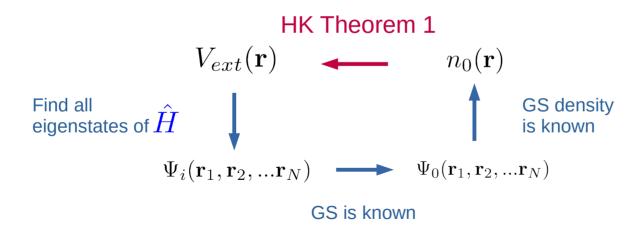
W. Kohn!

École Normale Superieure, 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) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 < < 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \to \infty$. 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.

Proof of Existence:

For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, there exists a ground-state particle density $n_o(\mathbf{r})$ that <u>uniquely</u> 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

Proof of Existence (reductio ad absurdum)

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

 V_{ext}

 V'_{ext}

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

Variational Theorem

There exists a universal functional $F[n(\mathbf{r})]$. For any potential $V_{ext}(\mathbf{r})$, 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 $n_o(\mathbf{r})$

The <u>density</u> is now the fundamental descriptor of the system

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

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

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

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

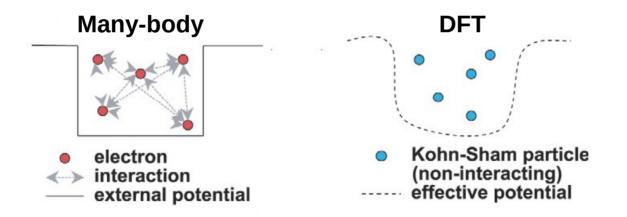
University of California, San Diego, La Jolla, California
(Received 21 June 1965)

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

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

Ansatz: the ground-state charge density of the <u>non-interacting</u> 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 <u>exact</u> many-body wavefunction

Kohn-Sham energy functional

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

$$= T[n(\mathbf{r})] + E_{Hartree}[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})] + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r})$$

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

$$T[n(\mathbf{r})] = \sum_{i}^{N} -\frac{1}{2} \int d\mathbf{r} \phi_{i}(\mathbf{r})^{*} \nabla^{2} \phi_{i}(\mathbf{r})$$
$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_{i}(\mathbf{r})|^{2}$$

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.

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

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

Kohn-sham eigenfunction and eigenvalue

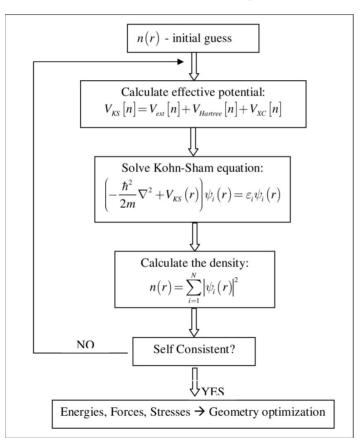
Kohn-Sham potential is an effective single-particle local potential

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

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
$$\frac{\partial E[n]}{\partial n_i} = \epsilon$$

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 <u>homogeneous electron gas</u> (in a similar spirit to Thomas-Fermi for quantum kinetic energy)

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

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

XC energy per particle in uniform electron gas

Ceperley and Alder:

Computed accurately with QMC

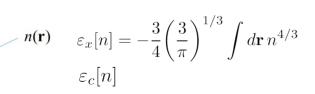
Phys Rev Lett 45, 566 (1980)

Perdew and Zunger:

Parametrized to get an analytic form

Phys. Rev. B 23, 5048 (1981)

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



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 << E_x)

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

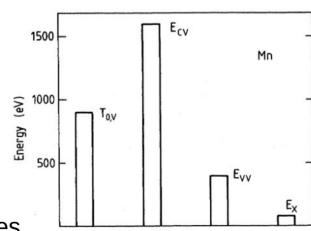


FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

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

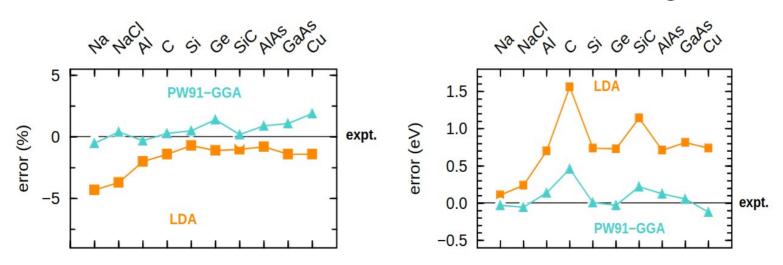
Usually not much more computationally expensive than LDA

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

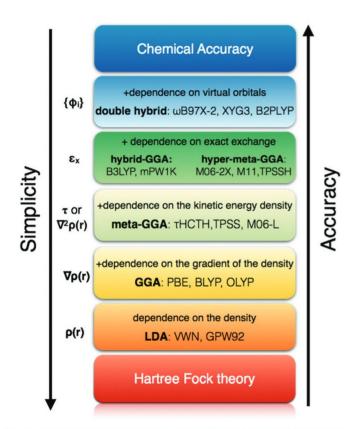


Fig. 5 The hierarchy of exchange—correlation functionals is often represented by the rungs of Jacob's ladder, according to the number and kind of local ingredients.



Informal poll of popular functionals

(like, neutral, hate)

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

Primera Divisió 2023

B3LYP, B3LYP-D, B97-D, B97-3c, B97M-V, CAM-B3LYP, HSE, LDA, PBE, PBE-D, PBE0 (PBE1PBE), PBEsol, PW91, RPA, r2SCAN-D4, SCAN, SCAN-rVV10, ωB97X-D, ωB97M-V, ωB97X-V

Segona Divisió 2023

B2PLVP, B3PW91, BEEF-vdW, BLYP, BP86, DM21, DSD-PBEP86, LC-PBE, LC-ΦPBE, M06, M06-2X, M06-L, optB88-vdW, PW6B95, PWPB95-D3, revPBE, revTPSS, revTPSS-D, RPBE, TPSSh

https://www.marcelswart.eu/dft-poll/

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 XC_LDA_X	LDA exchange	6.92 [00, 41]	XC.GGA.X.AM66 XC.GGA.X.PBEA XC.GGA.X.mPW91	Amiento & Mattsson 05 exchange Madson 67 mPW91 of Adamo & Bozone	61.38 [78, 79] 30.98 [80] 47.19 [81]	XC.GGA.XC.PBELYPIW XC.GGA.XC.TH.FL	PBELYPTW (functional fitted for water) Keel and Tozer, version 2 Tozer and Handy v. FL	79.12 [115] 31.73 [88] 94.64 [116]
XCLDA_X_ID	Slater exchange in 2D Slater exchange in 1D	9.36 3382 [42]	XC.GGA.X.2D.B86_MGC	Becke 86 with modified gradient correction for 2D	13.49 [62]	XC,GGA,XC,TH,FC	Torer and Handy v. FC	247.35 116
LDA Correlation		CONTRACT.	XC.GGA.X.BAYESIAN	Bayesian best fit for the enhancement	18.91 [83]	XC.GGA_XC.TH_FCPO XC.GGA_XC.TH_FCO	Tozer and Handy v. FCO	372.59 [116] 355.16 [116]
XCLDA_C_WIGNER XCLDA_C_RPA	Wigner parametrization Random Phase Approximation	6.55 [43] 11.96 [44]	XC_CCA_X_PBE_JSJR	factor Reparametrized PBE by Pedrom, Silva &	18.71 [84]	XCJGGA_XCJTH1 XCJGGA_XCJTH2	Tozer and Handy v. 2	383.44 [117] 352.52 [118]
XCLDA_C_HL XCLDA_C_GL	Hedia & Lundqvist Gunnarson & Lundqvist	9.86 [45] 12.19 [46]	XC.GGA.X.OPTB88.VDW	Capelle opt-Becke 88 for vdW	25.24 [85]	XC_GGA_XC_TH3 XC_GGA_XC_TH3		332.24 [119] 337.86 [119]
NCLDA_C_XALPHA	Slater's Xa (X-alpha)	9.33	XC.GGA.X.PBEKL.VDW XC.GGA.X.OPTPBE.VDW	Reparametrized PBE for vdW Reparametrized PBE for vdW	18.72 [85]	GGA Kinetic Energy		
NCLDA.C.VWN NCLDA.C.VWN.RPA	Vosko, Wilk, & Nussair Vosko, Wilk, & Nussair (RPA)	24.14 [47] 18.21 [47]	XC GGA X RGE2 XC GGA X RPW86	Regularized PRE Refitted Perdex & Wang 86	14.65 [86] 30.61 [87]	XC_GGA_K_VW	von Weiszaecker correction to Thomas- Fermi	18.49 [120]
XCLDA_C_PZ XC_LDA_C_OB_PZ	Perdew & Zunger Ortiz & Ballone (PZ parametrization)	8.90 [48] 12.08 [8, 48, 49]	XC GGA X KT1 XC GGA X HERMAN	Keal and Tozer, version 1 Herman Xalohabata GGA	23.96 [88] 17.44 [89, 90]	XC_GGA_K_GE2	Second-order gradient expansion of the ki-	16.08 [121, 122]
NCLDA_C_PW_ NCLDA_C_PW_RPA	Perdew & Wang Perdew & Wang fit to the RPA energy	17.63 [50] 28.16 [50]	XC.GGA.X.LBM	van Leeuwen & Barrends modified	30.98 [91]	XC.GGA_K_GOLDEN	netic energy density TF-lambda-vW form by Golden (l =	16.39 [123]
XCLDA_C_OB_PW XCLDA_C_2D_AMGB	Ortiz & Ballone (PW parametrization) Attacendite, Moroni, Gori-Giorgi, and	12.43 [8, 49, 50]	XC.GGA.X.OL2	Levy v.2	15.69 [92, 93]	XC_GGA_K_YT65	13/45) TF-lambda-vW form by Youci and	13.29 [124]
NCLDA-C-2D-PRM	Bachelet (LDA for 2D systems) Pittalis, Rissiner, and Marques (LDA for		XC,GGA,X,MB88 XC,GGA,X,APBE	Modified Becke 88 for proton transfer mu fixed from the semiclassical neutral	24.86 [94] 18.71 [95]	NC.GGA.K.BALTIN	Tomishims $(l = 1/5)$ TF-lombds-vW form by Baltin $(l = 5/9)$	
XCLDA.C.vBH	2D systems)	10.40 [53]	XC,GGA,X,HTBS	stom Hass, Tron. Blaha, and Schwarz	26.17 [96]	XC,GGA,K,LIEB	TF-bmbds-vW form by Lieb (l = 0.185909191)	14.68 126
NCJ.DAJC.JD.CSC	Casula, Sorella & Senatore (LDA correla- tion for 1D systems)		XC GGA X AJRY XC GGA X LAG	Constantin et al based on the Airy gas Local Airy Gas	47.48 97 49.75 98	NC_GGA_K_ABSR1	gamma-TFvW form by Acharya et al $[g = 1 - 1.412/N^{1/3}]$	17.54 [127]
NCLDA_C_ML1	Modified LDA (version 1) of Proyany and Salahub	37.02 [55]	XC.GGA.X.SOGGA11	Second-order generalized gradient approx- imation 2011		XCJGGAJK_ABSR2	gamma-TFvW form by Acharya et al $[g = 1 - 1.332/N^{1/3}]$	17.01 [127]
XCLDA.C.ML2	Modified LDA (version 2) of Proynov and Salabub	51.99 [55]	XC.GGA.X.C09X	C09x to be used with the VdW of Rutgers- Chalmers	19.86 [100]	NC_GGA_K_GR	gamma-TFvW form by Glasquez and Robles	13.89 [128]
XCLDA_C_COMBAS	Gombas	10.81 [56]	GGA Correlation			XC_GGA_K_LUDENA	gamma-TFvW form by Ludeña	18.72 [129]
LDA Exchange-Correla	ation		XC_GGA_C_PBE	Perdew, Burke & Ernzerhof correlation	39.69 [59, 60]	XC_CCA_K_CP85	gamma-TFvW form by Ghosh and Parr Backs 88	18.19 [130]
XCLDA_XC_TETER93	Teter 1903	9.22 [57]	XC GGA_C_XPBE XC GGA_C_LYP	Extended PBE by Xu & Goddard III Lee, Vang & Parr	43.85 [63] 25.88 [101, 10	XC.GGA.K.LLP XC.GGA.K.FR.B88	Fuentealba & Reyes (B88 version)	22.69 [131] 19.97 [92]
LDA Kinetic Energy			XC,GGA,C,P86	Pendew 86	51.36 [103]	XC_GGA_K_FR_PW86 XC_GGA_K_PEARSON	Fuentealha & Reyes (PW86 version) Pearson 1992	32.24 [92] 13.30 [132, 133]
NCLDA_K_TF NCLDA_K_LP	Thomas-Fermi kinetic energy Lee and Parr Gaussian ansatz for the ki-	6.74 [11, 12] 7.99 [58]	XC_GGA_C_PBE_SOL	Perdew, Burke & Erasserhof correlation SOL	00.32 [10]	XC_GGA_K_OL1	Ou-Yang and Lovy v.1	20.43 [93]
M. J. M. J. L.	netic energy	1.50 [00]	XC.GGA_C.PW91 XC.GGA_C.AM05	Perdew & Wang 91 Armiento & Matteson 05 correlation	51.17 [70, 104 25.88 [78]	XC_GGA_K_OL2 XC_GGA_K_DK	Ou-Yang and Levy v.2 DePrizzo and Kress	20.26 [93]
GGA Functionals			XC.GGA_C_LM XC.GGA_C_PBE_IRGX	Langreth & Mehl Reparametrized PBE by Pedroza, Silva &	42.87 [105]	XC_GGA_K_PERDEW XC_GGA_K_VSK	Perdew Vites, Skriver, and Kollar	16.21 [135] 17.05 [136]
GGA Exchange				Capelle		XC_GGA_K_VJKS	Vitos, Johansson, Kollar, and Skriver	18.61 [137]
XC_GGA_X_PBE	Perdew, Burke & Ernzenhof exchange	13.61 [59, 60]	XC_GGA_C_RGE2	Regularized PBE	40.55 [86]	NC_GGA_K_ERNZERHOF	Ernzerhof	18.72 138
XC_GGA_X_PBE_R	Perdew, Barko & Emzerhof exchange (revised)	19.27 [61]	XC.GGA.C.WL XC.GGA.C.WI	Wilson & Levy Wilson & Ivanov	20.95 106 16.48 107	XC_GGA_K_LC94 XC_GGA_K_APBE	Lembarki & Chermette mu fixed from the semiclassical neutral	46.63 [139] 19.48 [95]
XC.GGA_X_MPBE	Adamo & Barone modification to PBE	19.39 [62]	XC.GGA.C.APBE	Wilson & Ivanov initial version and fixed from the semiclossical neutral	19.42 [107]	XC GGA K THAKKAR	Thakker 1982	21.92 [140]
XC_GGA_X_XPBE XC_GGA_X_B86	Extended PBE by Xu & Goddard III Bocke 86 Xulfa beta gramma	18.90 [63] 18.64 [64, 65]	ACAMAD DAFBE	atom	arron (res)	NC GGA K TWI	Tran and Wesolowski set 1 (Table II)	18.70 [141]
XC,GGA,X,Bss,MGC	Becks 86 Xalfa,beta.gamma (with mod. grad, correction)		XC GGA C SOGGALL	Second-order generalized gradient approx- imation 2011	40.67 [99]	XC_GGA_K_TW2 XC_GGA_K_TW3	Tran and Wesolowski set 2 (Table II) Tran and Wesolowski set 3 (Table II)	18.30 141 19.01 141
NC_GGA_X_Bss NC_GGA_X_G96	Becke 88 GH 96	20.97 [67] 15.57 [68]	XC.GGA.C.SOGGAILX	to be used with XCHYB.GGA.X.SOGGAILX	37.05 [108]	XC_GGA_K_TW4	Tran and Wesolowski set 4 (Table II)	19.97 [141]
XC_GGA_X_PW86 XC_GGA_X_PW91	Perdew & Wang 86 Perdew & Wang 91	32.31 (69 48.02 [70]	GGA Exchange-Corre			MctaGGA Functionals		
XC_GGA_X_OPTX	Handy & Cohen OPTX 01	18.21 [71]	XC.GGA.XC.LB	van Leerwen & Barrends	29.27 [109]	MetaGGA Exchange		
NC_GGA_X_DK87_R1	dePristo & Kress 87 (version R1)	19.10 72	XC.GGA_XC.HCTH_93		155.10 [110]	XC_MGGA_X_LTA	Local tau approximation	24.07 [142]
NC_GGA_X_DK87_R2	dePristo & Kress 87 (version R2)	24 11 [72]	XC GGA XC HCTH 120		151.57 [111]	XC.MGGA.X.TPSS	Perdew, Tao, Staroverov & Scoreria	
XC_GGA_X_LG93 XC_GGA_X_FT97_A	Lucks & Gordon 93 Filatov & Thiel 97 (version A)	32.74 [73] 22.05 [74]	XC.GGA_XC.HCTH_147 XC.GGA_XC.HCTH_407		143.57 [111] 155.60 [112]		exchange	
NC_GGA_X_FT97_B	Filatov & Third 97 (version B)	26.86 [74]	XC.GGA.XC.EDF1	Empirical functional from Adamson, Gill.		XC_MGGA_X_TAU_HCTH.	Tau HCTH	23.45 [145]
NC.GGA.X.PBE.SOL	Perdew. Burks & Ernzerhof exchange (for		AND DESCRIPTION OF THE PARTY OF	and Pople	array famil	XC.MGGA.X.GVT4 XC.MGGA.X.M06L	GVT4 (exchange part of VSXC) M06-L	26.85 [106] 29.74 [147, 148]
	snlids)		XC.GGA.XC.XLYP	XLYP functional	106.30 [114]	XCMGGA.X.BR80	Becks-Roussel 89	49.39 [147, 148]
XC.GGA.X.RPBE XC.GGA.X.WC	Hammer, Hansen & Norskov (PBE-like) Wu & Cohen	17.14 [76] 17.91 [77]	XC_GGA_XC_PBE1W XC_GGA_XC_MPWLYP1W	PBEIW (functional fitted for water) mPWLYPIw (functional fitted for water)	94.72 115	XC_MGGA_X_B306	Becke & Johnson 06	35.28 150
						XC_MGGA_X_TB09	Trun & Blaha 09	31.96 [151]

Things you can compute with DFT

Solving the KS equations gives you KS eigenenergies and wavefunctions

Crystal structure of solids, bulk modulus Reaction energies, electrochemical voltages 1 hour Thermodynamic phase stability Ionic transport: activation energies Computation complexity Dielectric properties, piezoelectric coefficients 1 day Vibrational spectra Thermo-mechanical properties, heat capacity, expansion Liquid structure, amorphous materials 1 week Raman spectra, NMR spectra Structure and transport on surfaces, interfaces Electronic conductivity, electron-phonon coupling Thermal conductivity, phonon-phonon scattering accuracy limit Optical excitations, photo-electricity

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

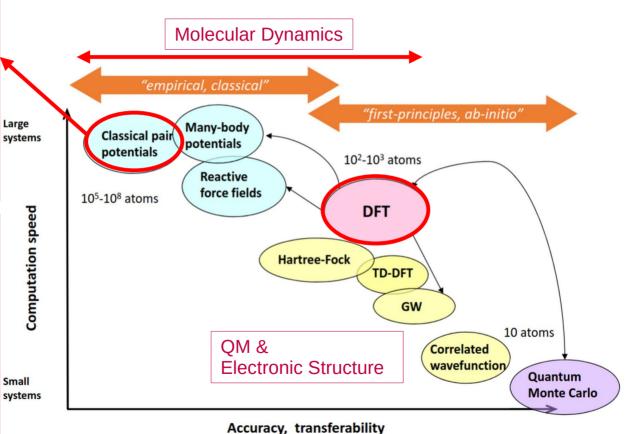
Lattice Sums and defects

Research practices with Python:

Data visualization

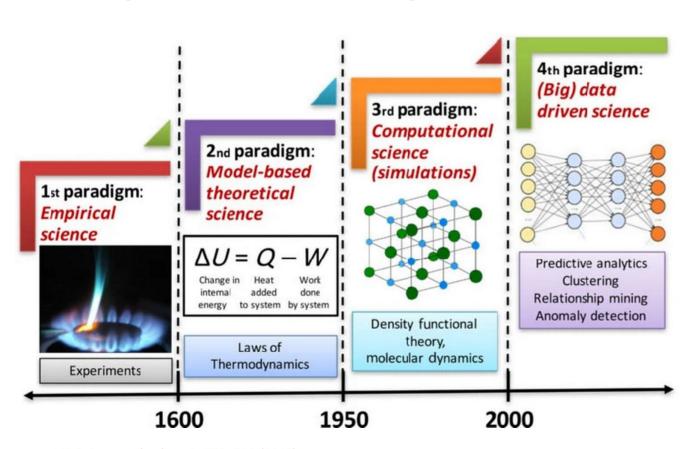
Coding environment/conventions

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

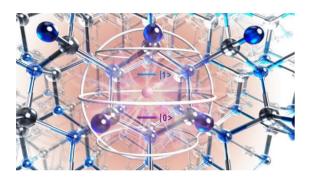
Active learning for interatomic potentials

Bayesian inference for experimental decision making

MRS Communications 9, 779–792 (2019).

Future directions in computational materials science

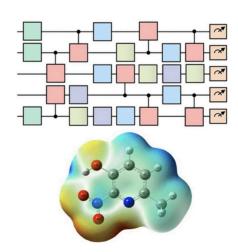
Quantum computers for the electronic structure problem



Engineering solid-state qubits

Implementing and running simulations of materials on quantum computers

Chem. Rev. 2020, 120, 22, 12685–12717 npj Comput Mater 6, 85 (2020).



Guest Lecturer:Dr. Roozbeh Anvari

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!



https://go.bl ueja.io/H3h PINxz2EmE 2v7NoAiKtA



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

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