TYC Materials Modelling

DFT Practicalities

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Kohn and Sham rewrote the Hohenberg–Kohn total energy functional as

$$egin{aligned} F_{ ext{HK}}[oldsymbol{
ho}] &= F_{ ext{KS}}[oldsymbol{
ho}] = T_s[oldsymbol{
ho}] + rac{1}{2} \iint rac{
ho(\mathbf{r})
ho\left(\mathbf{r}'
ight)}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' + E_{ ext{xc}}[oldsymbol{
ho}] \ &= T_s[oldsymbol{
ho}] + E_{ ext{Hartree}}\left[oldsymbol{
ho}
ight] + E_{ ext{xc}}[oldsymbol{
ho}] \end{aligned}$$

Where $T_{\rm s}$ is the kinetic energy of the particles in the noninteracting Kohn–Sham system. $E_{\rm xc}$ is then **defined** by this equation (thus transferring what we don't know from $F_{\rm HK}$ to $E_{\rm xc}$

Quick recap

Taking the functional derivative of the KS expression with respect to the density or the orbitals leads to the Kohn–Sham equations

$$igg[-rac{\hbar}{2m}
abla^2+V_{ ext{KS}}[oldsymbol{
ho}](extbf{r})igg]\phi_i(extbf{r})=arepsilon_i\phi_i(extbf{r})$$

Where the Kohn–Sham potential is given as:

$$egin{aligned} V_{ ext{KS}}[oldsymbol{
ho}](\mathbf{r}) &= V_{ ext{ext}}\left(\mathbf{r}
ight) + V_{ ext{Hartree}}\left[oldsymbol{
ho}](\mathbf{r}) + V_{ ext{xc}}[oldsymbol{
ho}](\mathbf{r}) \ V_{ ext{Hartree}}\left[oldsymbol{
ho}](\mathbf{r}) &= \int rac{
ho\left(\mathbf{r}'
ight)}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' \ V_{ ext{xc}}[
ho](\mathbf{r}) &= rac{\delta E_{ ext{xc}}[oldsymbol{
ho}]}{\delta
ho(\mathbf{r})} \end{aligned}$$

Quick recap

Clarification: Non-interacting particles but interacting density

$$\left[-rac{\hbar}{2m}
abla^2+V_{
m KS}[oldsymbol{
ho}]({f r})
ight]\phi_i({f r})=arepsilon_i\phi_i({f r})$$

Rather than feel the effect of the other electrons in a direct, particleby-particle way, Kohn–Sham particles feel the presence of each other through their effect on the Kohn–Sham potential

Put another way



Density functional theory (DFT) replaces the many-body N-dimensional electronic wavefunction with the 3-dimensional electron density

Lecture overview

DFT Practicalities

A. Where are the electrons?

B. Where are the atoms?

C. Which functional should I use?

Lecture overview

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Solving the KS equations

Finding the solutions of the KS is a chicken and egg problem

$$igg[-rac{\hbar}{2m}
abla^2+V_{ ext{KS}}[oldsymbol{
ho}](extbf{r})igg]\phi_i(extbf{r})=arepsilon_i\phi_i(extbf{r})$$

The KS potential $V_{\rm KS}$ depends on the density ρ . So, if we find the ρ that minimises the energy for a particular $V_{\rm KS}$, $V_{\rm KS}$ will change as a result.

Goal: We seek a self-consistent value of ρ , such that the energy is minimised and $V_{\rm KS}$ remains unchanged

Self consistent field cycle



Self consistent field cycle



Picking the next density

Large charge redistributions occur from one iteration to the next

Simply doing:

$oldsymbol{ ho}_{\mathrm{in}} = oldsymbol{ ho}_{\mathrm{out}}$

will typically not converge if iterated

Density mixing

The most obvious strategy is to damp the change by keeping some of the first input density in constructing the new output density



Example of direct mixing for a 2x2x2 supercell of pristine MgO

Density mixing

However, this is not guaranteed to converge and doesn't work for more complex examples due to charge sloshing instabilities



Example of direct mixing for a 2 × 2 × 2 supercell of MgO containing an oxygen vacancy

Density mixing – advanced

More complex mixing algorithms keep a record of all densities calculated and mix many densities together

Broyden and Pulay mixing are the most common



Mixing algorithms for a 2 × 2 × 2 supercell of MgO containing an oxygen vacancy

Self consistent field cycle



Self consistent field cycle



Diagonalisation schemes

Direct diagonalization works well for small problems but with plane waves the matrix can be huge and computationally intractable

$$\sum_{m'} = H_{m,m'}(\mathbf{k})c_{i,m'}(\mathbf{k}) = arepsilon_i(\mathbf{k})c_{i,m}(\mathbf{k})$$

Iterative methods (e.g. Blocked-Davidson) only require knowledge of how the Hamiltonian acts on a particular vector. Iteratively applying an operator allows one to extract the lowest-lying eigenstates (default in VASP)

Alternative methods include the "residual-minimization method with direct inversion in the iterative subspace (RMM-DIIS)"

If a band lies near to the Fermi level, it can be fully occupied in one iteration and fully deoccupied in the next, leading to instabilities

This is always going to happen for metals



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This is always going to happen for metals



A solution is to allow partial occupancy of bands near the Fermi level

$$ho(\mathbf{r}) = \sum_n f_n(T) |\psi_n(\mathbf{r})|^2$$

A "temperature" is used to define the distribution – not a physical temperature but a convergence parameter where we want the $T \rightarrow 0$ limit

A solution is to allow partial occupancy of bands near the Fermi level



A "temperature" is used to define the distribution – not a physical temperature but a convergence parameter where we want the $T \rightarrow 0$ limit

Smearing – insulators

For insulators, the bands should never be partially occupied but an incorrect smearing can sometimes cause this



The red colour indicates partial occupancy of the bands. The width of the smearing is too high and can give rise to incorrect energies and forces.

Smearing – insulators

For insulators, the bands should never be partially occupied but an incorrect smearing can sometimes cause this



One solution is to set a very small broadening width in semiconductors (e.g., SIGMA = 0.02) for VASP

Smearing – insulators

For insulators, the bands should never be partially occupied but an incorrect smearing can sometimes cause this



The best option is to use tetrahedron integration with Blöchl corrections instead (e.g., ISMEAR = -5 in VASP). However, you need at least 4 k-points

Impact of smearing functions

The choice of smearing can have a large impact on integrated properties, e.g. the density of states or response functions



"How to analyse a density of states", *Materials Today Electronics* 1, 100002 (2022)

You should always test the k-point sampling for your system. The sampling ratios depend on the reciprocal lattice dimensions

	Length cutoff	KSPACING	Sam	Samples	
	5.588	0.5622	2	2	2
FFFFF	11.176	0.3748 0.2811	3 4	3 4	3 4
	13.970 16.764	0.2249 0.1874	5 6	5 6	5 6

Different properties can converge differently with k-point sampling. For example, total energies will converge much faster than Raman intensitites

You should always test the k-point sampling for your system. The sampling ratios depend on the reciprocal lattice dimensions

Po P	Length cutoff	KSPACING	San	Samples	
	6.277	0.5005	3	4	2
	7.488	0.4196	3	5	2
	7.559	0.4156	4	5	2
	7.846	0.4004	4	5	3
	9.416	0.3337	4	6	3

For anisotropic systems, selecting the k-point meshes to test is non-trival Recommended to use: https://github.com/WMD-group/kgrid

Where does the total energy converge?



Note: metals typically require much denser meshes to converge

Where does the total energy converge?



Note: metals typically require much denser meshes to converge

Where does the total energy converge?



Note: metals typically require much denser meshes to converge

Basis set choices

Basis sets are used to represent the electronic wavefunctions



Other types include real-space grids, mixed basis sets and augmented methods

Basis set choices

Basis sets are used to represent the electronic wavefunctions

Plane waves

Good for periodic systems
 Straight-forward to converge
 Straight-forward to converge
 No geometry dependence
 Mathematically simple
 Not good for sharp features
 Required even in empty space
 Need many PWs to converge

Atom centred

- ✓ Good for core states
- Correspond to atomic orbitals
- Relatively few functions needed
- Better scaling for large systems
- × Not orthogonal
- ✗ Basis set superposition errors
- X Linear dependencies

Different types: Gaussian, Slater

Other types include real-space grids, mixed basis sets and augmented methods

Plane wave cutoff convergence

You should always test the plane wave cutoff for your system. This only needs to be done once per composition-structure combo



Different properties can converge at different cutoff. For example, total energies will often converge faster than the stress

Spin State



Notes on spin

If your system is spin-polarized you should carefully consider the spin states before running any calculations

A DFT code will normally guess that systems with an even number of electrons are singlets and that systems with odd numbers of electrons are doublets

Although there are methods that will optimize the spin states, they are not very good and normally get stuck on the initial guess. You will normally need to try higher spin states by hand if you think they might be lower in energy
Example – oxygen

Both atomic and molecular oxygen have a triplet ground state





Example with VASP – oxygen

Example INCAR tags needed to set the triplet spin state of O₂

- ISPIN = 2 ! Enable spin polarisation
- MAGMOM = 1 1 ! Initial magnetic moment on each ion
- NUPDOWN = 2 ! Enforce spin multiplet



Other DFT codes such as CASTEP will have similar settings

Example – ferromagnets

In ferromagnetic materials, all the spins point the same way. E.g., CrO_2 where Cr is d² and there are 2 Cr atoms in the unit cell



ISPIN	=	2		
MAGMOM	=	2	2	6*0
NUPDOWN	=	4		

Example – antiferromagnets

Alternatively, if the system is antiferromagnetic, the spins point in opposite directions and the total magnetisation is cancelled



ISPIN	=	2		
MAGMOM	=	2	-2	6*0
NUPDOWN	=	0		

Lecture overview

DFT Practicalities

A. Where are the electrons?

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Geometry optimisation

We can either calculate energies given the input atomic positions or we can geometry optimise to find the low energy structure



For a NaCl dimer, the only structural parameter is the separation



Geometry optimisation finds local minima not the global minimum



Generalised coordinate

Local minima are still important

Local minima can represent allotropes that are stable. Relaxing these structures would not find the global minimum (graphite)



A. R. Oganov et al. *Reviews in Mineralogy and Geochemistry* 75, 1, (2013)

Geometry optimisation – theory

Problem is to find the set of atomic positions $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\}$ and lattice vectors $\mathbf{a} = \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$ that define the minimum (stationary point) on the potential-energy surface

$$\mathbf{F}_{i} = -rac{\partial E_{0}}{\partial \mathbf{r}_{i}} = -\left\langle \Psi_{0}(\mathbf{R}, \mathbf{a}) \left| rac{\partial H(\mathbf{R}, \mathbf{a})}{\partial \mathbf{r}_{i}}
ight| \Psi_{0}(\mathbf{R}, \mathbf{a})
ight
angle$$

$$\sigma_{ij} = -rac{\partial \, E_0}{\partial \, \sigma_{ij}} = - \left\langle \Psi_0({f R},{f a}) \left| rac{\partial \, H({f R},{f a})}{\partial \, \sigma_{ij}}
ight| \Psi_0({f R},{f a})
ight
angle$$

Approach: Adjust an initial **R** and **a** to minimize E_0 , F_i and/or σ_{ij} via an optimisation algorithm

Optimisation and symmetry

Performing an optimisation involves using an algorithm to locate a minimum on a multidimensional potential energy surface (PES)



Optimisation and symmetry

Crystal symmetry can significantly reduce the number of degrees of freedom



Atoms fixed at
$$(0,0,0)$$
 and $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$

$$a = b = c$$
 and $a = eta = \gamma = 90^\circ$

One DoF: the lattice constant a

NaCl $Fm\bar{3}m$

Optimisation and symmetry

Crystal symmetry can significantly reduce the number of degrees of freedom



Atoms in the a/b plane fixed

$$a = b
eq c$$
 and $a = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$

Three DoFs: a, c and u

Wurtzite ZnS $P6_3mc$

Gradient descent

Follow the forces/stresses to the nearest minimum

$$egin{aligned} \mathbf{R}_{n+1} &= \mathbf{R}_n - \gamma
abla E(\mathbf{R}_n) \ &= \mathbf{R}_n + \gamma \mathbf{F}(\mathbf{R}_n) \end{aligned}$$



Pros and cons: Slow "zig-zag" convergence to the minimum; requires many iterations

Newton-Raphson

Follow the forces/stresses to the nearest minimum

$$egin{aligned} \mathbf{R}_{n+1} &= \mathbf{R}_n - \gamma \mathbf{H}(\mathbf{R}_n)^{-1}
abla E(\mathbf{R}_n) \ &= rac{\partial^2 E}{\partial \mathbf{R}_n^2} \end{aligned}$$



Pros and cons: Fast convergence but requires a cheap (approximate) inverse Hessian

Conjugate gradient

Follow the forces/stresses to the nearest minimum

$$egin{aligned} \mathbf{R}_{n+1} &= \mathbf{R}_n - k_n \mathbf{h}_n \ \mathbf{h}_n &= rac{\partial \, E}{\partial \, \mathbf{R}_n} + \gamma_n \mathbf{h}_{n-1} \end{aligned}$$



Pros and cons: A good middle ground between steepest descent and Newton-Raphson for convergence speed and cost

Other optimisation algorithms exist

The implementation of optimisation methods is not consistent across DFT packages – other approaches include

- **BFGS**: Robust and fast for most problems
- L-BFGS: Low memory version that can be useful for large systems
- **FIRE**: More modern method, worth trying for difficult cases

Performance will depend on your application and it is worth testing if you can speed a calculation up by changing algorithm

Choosing the optimisation method – VASP



Image from: https://www.vasp.at/wiki/index.php/VASP_workshop

Types of geometry optimisation

There is a lot of flexibility in what to optimise in a calculation

- **Geometry optimisation**: Minimise the total energy by moving the atoms and minimising forces
- **Cell optimisation**: Minimise the stress tensor by modifying the cell vectors (lengths and angles)
- **Both**: Attempt both kinds of optimisation at the same time

Different DFT codes treat geometry and cell optimisation differently – some will treat them as different types of calculations (CP2K) and others as the same type (Castep, VASP)

Example optimisation – VASP

The ISIF tag sets the details of what to optimise

ISIF	Positions	Cell shape	Cell volume
2	\checkmark	×	×
3	\checkmark		\checkmark
4	\checkmark		×
5	×		×
6	×		\checkmark
7	×	×	\checkmark

Pulay stress

The plane wave basis depends on the reciprocal lattice vectors and hence the cell shape and volume

During a variable cell optimisation, the basis set can become incomplete and lead to artificial (Pulay) forces



To mitigate: Increase plane wave cutoff to 1.3–2 times the converged value

Energy/volume curves

An alternative way to obtain the equilibrium volume is to calculate an energy-volume curve

- 1. Perform a series of constant-volume relaxation
- 2. Locate the minimum by fitting to an equation of state such as Birch-Murnaghan this gives equilibrium volume V_0 , energy E_0 , and bulk modulus B_0

$$E(V) = E_0 + rac{9V_0B_0}{16} \left\{ \left[\left(rac{V_0}{V}
ight)^{rac{2}{3}} - 1
ight]^3 B_0' + \left[\left(rac{V_0}{V}
ight)^{rac{2}{3}} - 1
ight]^2 \left[6 - 4 \left(rac{V_0}{V}
ight)^{rac{2}{3}}
ight]
ight\}$$



Comparison of wurtzite (w) vs zinc blende (c) ZnO



Troubleshooting

Problem

My optimisation is taking a long time to converge

Things to check

- Are your electronic SCF steps converging properly? One failed SCF can undo several optimisation steps
- Is your force convergence criteria reasonable large low-symmetry structures are hard to converge to high tolerances

Things to try

- Change your optimisation algorithm
- Change the step size if the PES is very shallow (e.g. POTIM in VASP)

Troubleshooting

Problem

My optimisation is diverging

Things to check

- Are your electronic SCF steps converging?
- Is your input structure reasonable? Experimental structures are definitely not infallible. Check for badly placed H atoms, partial occupancies and dodgy CIFs
- Is your POTCAR ordered correctly?
- If using spin polarisation, are your settings correct?

Things to try

- Change your optimisation algorithm
- Change the step size if the PES is very shallow (e.g. POTIM in VASP)

Troubleshooting

Problem

My optimised structure doesn't match experiment/previous calculations

Things to check

- If comparing to experiment: i) is the experimental structure good quality? ii) Have you considered thermal expansion? iii) Ideally you want single-crystal Xray or neutron data recorded close to O K.
- If comparing to calculations: i) Are you using a comparable setup (XC function, cutoff, k-point sampling, ...). ii) Are your chosen parameters more appropriate than those used in previous work?

Things to try

• Different XC functions – PBEsol or PBE-D3 instead of PBE.

Not all stationary points are equal

Problem is to find the set of atomic positions $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\}$ and lattice vectors $\mathbf{a} = \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$ that define the minimum (stationary point) on the potential-energy surface



Not all stationary points are equal

Computing the force constants and obtaining the harmonic phonon frequences from the dynamic matrix allows us to confirm we have located a minimum



Comparing with experiment

A range of excellent databases of crystal structures exist



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Detailed View							Entry 1 of 1 😧
Q Back to Query	E Back to List			r CCDC	Export Cif	🔒 Print	Eeedback to Editor
Summary							Collection Code 9863
Struct. formula	Mg O		Structure type	NaCl			
Cell parameter	4.217(1) 4.217((1) 4.217(1) 90. 90. 90.	Space group	F m -3 m (225)			
Cell volume	74.99 [Å ³]		Z	4			
Temperature	room temperat	ture	Pressure	atmospheric			
Data quality	High quality		R-value	0.0126			
Author	Sasaki, S.; Fuj	jino, K.; Takeuchi, Y.;	Title	X-ray determination of ele and Ni O, and atomic sca	ectron-density dist attering factors of t	ributions in ox heir constitue	kides, Mg O, Mn O, Co O, nt atoms
Reference	Proceedings of	f the Japan Academy (1979) 55, p. 43-48 (4 structures) 🔗	DOI	10.2183/pjab.55.43 🗹			
Details						د ^م Expand	all 🦽 Collapse all 👔
 Visualization 							

Published Crystal Structure





Lul Interactive Visualization

Lecture overview

DFT Practicalities

A. Where are the electrons?

B. Where are the atoms?

C. Which functional should I use?

Jacob's ladder of DFT functionals

The Jacob's ladder of density functional approximations to the exchange-correlation energy adds local ingredients successively, leading up in five steps from the Hartree world ($E_{xc} = 0$) of weak or no chemical bonding to the heaven of chemical accuracy



J. P. Perdew et al. "Some fundamental issues in ground-state density functional theory: A guide for the perplexed", *J. Chem. Theory Comput.* 5 4 (2009)

Local density approximation (LDA)

XC energy is locally approximated with the value of a homogeneous electron gas of the same density. Computationally the cheapest

$$E_{
m x}^{
m LDA}[m{
ho}] = -rac{3}{4}igg(rac{3}{\pi}igg)^{1/3}\int
ho({f r})^{4/3}{
m d}{f r}$$

Only run of the ladder that doesn't include any empirical parameters

Generalised gradient approximation (GGA)

A family of functionals including PBE, PBEsol, PW91, BLYP

$$E_{\mathrm{x}}^{\mathrm{GGA}} = E_{\mathrm{x}}^{\mathrm{GGA}} \left[
ho(\mathbf{r}),
abla
ho(\mathbf{r})
ight]$$

- Negligible computational cost increase on LDA but greater range
 of available parameters
- PBE is considered one of the best general purpose GGA
- Other GGAs might be better for a specific purpose but tend to be weaker in other areas (PBEsol best for solids)
- At the limit of improving GGA performance (PBE is from 1996)

Meta-GGAs

Include a dependence on the kinetic energy density of electrons

$$E_{\mathrm{x}}^{\mathrm{mGGA}} = E_{\mathrm{x}}^{\mathrm{mGGA}} \left[
ho(\mathbf{r}),
abla
ho(\mathbf{r}),
abla^2
ho(\mathbf{r}), au(\mathbf{r})
ight]$$

- In meta-GGAs the XC potential becomes orbital dependent
- Small computational cost increase on GGA. Making meta-GGAs better than GGAs is very hard. They are often less transferable
- Earlier attempts like the TPSS functional (2003) have not been used much in practice
- Newer GGAs like r²SCAN (2020) seem more promising

The need to go beyond DFT and Hartree-Fock

More accurate treatment of electronic correlation needed for band gaps, atomization energies, reaction barriers, VDW interactions



Atomization energy			
	LDA	PBE	
MRE (%)	17.3	-1.9	
MARE (%)	17.3	3.4	
ME (eV)	0.76	0.14	

Hybrid functionals

XC functionals that mix some Fock exchange with semi-local DFT

$$E_{\mathrm{x}}^{\mathrm{hybrid}} = lpha E_{\mathrm{x}}^{\mathrm{HF}} + (1-lpha) E_{\mathrm{x}}^{\mathrm{GGA}}[
ho(\mathbf{r}),
abla
ho(\mathbf{r})]$$

- Using non-local exchange is extremely computationally expensive. Guaranteed to be most expensive part of resulting DFT calculation
- Importance choice is how much non-local exchange to use
- Functionals also differ in how they treat long range exchange
- Started out as empirical method by now well justified through the adiabatic connection theorem (see 10.1103/RevModPhys.80.3)


Empirical functional fitted to reproduce atomization energies, ionization potentials, proton affinities, and atomic energies

$$egin{aligned} E_{ ext{xc}}^{ ext{B3LYP}} &= 0.8 E_{ ext{x}}^{ ext{LDA}} + 0.2 E_{ ext{x}}^{ ext{HF}} + 0.72 (E_{ ext{x}}^{ ext{GGA}} - E_{ ext{x}}^{ ext{LDA}}) \ &+ 0.19 E_{ ext{c}}^{ ext{LDA}} + 0.81 (E_{ ext{c}}^{ ext{GGA}} - E_{ ext{c}}^{ ext{LDA}}) \end{aligned}$$

- B3LYP is more reliable for lighter elements as this is what it was fitted to (atoms and simple molecules)
- The most popular hybrid functional for organic molecules
- Arbitrary mix of GGA/LDA not common in most hybrid functionals



The PBEO functional uses ¼ exact exchange – justified according to MP4 theory

$$E_{\mathrm{xc}}^{\mathrm{PBE0}} = rac{1}{4}E_{\mathrm{x}}^{\mathrm{HF}} + rac{3}{4}E_{\mathrm{x}}^{\mathrm{PBE}} + E_{\mathrm{c}}^{\mathrm{PBE}}$$

- Significantly more costly to apply to solids than B3LYP is to molecules as it is hard to converge with respect to k-points (B3LYP would have same issues if it were used with solids)
- A popular hybrid functional in Physics

HSE06

Designed to be better behaved with k-point sampling – Long range exchange is turned off using the parameter ω

$$E_{ ext{xc}}^{ ext{HSE06}} = rac{1}{4} E_{ ext{x}}^{ ext{HF,SR}}(\omega) + rac{3}{4} E_{ ext{x}}^{ ext{PBE,SR}}(\omega) + E_{ ext{x}}^{ ext{PBE,LR}}(\omega) + E_{ ext{c}}^{ ext{PBE}}$$

- The standard value of $\omega = 0.2$ is used (reduces to PBEO for $\omega = 0$)
- Screening exchange in this manner reduces the computational cost significantly
- Although motivated by computational considerations, HSE06 outperforms PBE0 for small and medium gap semiconductors

Performance for solids

Hybrids significantly improve on GGA but still aren't perfect



Marsman et al. J. Phys.: Condens. Matter 20 064201 (2008)

Performance for solids

Table 1. The mean absolute error (MAE) in lattice constants a_0 (Å), cohesive energies E_0 (eV/atom), and bulk moduli B_0 (GPa) on testing sets of bulk crystals using different density-functional approximations reported from literature benchmarks^a. The mean absolute relative error (MARE) and the maximum absolute relative error (MAX) are given in percentage.

		LDA	PBE	PBEsol	TPSS	revTPSS	HSE06
<i>a</i> ₀	MAE	0.071	0.061	0.030	0.054	0.039	0.033
	MARE	1.5	1.2	0.6	1.1	0.8	0.7
	MAX	4.9	2.8	2.3	4.1	3.3	2.0
<i>B</i> ₀	MAE	11.5	12.2	7.8	9.6	9.6	7.3
	MARE	9.4	11.0	7.0	10.3	9.4	4.0
	MAX	32.8	25.5	19.5	29.6	25.8	23.4
E ₀	MAE	0.77	0.19	0.31	0.20	0.22	0.25
	MARE	17.2	5.0	6.9	4.9	5.1	6.5
	MAX	38.7	21.0	22.8	15.3	17.7	25.0

Hybrid exchange

The amount of exchange needed to describe a material is related to the dielectric screening (itself a material-specific property)



J. H. Skone et al. *Phys. Rev. B* 89, 19 (2014); D. Fritsch et al. *Nano. Res. Lett.* 12, 19 (2017)

Failures of XC functionals

- You can't mix and match XC functionals systematically, so hard to describe systems where different functionals are appropriate, e.g., molecule on metal, metal/semiconductor interface
- Very poor description of long-range interactions, such as van der Waals (need empirical corrections such as D3)
- Better at molecular binding energies (does chemical reaction happen) vs barriers (how fast does chemical reaction happen)
- Routes to XC functional improvement seem to require calculations to be very expensive (see double hybrid functionals)

Failures of hybrid functionals

Care needs to be taken with transition metals – the set values of exchange are not always correct

Table 2 Table comparing the GGA, HSE06 and HF calculated $t_{2g}^{6}-e_{g}^{0}$ splitting for $[M^{III}(NH_{3})_{6}]^{3+}(M^{III} = Co, Rh, Ir)$ octahedral complexes with their experimental values. All splittings are given in eV

Material	PBE	HSE06	HF	Expt. ⁷⁵
$[Co(NH_3)_6]^{3+}$	2.61	6.24	24.51	2.85
$[Rh(NH_3)_6]^{3+}$	3.73	6.10	17.20	4.22
$[Ir(NH_3)_6]^{3+}$	4.36	6.45	16.74	5.08

D. O. Scanlon and G. W. Watson Phys. Chem. Chem. Phys. 13, 9667 (2011)

Beyond DFT

GW theory and its many flavours can correct many issues with hybrid functionals – but expect a high computational price



Forces are not readily available from GW calculations - instead use RPA

Conclusions

- 1. Density mixing is an important part of SCF calculations
- 2. Geometry optimisation can find local minima in the energy landscape, which may or may not be the global minimum
- 3. Local functionals are cheap and good for many properties. Difficult to find better general-purpose functionals than PBE
- 4. Hybrid functionals require significant computational resources but offer improved band gaps

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