

# An (Opinionated) Introduction to Density-Functional Theory

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# Partnership between theory and experiment

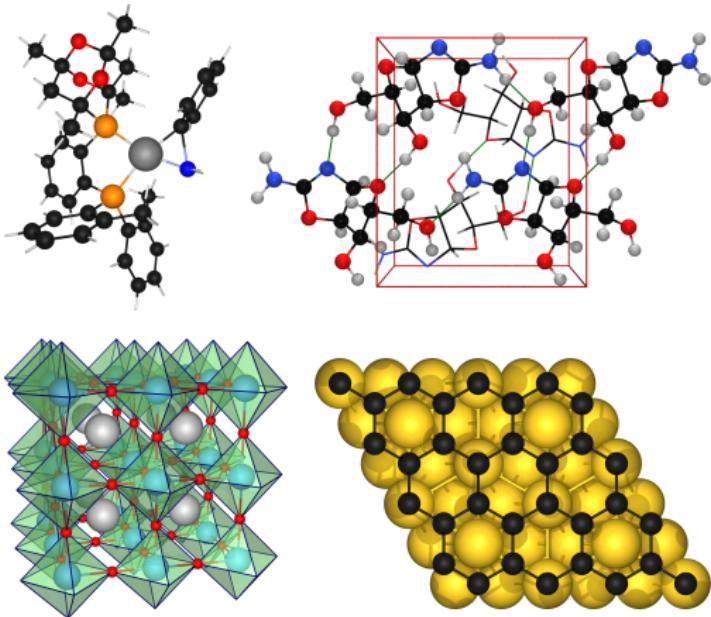
Simulating chemical processes computationally can help interpret and inform experiment.



# What can theory predict?

The aim of quantum chemistry is to accurately predict molecular and materials properties from first principles.

- molecular or crystal geometries
- thermodynamic quantities
- mechanisms and chemical kinetics
- spectroscopic quantities
- mechanical properties



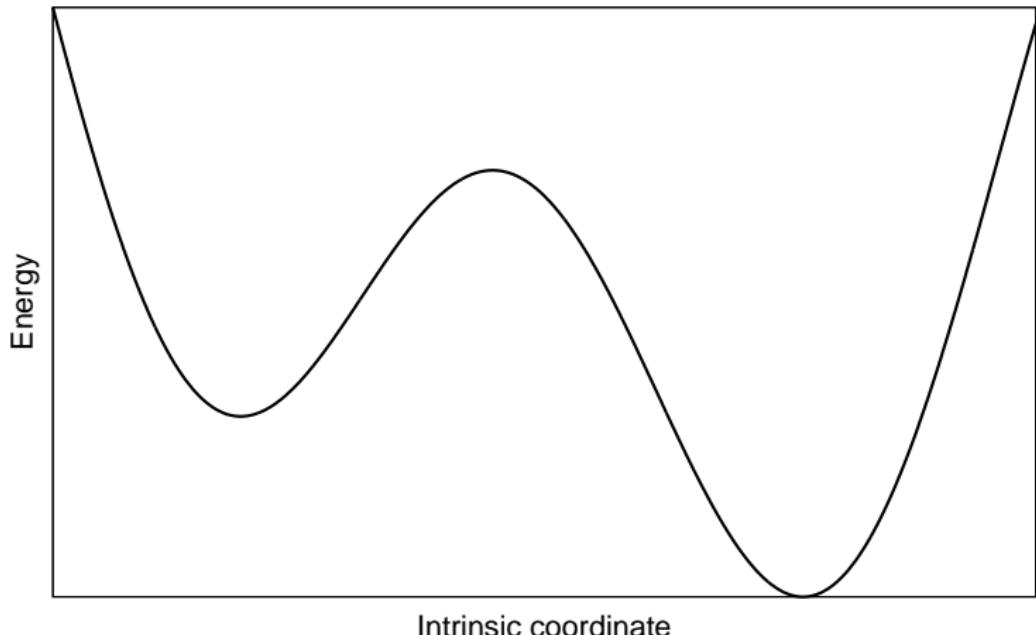
# Calculation details

When setting up a calculation it is important to consider:

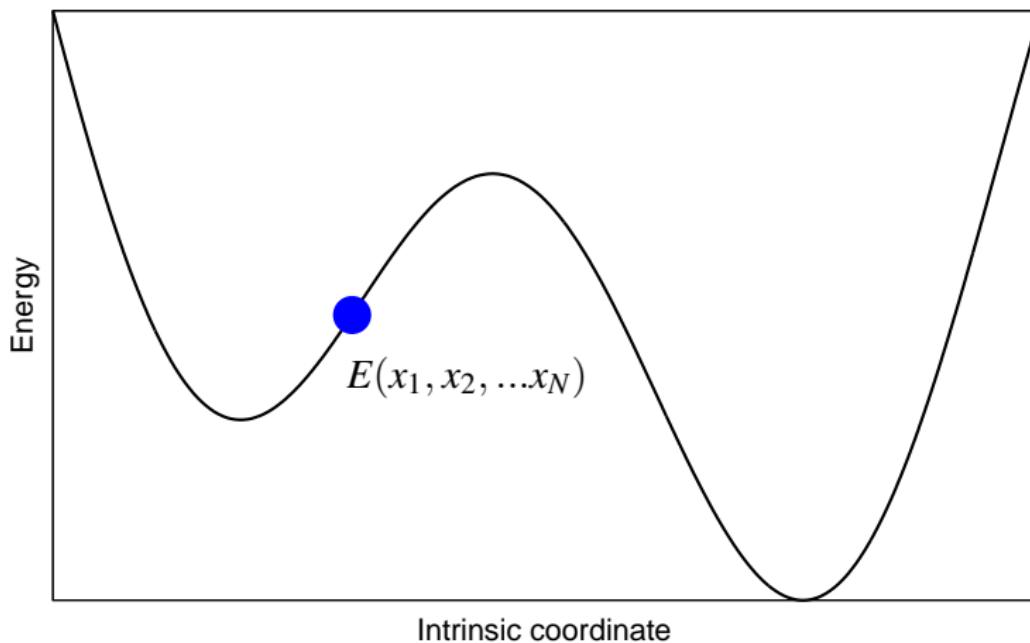
- The geometry of the system under study, including atom positions, charge, spin, and unit-cell
- The choice of density functional (and dispersion correction)
- The basis set and ECPs/pseudopotentials
- Any other specific options (solvent, relativistic corrections, etc.)

# What types of calculations are possible?

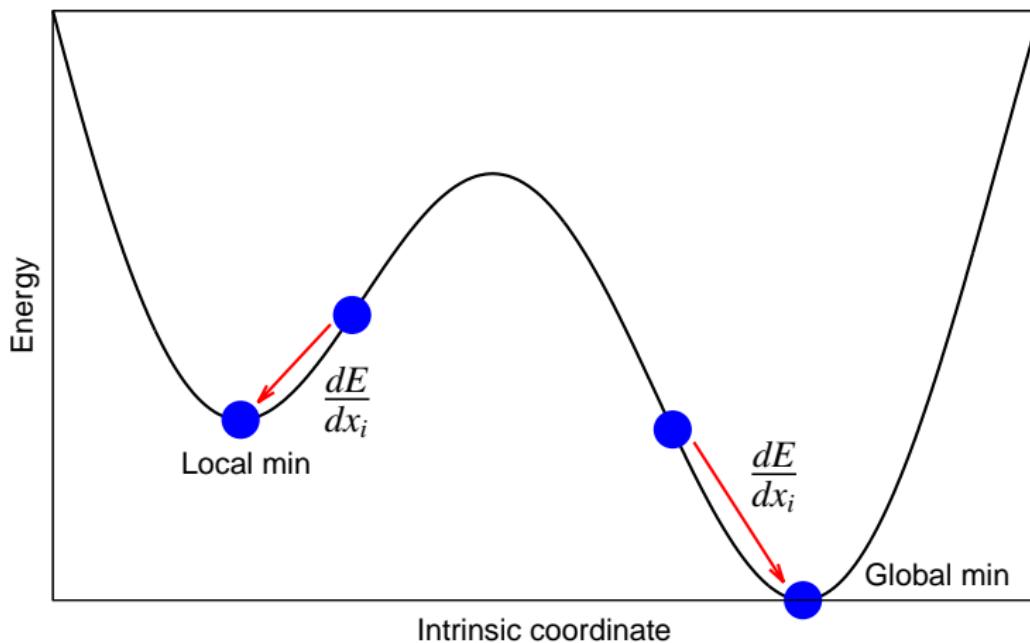
Consider a potential energy surface (PES):



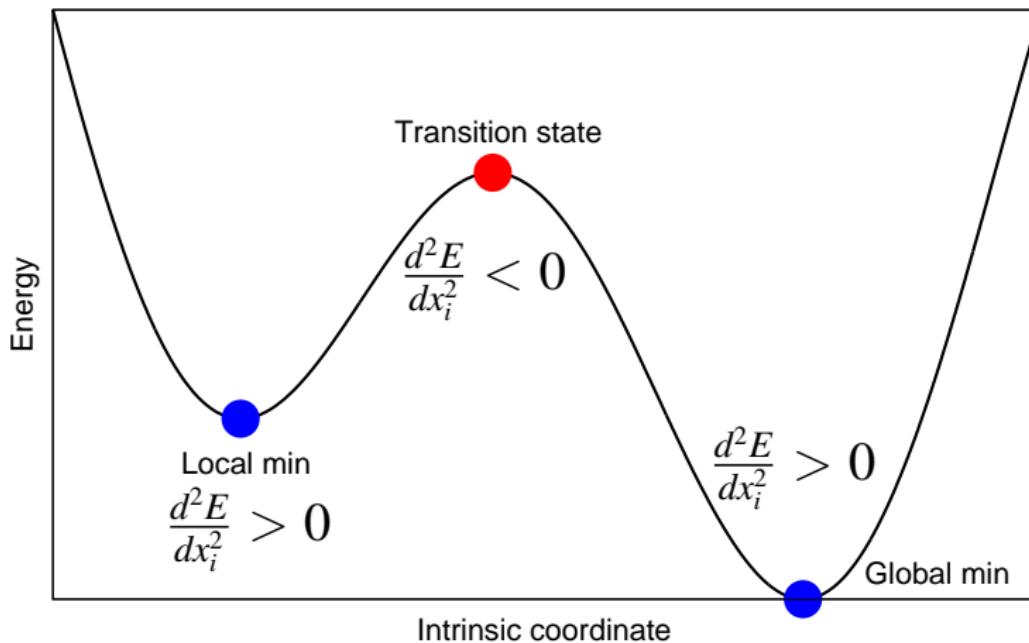
# Calculation types — single-point energy



# Calculation types — geometry optimization



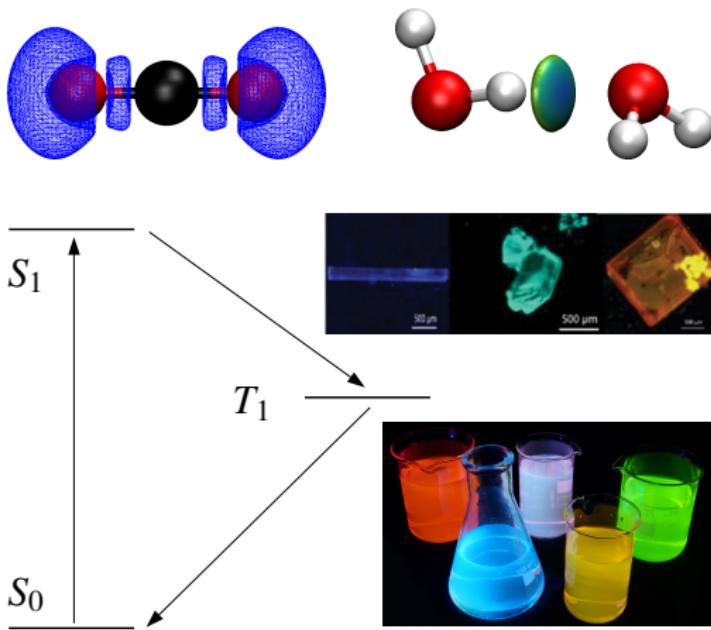
# Calculation types — frequencies



# Other calculation types

Detailed analysis of a particular property can also be done as part of a single-point energy calculation.

- Charge analysis
- Energy decomposition
- ELF and NCI plots
- Band structures
- Density of states
- Excitation energies
- NMR shieldings



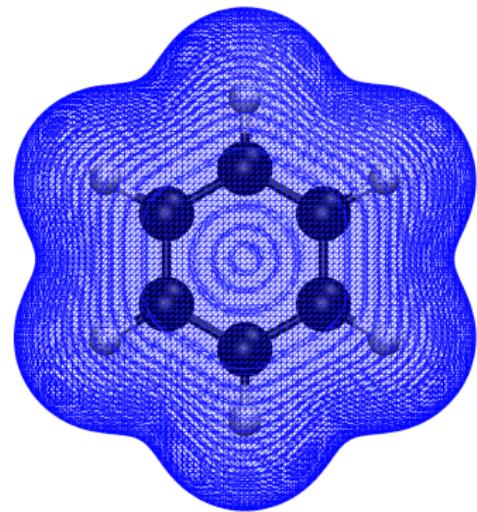
# Electron density and energy

The occupied MOs generate the 3D electron density,  $\rho$ .

$$\rho = \sum_i |\phi_i|^2$$

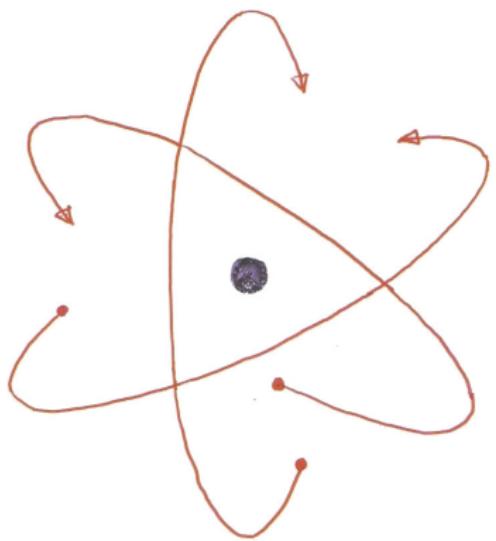
The energy is written as a functional of the density:

$$E = E[\rho(x, y, z)]$$

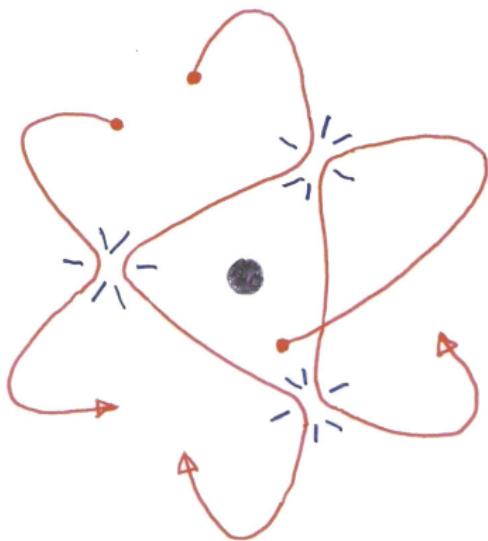


# What is the challenge?

Electrons cannot be treated as classical, independent particles.



vs.



# Density-functional theory (DFT)

The DFT energy is written as a sum of terms:

$$E = T_0 + V(\rho) + J_0(\rho) + E_{XC}(\rho)$$

- $T_0$  is the kinetic energy of the electrons
- $V$  is the electron-nuclear potential energy
- $J_0$  is the classical electron-electron repulsion energy
- $E_{XC}$  is the exchange-correlation energy

$E_{XC}$  is the difference between the classical and quantum-mechanical electron-electron interactions.

# Density-functional approximations (DFAs)

The DFT energy is written as a sum of terms:

$$E = T_0 + V(\rho) + J_0(\rho) + E_{\text{XC}}(\rho)$$

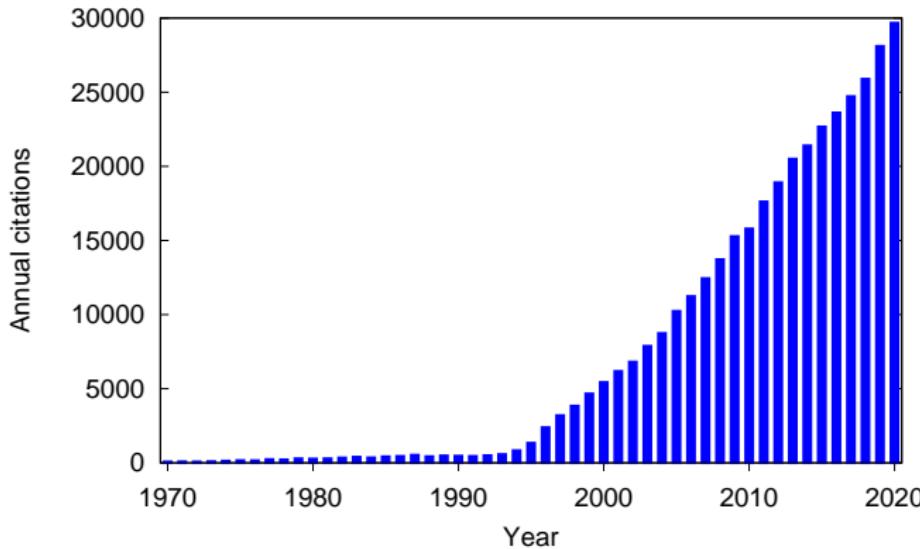


The forms of  $T_0$ ,  $V$ , and  $J_0$  are known and straightforward to compute.

The exact form of  $E_{\text{XC}}$  is unknown and there is no systematic route to obtain it – very many DFAs have been proposed over 4 decades.

# Density-functional approximations (DFAs)

While DFT was formulated in 1965, the most popular DFAs were developed between 1986-1996.



Walter Kohn



Axel Becke

Their use is increasing with advances in computer technologies.

# Hierarchy of DFAs

In order of roughly increasing accuracy and computational time:

- The local spin-density approximation (LSDA) —  $E(\rho)$
- Generalized gradient approximations (GGAs) —  $E(\rho, \nabla\rho)$ 
  - ▶ common examples: BLYP, PW91, PBE, PBEsol, B86bPBE
- meta-GGAs —  $E(\rho, \nabla\rho, \nabla^2\rho, \tau)$ 
  - ▶ common examples: BR, M06-L, SCAN
- Global hybrids — global mixing of DFAs with Hartree-Fock (HF)
  - ▶ common examples: B3LYP, PBE0, M06-2X
- Range-separated hybrids — variable mixing of DFAs with HF
  - ▶ common examples: LC-BLYP, LC- $\omega$ PBE,  $\omega$ B97X

# Density-functional thermochemistry

Mean absolute errors, in kcal/mol, for 222 heats of formation:

<i>Method type</i>	<i>MAE</i>
Hartree-Fock	225
LSDA	120
(meta-)GGAs	~ 10
Hybrids	~ 2-5

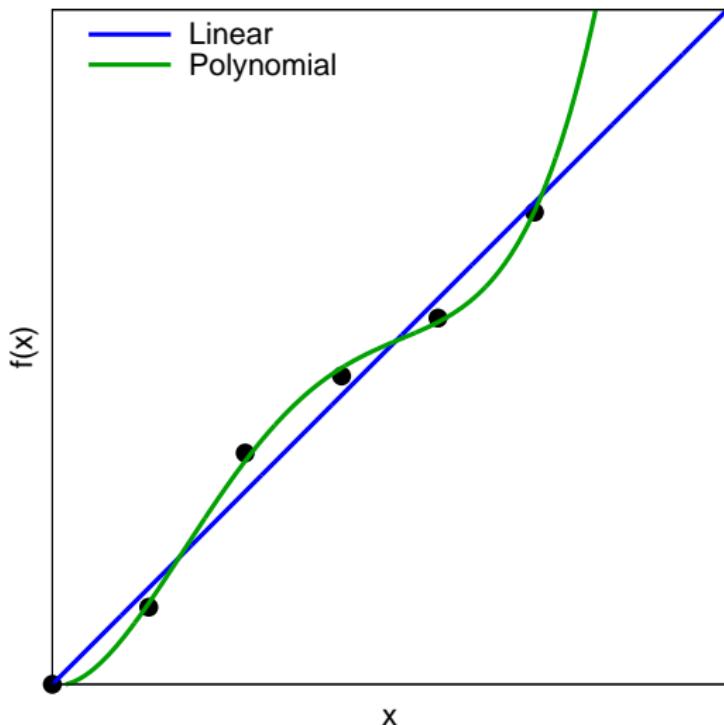
Hybrid functionals are quite accurate for intramolecular bonding.

# Physics vs. parameterization

Two schools of thought in functional development:

- Physical constraints
- Empirical parameters

“With four parameters I can fit an elephant, and with five I can make him wiggle his trunk.”



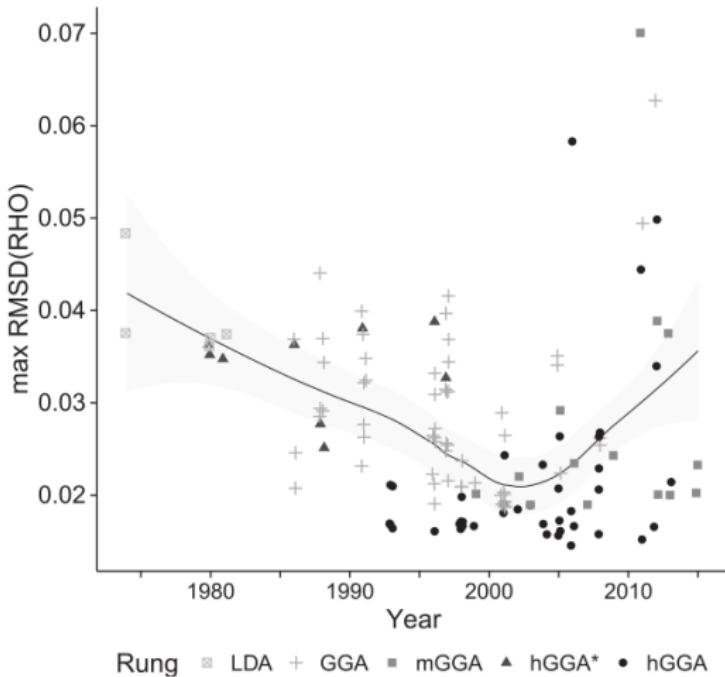
John von Neumann

# Physics vs. parameterization

Two schools of thought in functional development:

- Physical constraints
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Too many parameters can lead to over-fitting and errors outside the fit set.



## What type of DFA should I use when?

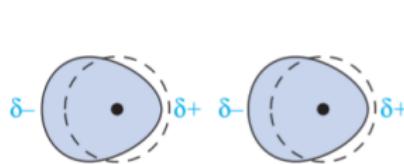
Solid-state: use GGAs, like PBE or B86bPBE, since hybrids are too expensive (at least with plane waves).

Molecular: use global hybrids like B3LYP or PBE0, unless you have:

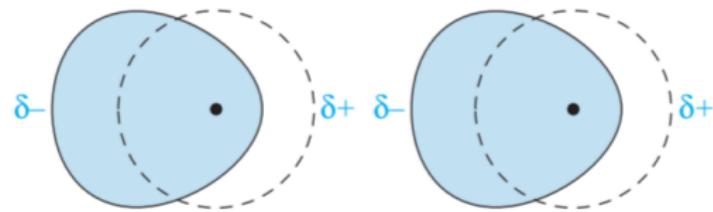
- Delocalization/self-interaction error:
  - ▶ Examples include charge-transfer complexes, halogen bonding, H-atom transfer transition states, etc.
  - ▶ use range-separated hybrids like LC- $\omega$ PBE,  $\omega$ B97X
- Multi-reference systems/strong correlation error:
  - ▶ Examples include open-shell singlet biradicals ( $^1\text{O}_2$ ), some transition-metal compounds ( $\text{Cr}_2$ )
  - ▶ Use correlated-wavefunction theory, not DFT, if possible
  - ▶ Otherwise, use GGAs, like PBE or B86bPBE

# Dispersion corrections

London dispersion is responsible for condensation of non-polar species, like noble gases and hydrocarbons.



Neon (10 electrons)

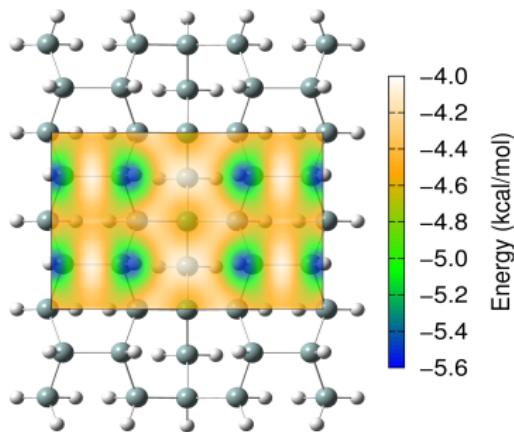
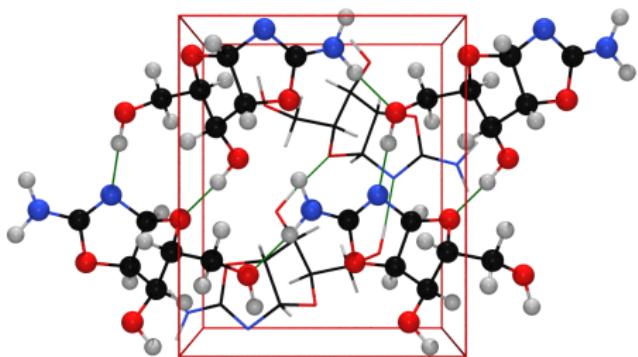


Xenon (54 electrons)

The strength of dispersion interactions increases with polarizability, explaining boiling-point trends.

This long-range non-local interaction is not captured by most density functionals.

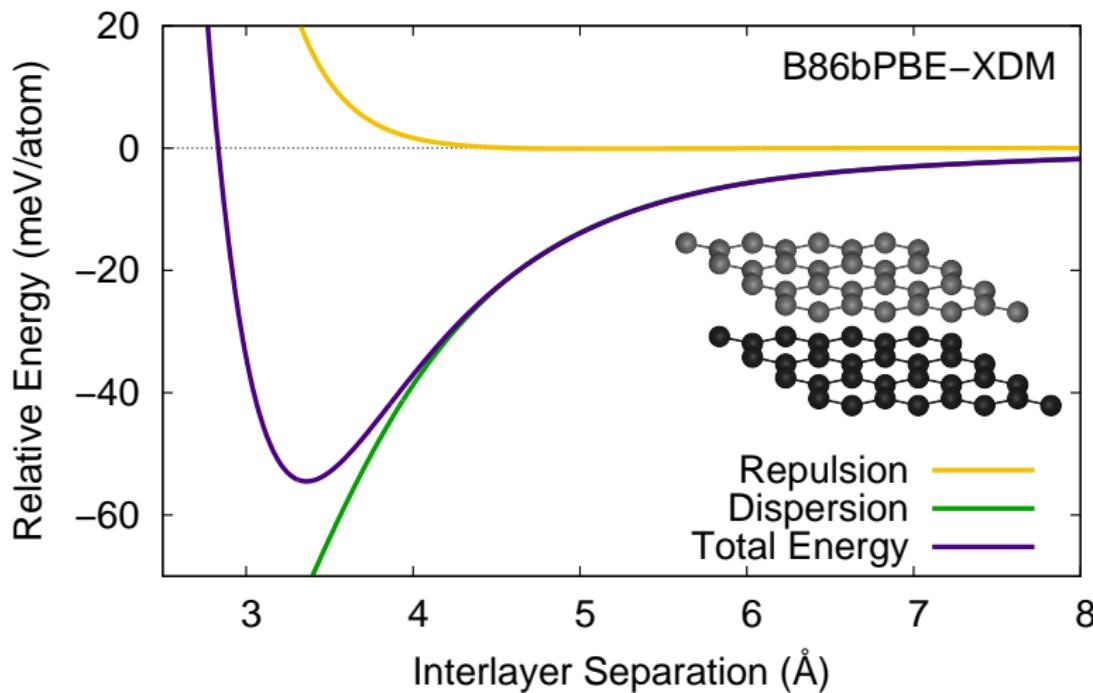
# Dispersion interactions



- Biomolecular structure
- Self-assembly
- Layered materials
- Surface adsorption
- Phase transitions
- Crystal packing

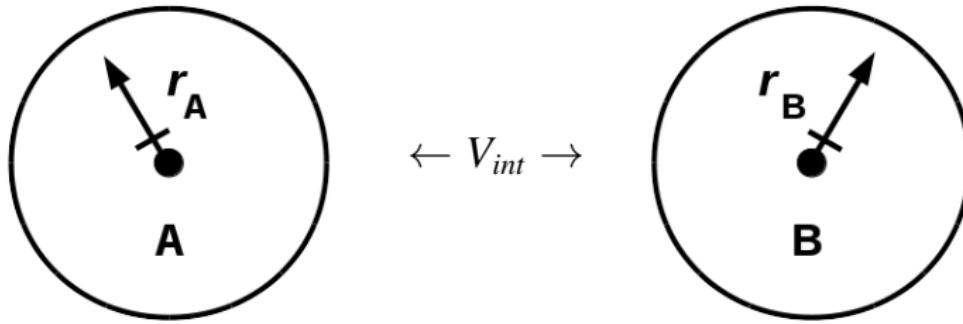
# Dispersion interactions: graphite

Explicit dispersion-energy terms need to be added to DFT methods.



# The dispersion energy

Dispersion arises from interaction of instantaneous dipoles (and higher-order multipoles) in the electron density distribution.



The dispersion energy can be written as a sum over all atom pairs:

$$E_{\text{disp}} = - \sum_{i < j} \left( \frac{C_6}{R_{ij}^6} + \frac{C_8}{R_{ij}^8} + \dots \right)$$

# Hierarchy of dispersion corrections

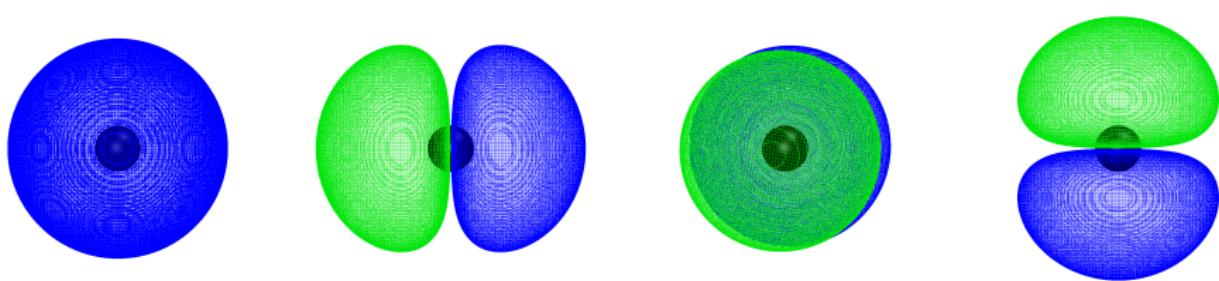
In order of roughly increasing accuracy and computational time:

- D2, TS —  $C_6$ 's are fixed or weakly dependent on environment
- D3, D3(BJ) — dispersion coefficients depend on coordination
- XDM, MBD — highly dependent on environment
- vdW-DF, rVV10 — explicitly non-local XC functional

Choosing any is better than nothing — dispersion corrections are physically important and should not be viewed as optional.

## Atom-centered basis sets

Take linear combinations of atomic orbitals to form molecular orbitals:



$$\phi = c_1\chi_1 + c_2\chi_2 + \dots + c_n\chi_n = \sum_{i=0}^n c_i\chi_i$$

However, using hydrogen-like AOs is not practical for computing the electron-electron repulsion integrals.

# Gaussian basis sets

Use a sum of Gaussians to represent each AO:

$$\chi = Nx^i y^j z^k e^{-ar^2}$$

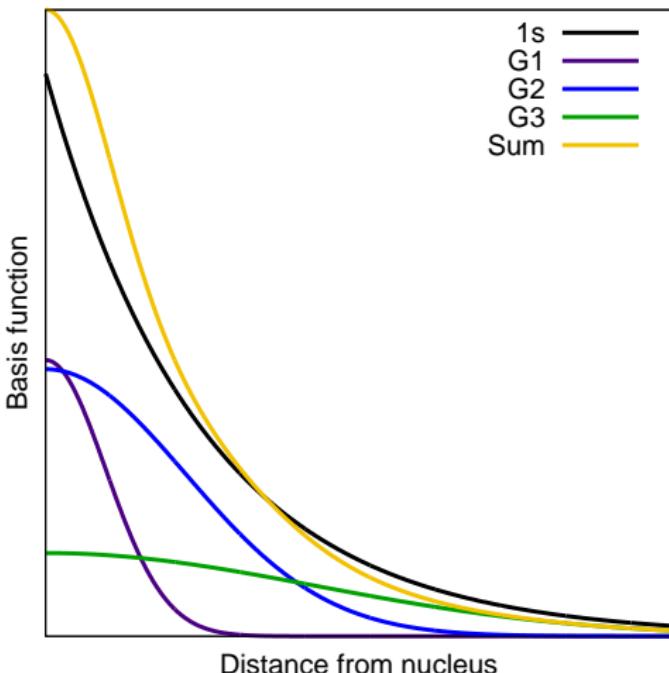
$i = j = k = 0 \rightarrow s$  orbital

$i + j + k = 1 \rightarrow p$  orbital

$i + j + k = 2 \rightarrow d$  orbital

$i + j + k = 3 \rightarrow f$  orbital

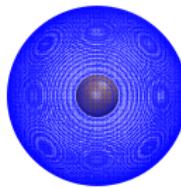
Using 2 or more sets of Gaussians per orbital allows them to expand or contract.



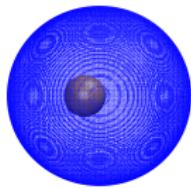
## Gaussian basis sets — building flexibility

Polarization functions (\*):

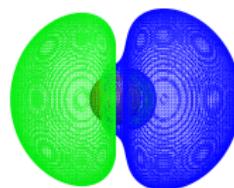
- include higher angular-momentum functions
  - add  $p$  functions to  $s$ -block and  $d$  functions to  $p$ -block elements
  - allows polarization of the density along bonds and for lone pairs



Spherical  
density



Polarized  
density

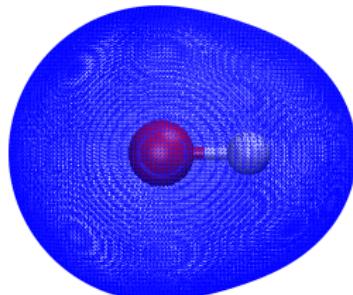


## Density difference

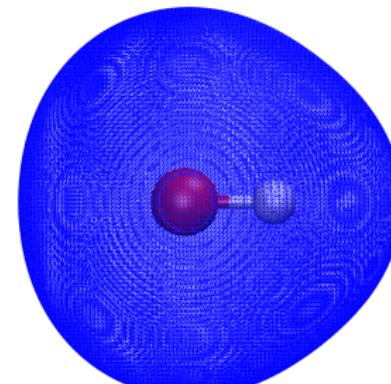
# Gaussian basis sets — building flexibility

Diffuse functions (+):

- add broad Gaussians with small exponents
- important for anions, which have large atomic radii
- important for intermolecular interactions, like H-bonding



Neutral



Anion

# Which basis sets should I use?

Geometry optimization and frequency calculations:

- time-consuming, require many energy evaluations
- fairly insensitive to basis set
- use small basis sets: 6-31G\*, cc-pVDZ, def-SVP
- for anions and very electronegative atoms, add diffuse functions: 6-31+G\*, aug-cc-pVDZ, def-SVPD

Single-point energy calculations:

- fairly quick, require only one energy evaluation
- quite sensitive to basis set
- use large basis sets: 6-311+G(2d,2p), aug-cc-pVTZ, def-TVZPD

## Effective core potentials (ECPs)

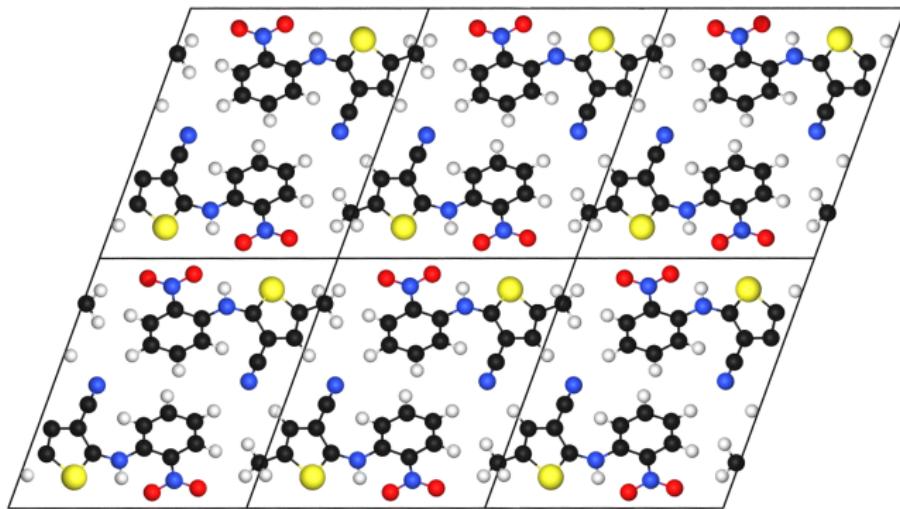
For heavy elements, core electrons are replaced by an ECP to

- save computational time since core electrons are unreactive
  - include scalar relativistic effects
  - ECPs are typically necessary for  $Z \geq 37$  (i.e. beyond Kr)
  - For transition metals, the outermost  $s$  and  $p$  electrons should be modeled explicitly, not included in the ECP



# Periodic boundary conditions

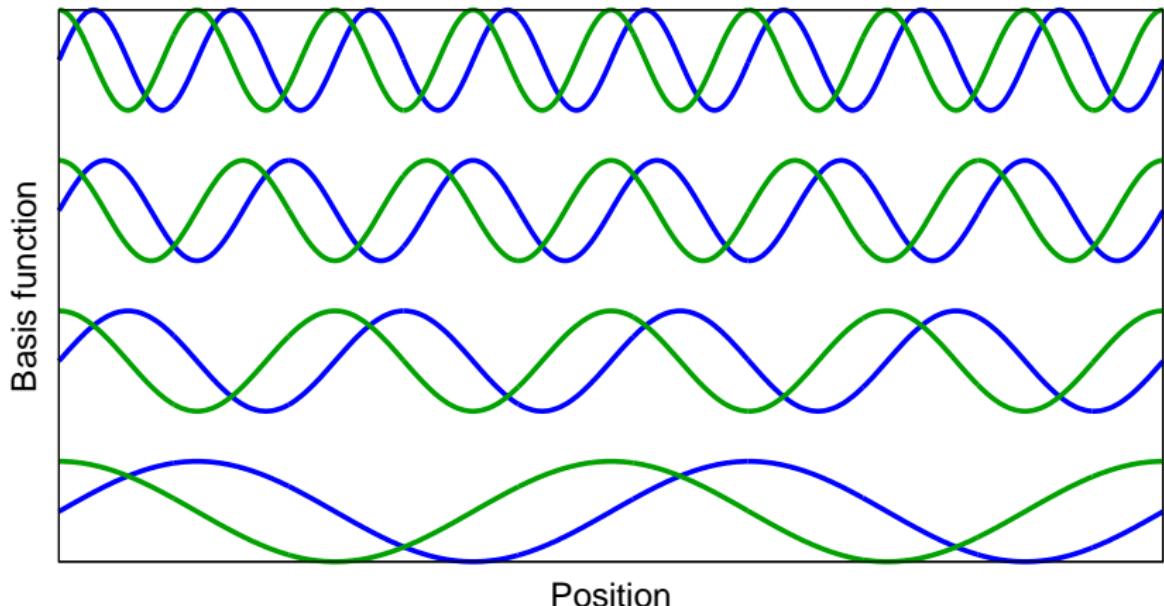
Most solids are crystals than can be represented by a single unit cell, repeatedly replicated in 3D.



The basis functions should have the same periodicity as the lattice.

# Plane-wave basis sets

All plane waves are included up to some energy (frequency) cutoff.



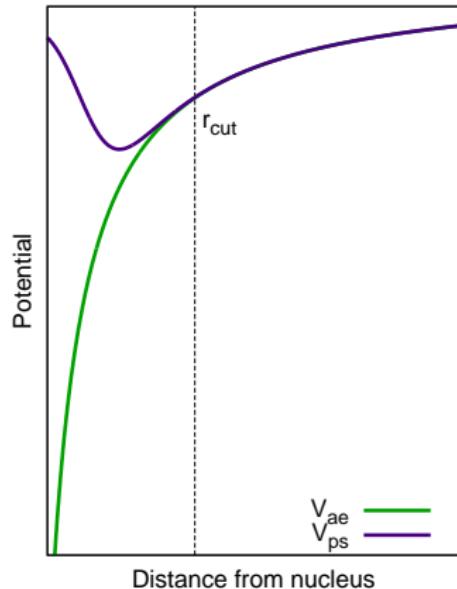
# Pseudopotentials

Sharp electron-density peaks near nuclei are hard to represent using plane waves.

Replace the potential (and the density) within some cut-off radius,  $r_{\text{cut}}$ .

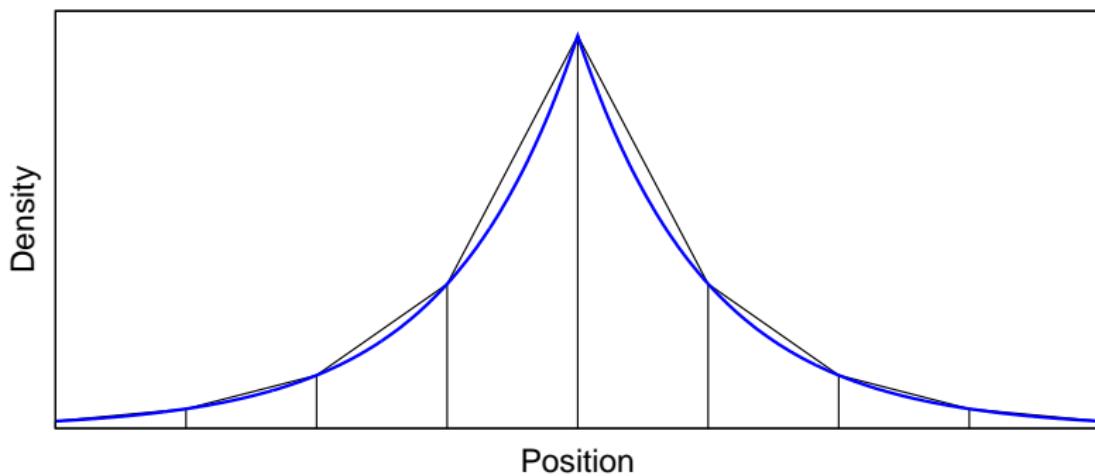
Pseudopotentials are used for all elements.

Core regions between bonded atoms must never overlap.



## Integrals: k-point mesh

Integrals to evaluate the energy are done numerically – need a dense enough mesh to obtain converged values.



In reciprocal space – more points for small cell dimensions and few points for large cell dimensions.

# Summary

DFT is a powerful tool for chemistry, physics, materials science, and engineering, but is not a black box. Be sure to consider:

- Geometry details for the system under study
  - ▶ cif files or xyz coordinates
  - ▶ charge and magnetization
- The choice of density functional
  - ▶ base functional
  - ▶ dispersion correction
- Basis set or plane-wave/pseudopotential details
  - ▶ basis set and ECP
  - ▶ pseudopotential type, plane-wave cutoffs, k-point mesh