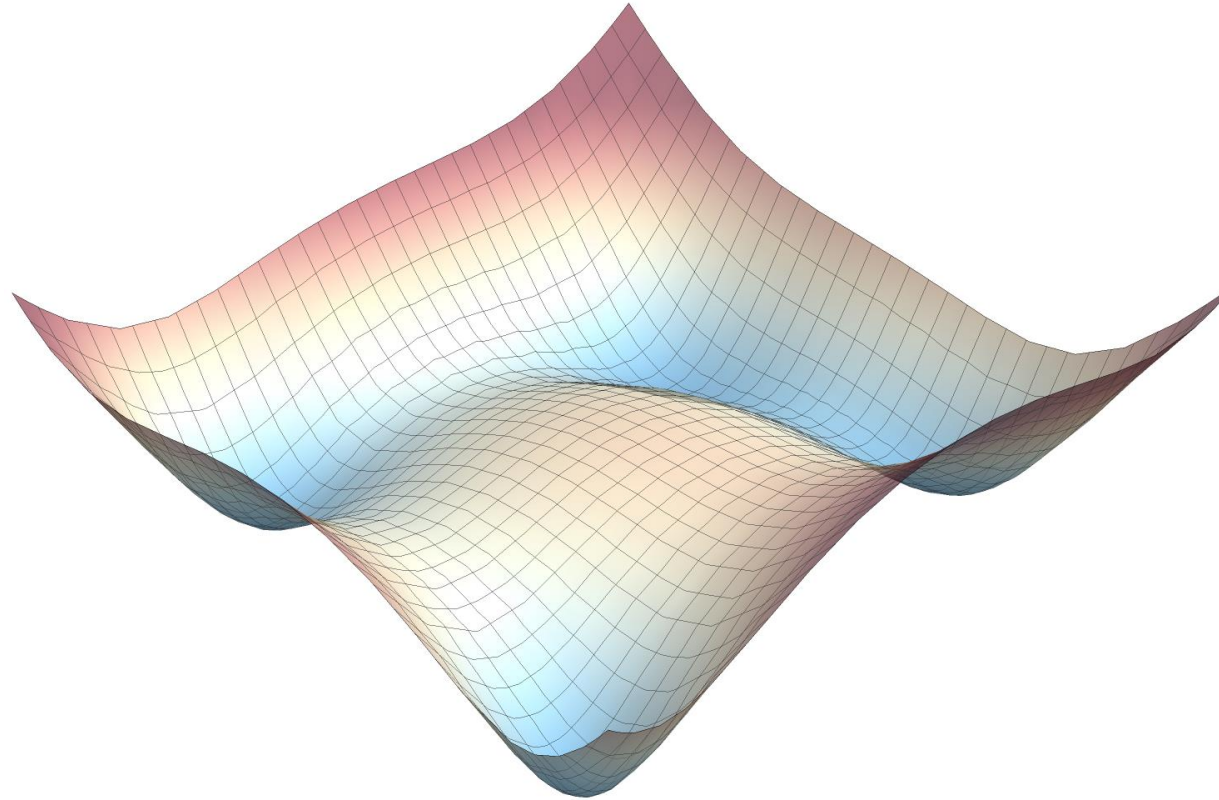




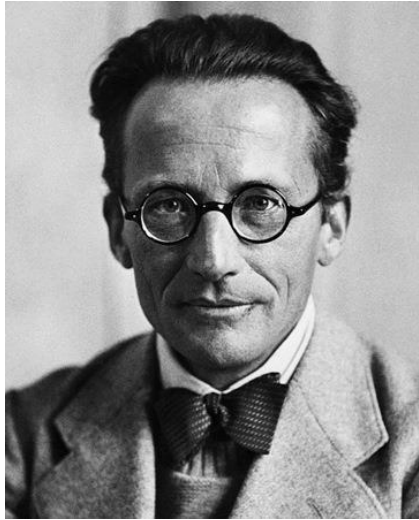
Fundamentals of Density Functional Theory



Jackson Deobald
Knowles Lab
September 9, 2022



Schrödinger Equation



Time-Independent Form:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$\hat{H} = \hat{T} + \hat{V}$$

kinetic energy potential energy

Variational Theorem:

$$E = \langle \Psi | \hat{H} | \Psi \rangle \leq \langle \Phi | \hat{H} | \Phi \rangle$$

“The ground state energy of any approximate wavefunction is always an upper bound to the exact ground state energy”

The exact wavefunction can be approximated by finding a solution that minimizes energy



Schrödinger Equation



Born-Oppenheimer Hamiltonian:

$$\hat{H} = \sum_i^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_i^{N_n} \sum_j^{N_e} \frac{e^2 Z_i}{|\vec{r}_j - \vec{R}_i|} + \sum_{i < j}^{N_n} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{i < j}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

electronic kinetic energy nuclear-electronic attraction nuclear-nuclear repulsion electron-electron repulsion



The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

– Paul Dirac, 1929



Simplifying Approximations

$$\hat{H} = \sum_i^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_i^{N_n} \sum_j^{N_e} \frac{e^2 Z_i}{|\vec{r}_j - \vec{R}_i|} + \sum_{i < j}^{N_n} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{i < j}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

electronic kinetic energy nuclear-electronic attraction nuclear-nuclear repulsion electron-electron repulsion

Trivial to calculate No known solution (many-body problem)

Born-Oppenheimer Approximation:

The motion of nuclei is slow relative to the motion of electrons, so we can treat them as stationary

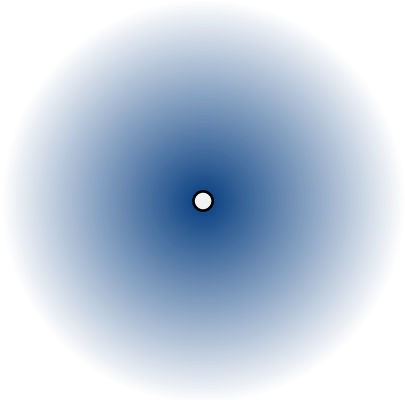
- No nuclear kinetic energy term in Hamiltonian
- Nuclear-electronic attraction term depends only on position of electrons
- Nuclear-nuclear repulsion term becomes a constant



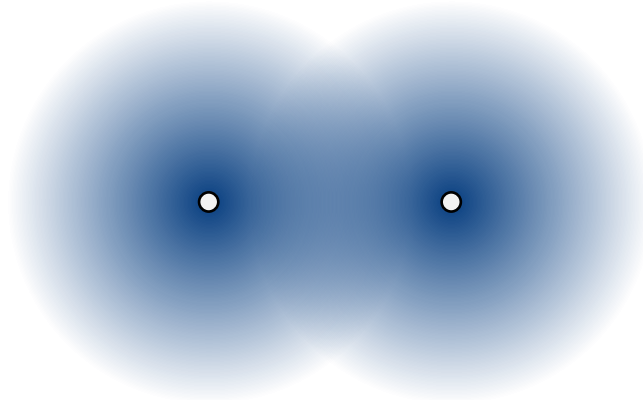
Simplifying Approximations

Linear Combination of Atomic Orbitals (LCAO):

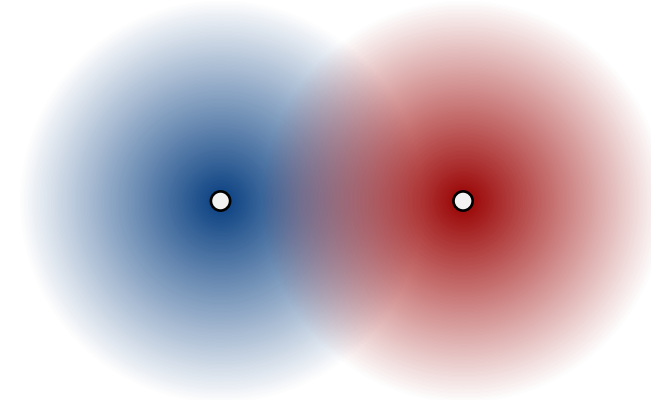
- Molecular orbitals are expressed in terms of hydrogen-like atomic orbitals (known exactly)
- Bonding interactions correspond to constructive interference
- Antibonding interactions correspond to destructive interference



Hydrogen 1s
orbital



H₂ σ -bonding
orbital



H₂ σ -antibonding
orbital

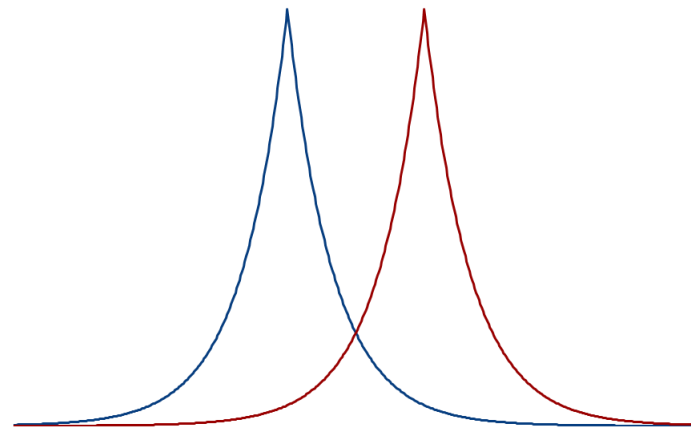
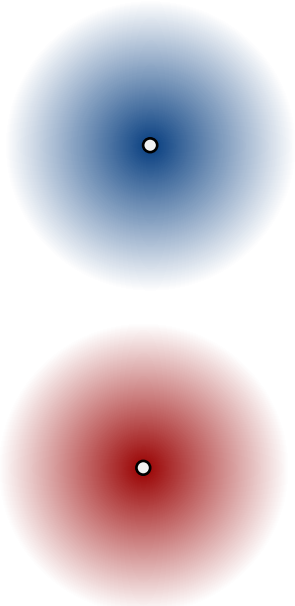


Simplifying Approximations

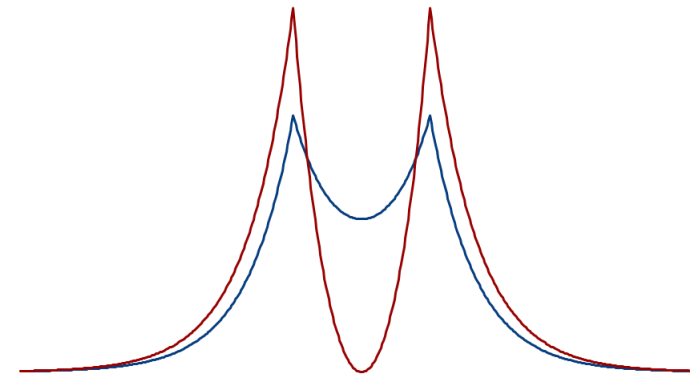
Linear Combination of Atomic Orbitals (LCAO):

- Molecular orbitals are expressed in terms of hydrogen-like atomic orbitals (known exactly)
- Bonding interactions correspond to constructive interference
- Antibonding interactions correspond to destructive interference

Probability densities:



1s orbitals



σ -orbitals



Simplifying Approximations



$$\hat{H} = \sum_i^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_i^{N_n} \sum_j^{N_e} \frac{e^2 Z_i}{|\vec{r}_j - \vec{R}_i|} + \sum_{i < j}^{N_n} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{i < j}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

electronic kinetic energy nuclear-electronic attraction nuclear-nuclear repulsion electron-electron repulsion

Hartree-Fock:

- Assume that the wavefunction can be expressed as the product of one-electron wavefunctions (orbitals)
- Electrons interact with electric field from average position of other electrons
- *Antisymmetrized* to satisfy Pauli exclusion principle (permutation of electrons changes sign)
- Variational principle used to find minimum-energy electronic state

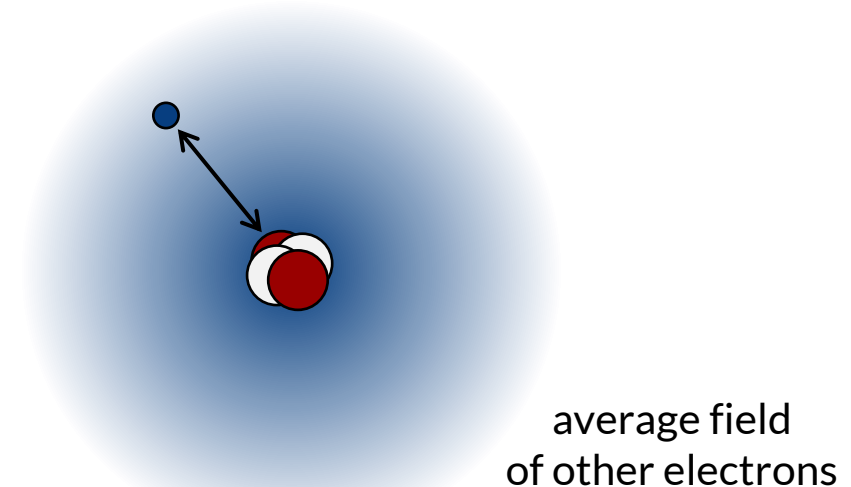
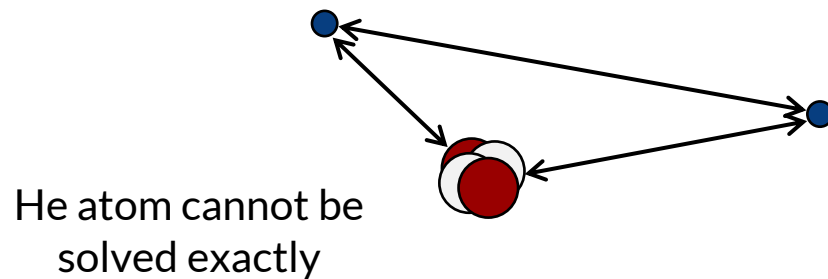


Simplifying Approximations

$$\hat{H} = \sum_i^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_i^{N_n} \sum_j^{N_e} \frac{e^2 Z_i}{|\vec{r}_j - \vec{R}_i|} + \sum_{i < j}^{N_n} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{i < j}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

electronic kinetic energy nuclear-electronic attraction nuclear-nuclear repulsion electron-electron repulsion

Hartree-Fock:





Simplifying Approximations

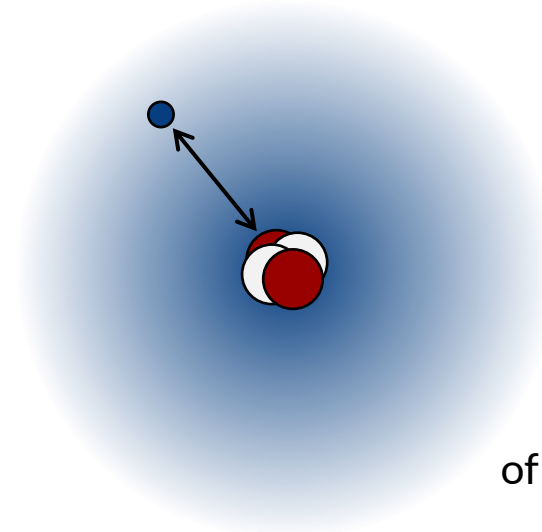
$$\hat{H} = \sum_i^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_i^{N_n} \sum_j^{N_e} \frac{e^2 Z_i}{|\vec{r}_j - \vec{R}_i|} + \sum_{i < j}^{N_n} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{i < j}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

electronic kinetic energy nuclear-electronic attraction nuclear-nuclear repulsion electron-electron repulsion

Hartree-Fock:

Self-consistent field (SCF): electronic charge distribution must be consistent with its own electrostatic field

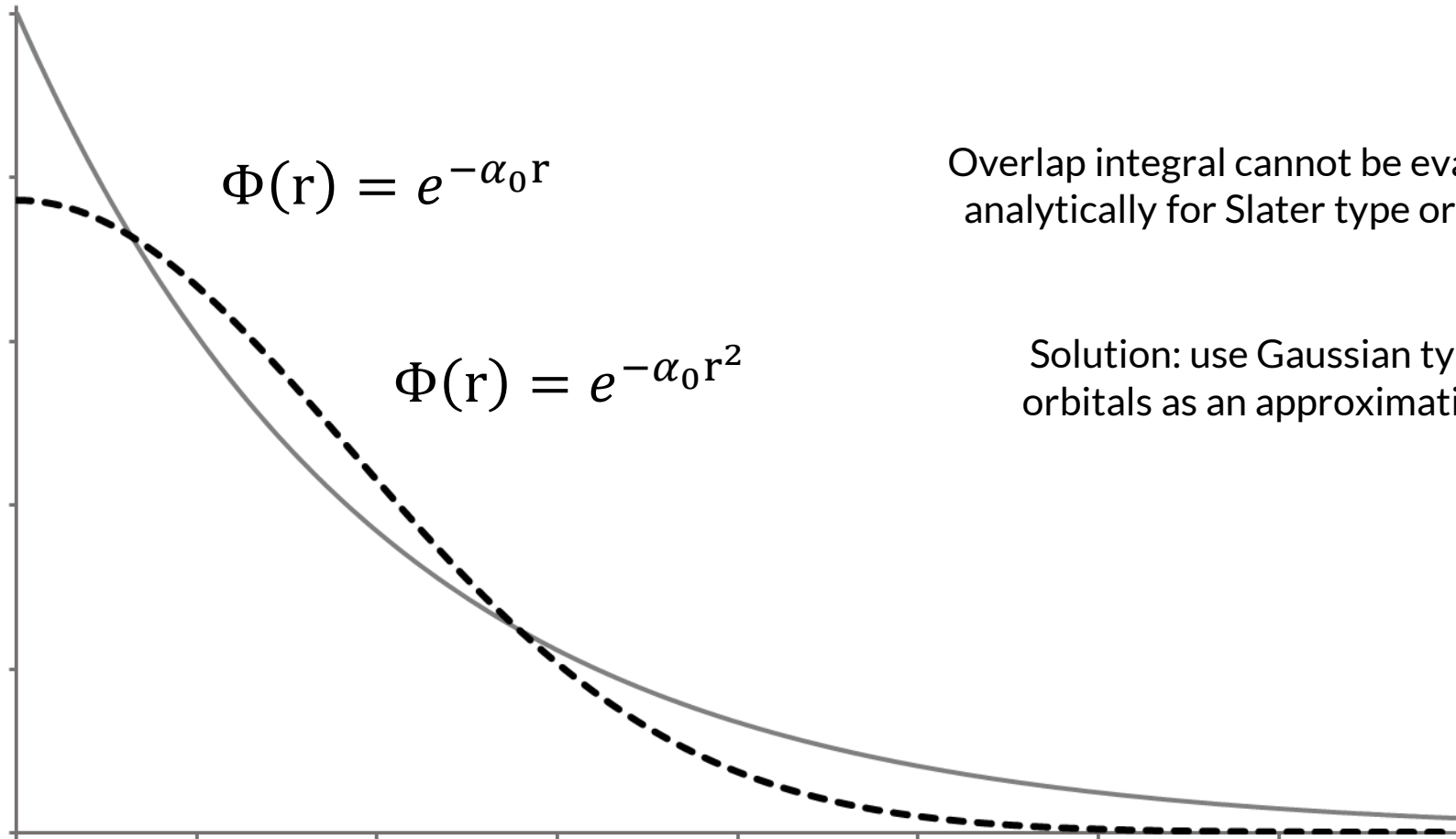
Provides a method for determining orbital coefficients



average field
of other electrons



Gaussian Basis Sets

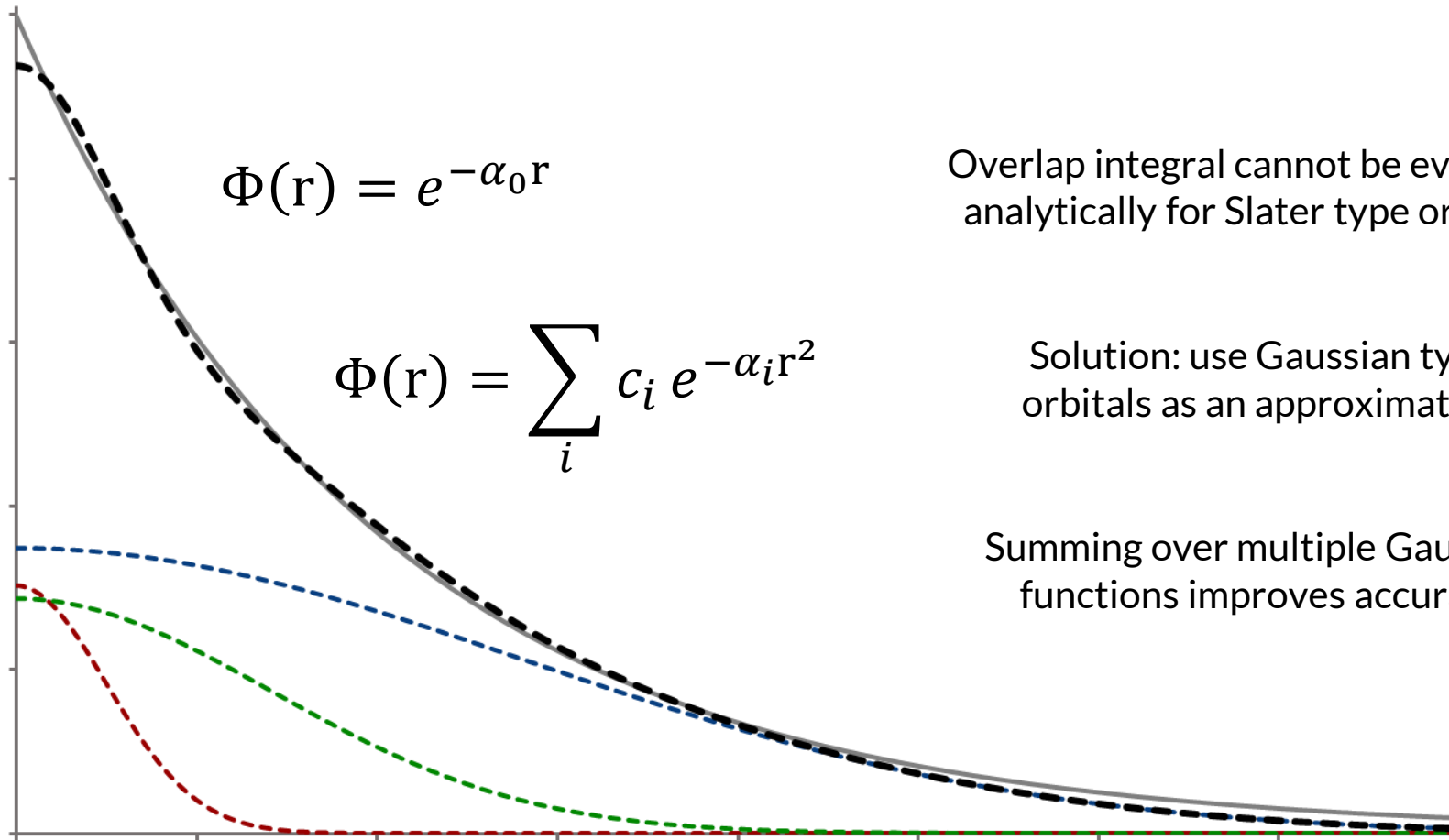


Overlap integral cannot be evaluated analytically for Slater type orbitals!

Solution: use Gaussian type orbitals as an approximation



Gaussian Basis Sets



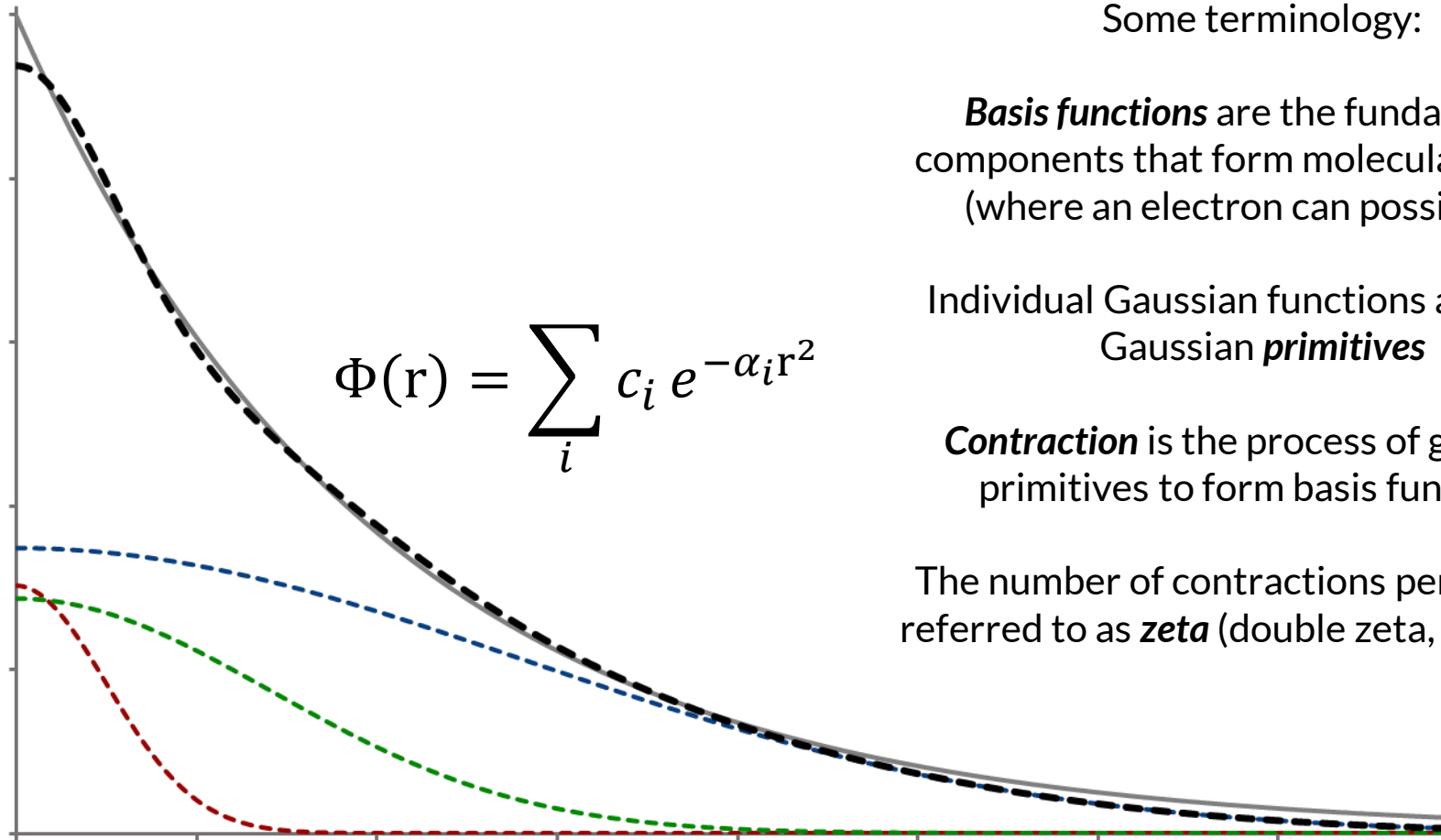
Overlap integral cannot be evaluated analytically for Slater type orbitals!

Solution: use Gaussian type orbitals as an approximation

Summing over multiple Gaussian functions improves accuracy



Gaussian Basis Sets



Some terminology:

Basis functions are the fundamental components that form molecular orbitals (where an electron can possibly be)

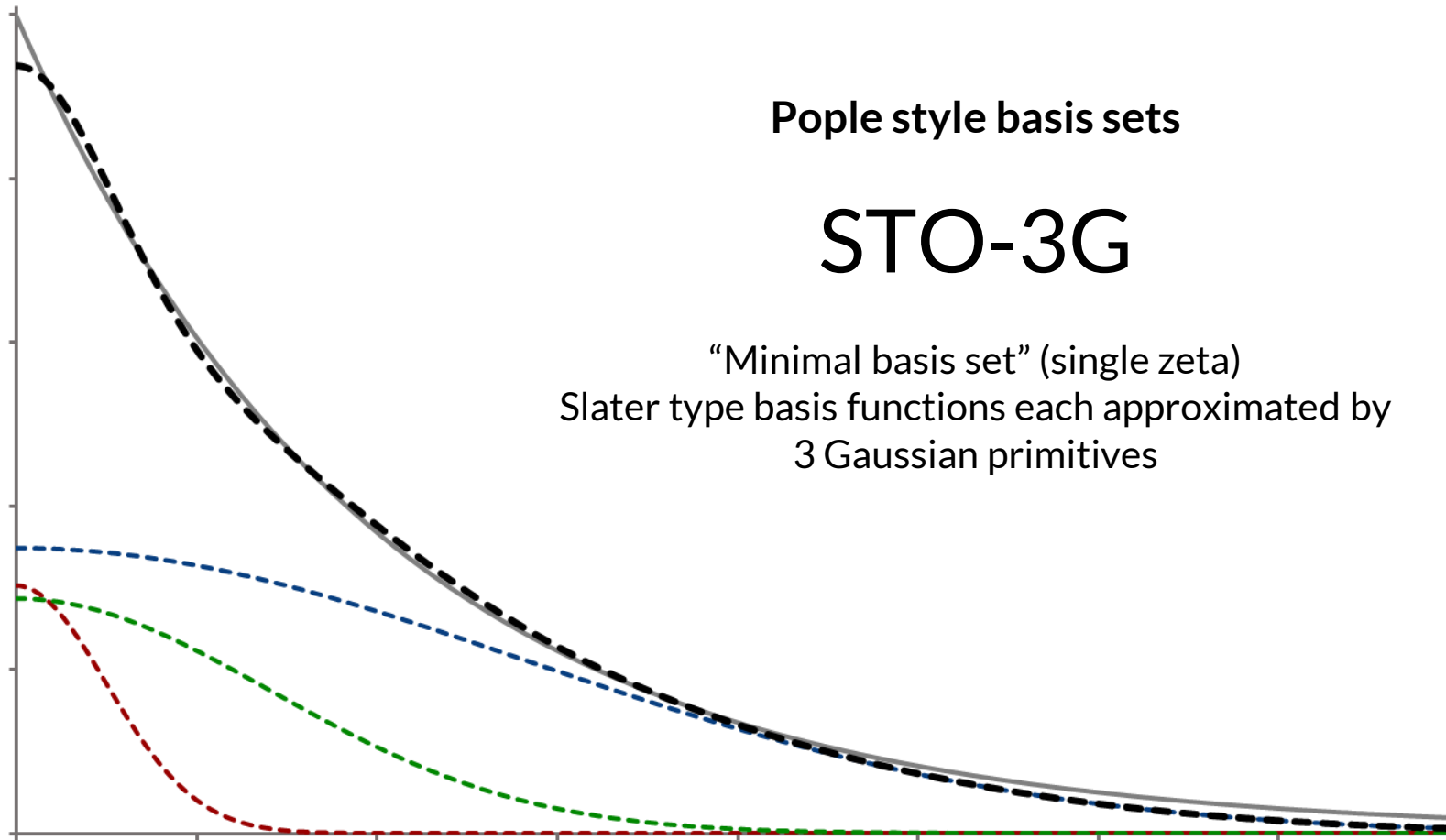
Individual Gaussian functions are called Gaussian **primitives**

Contraction is the process of grouping primitives to form basis functions

The number of contractions per orbital is referred to as **zeta** (double zeta, triple, etc.)

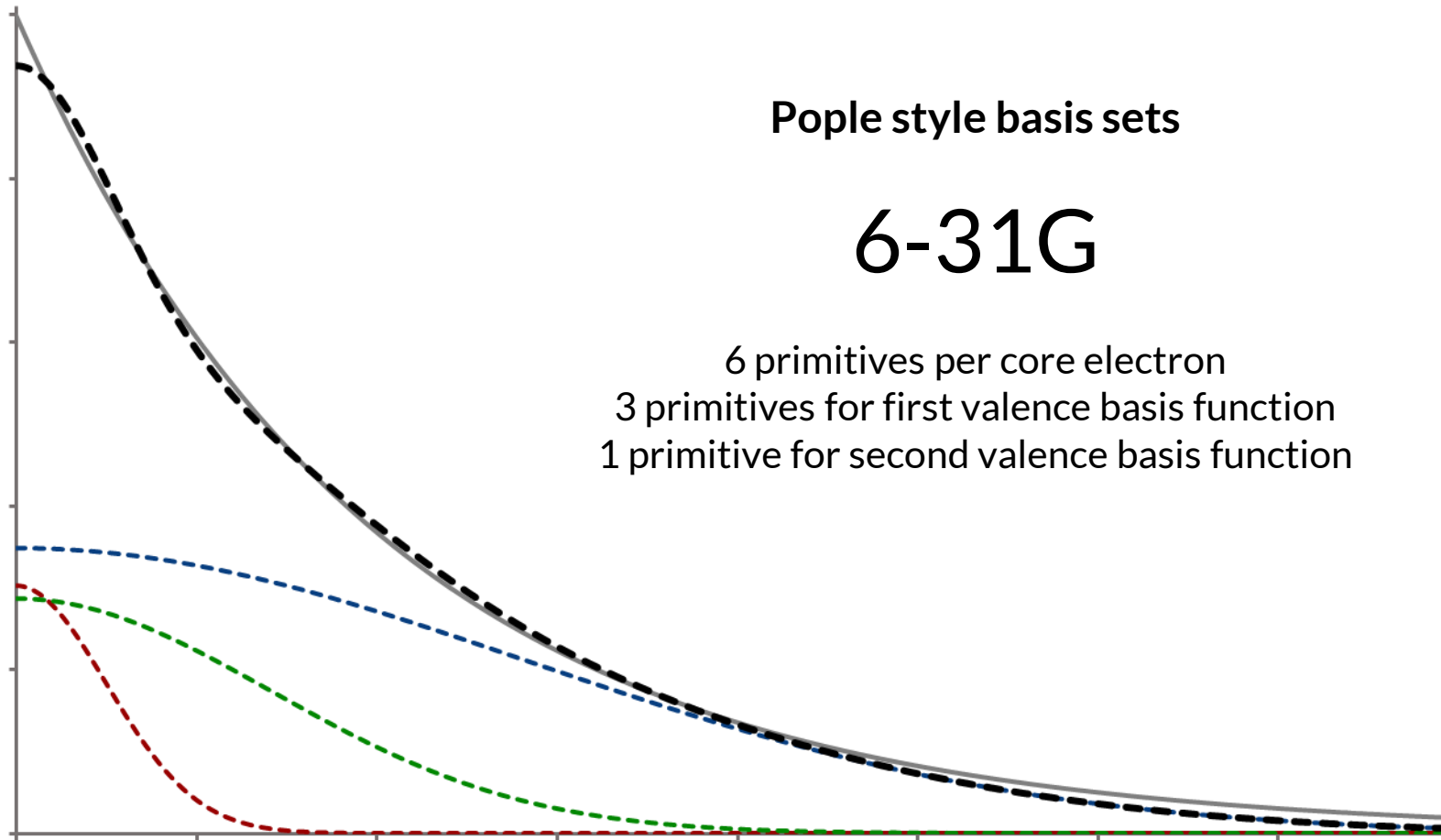


Gaussian Basis Sets



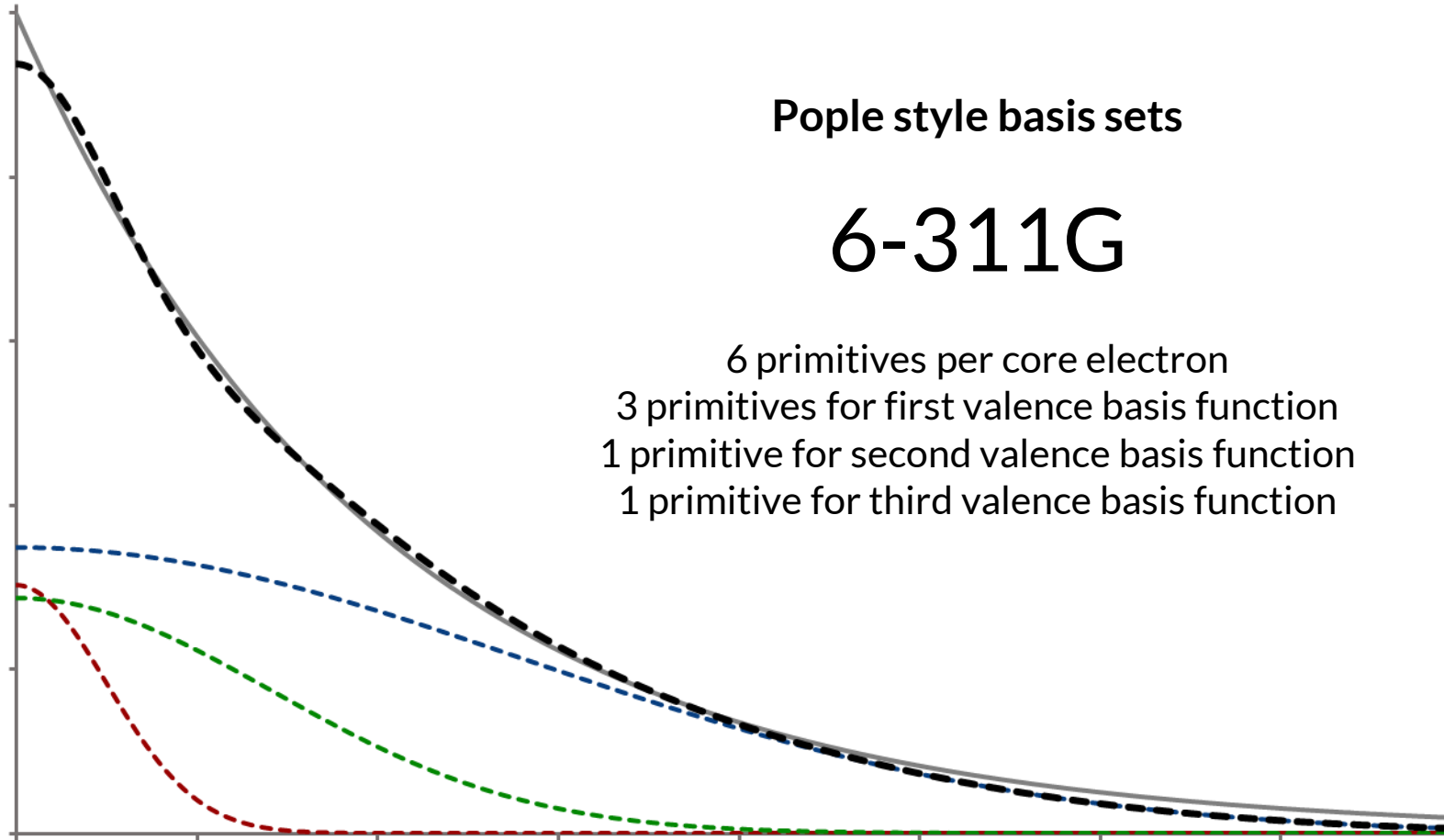


Gaussian Basis Sets



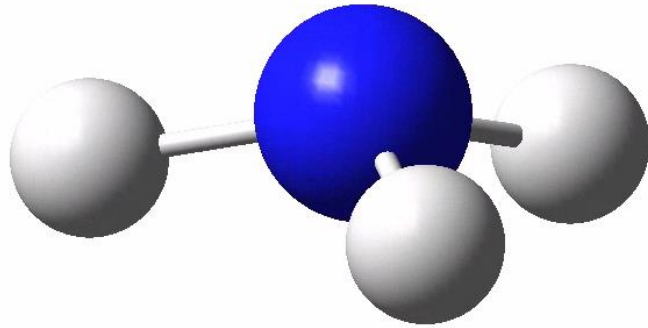


Gaussian Basis Sets

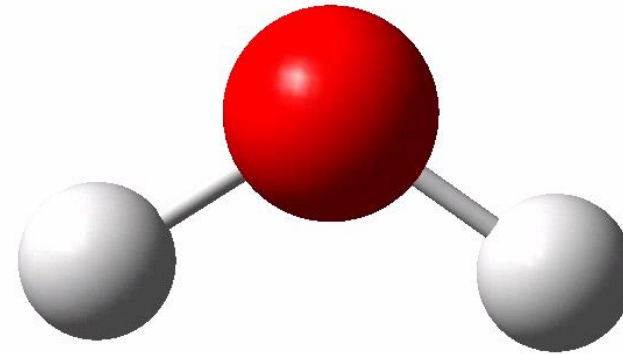




Polarization Functions



114.4° (107.8° expt.)



111.9° (104.5° expt.)

Geometries predicted by large basis set of only s and p symmetry


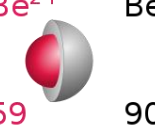
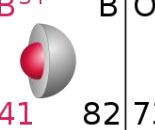

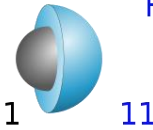




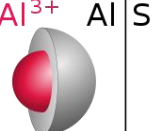
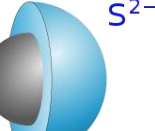
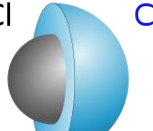


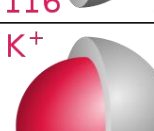
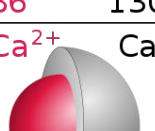
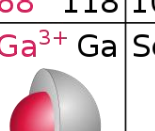
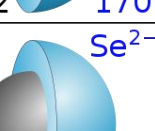
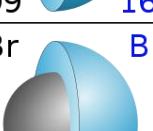



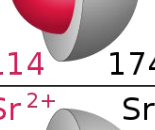
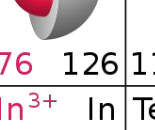
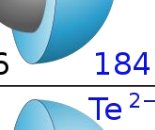
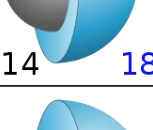


Limitation of LCAO: molecular orbitals cannot be described using only *occupied atomic orbitals*

Solution: add additional basis functions of *higher angular momentum (polarization functions)*

(The true space of possible electronic configurations has *infinite* dimension)



Diffuse functions

Li^+  90	Li 134	Be^{2+}  59	Be 90	B^{3+}  41	B 82	O  73	O^{2-}  126	F  71	F^-  119
Na^+  116	Na 154	Mg^{2+}  86	Mg 130	Al^{3+}  68	Al 118	S  102	S^{2-}  170	Cl  99	Cl^-  167
K^+  152	K 196	Ca^{2+}  114	Ca 174	Ga^{3+}  76	Ga 126	Se  116	Se^{2-}  184	Br  114	Br^-  182
Rb^+  166	Rb 211	Sr^{2+}  132	Sr 192	In^{3+}  94	In 144	Te  135	Te^{2-}  207	I  133	I^-  206

Describing negatively charged molecules becomes difficult using only neutral hydrogen-like atomic orbitals

Add extra basis functions with larger radius (simulate shielding effect)



Gaussian Basis Sets



Pople style basis sets

6-31+G(d,p)

6 primitives per core electron

3 primitives for first valence basis function

1 primitive for second valence basis function

+ diffuse function on heavy atoms (Li and beyond)

d polarization on heavy atoms, p polarization on light atoms (H, He)



Gaussian Basis Sets



Pople style basis sets

6-311++G(2d,2p)

- 6 primitives per core electron
- 3 primitives for first valence basis function
- 1 primitive for second valence basis function
- 1 primitive for third valence basis function
 - + diffuse function on heavy atoms
 - + diffuse function on light atoms
- 2 d polarization functions on heavy atoms
- 2 p polarization functions on light atoms



Choice of Basis Set



Pople style basis sets

STO-3G
3-21G
6-31G(d,p)
6-31+G(2d,2p)
6-311G(d,p)
6-311+G(2d,2p)
6-311++G(2df,2pd)

Ahlrichs basis sets

def2-SV(P)
def2-SVP
def2-TZVP(-f)
def2-TZVP
def2-TZVPP
def2-QZVP
def2-QZVPP

Dunning basis sets

cc-pVDZ
cc-pVTZ
cc-pVQZ
cc-pV5Z
aug-cc-pVDZ
aug-cc-pVTZ
aug-cc-pVQZ

LanL2DZ: Ignores core electrons, replaces them with a potential
(often used for metals)



Choice of Basis Set



Pople style basis sets

STO-3G
3-21G
6-31G(d,p)
6-31+G(2d,2p)
6-311G(d,p)
6-311+G(2d,2p)
6-311++G(2df,2pd)

Ahlrichs basis sets

def2-SV(P)
def2-SVP
def2-TZVP(-f)
def2-TZVP
def2-TZVPP
def2-QZVP
def2-QZVPP

Dunning basis sets

cc-pVDZ
cc-pVTZ
cc-pVQZ
cc-pV5Z
aug-cc-pVDZ
aug-cc-pVTZ
aug-cc-pVQZ

- Converge energy quickly
- “Well balanced” with polarization functions built in
- Matching auxiliary basis sets speed up integral evaluation
- def2-TZVP usually “good enough” for organic molecules



Choice of Basis Set



Pople style basis sets

STO-3G
3-21G
6-31G(d,p)
6-31+G(2d,2p)
6-311G(d,p)
6-311+G(2d,2p)
6-311++G(2df,2pd)

Ahlrichs basis sets

def2-SV(P)
def2-SVP
def2-TZVP(-f)
def2-TZVP
def2-TZVPP
def2-QZVP
def2-QZVPP

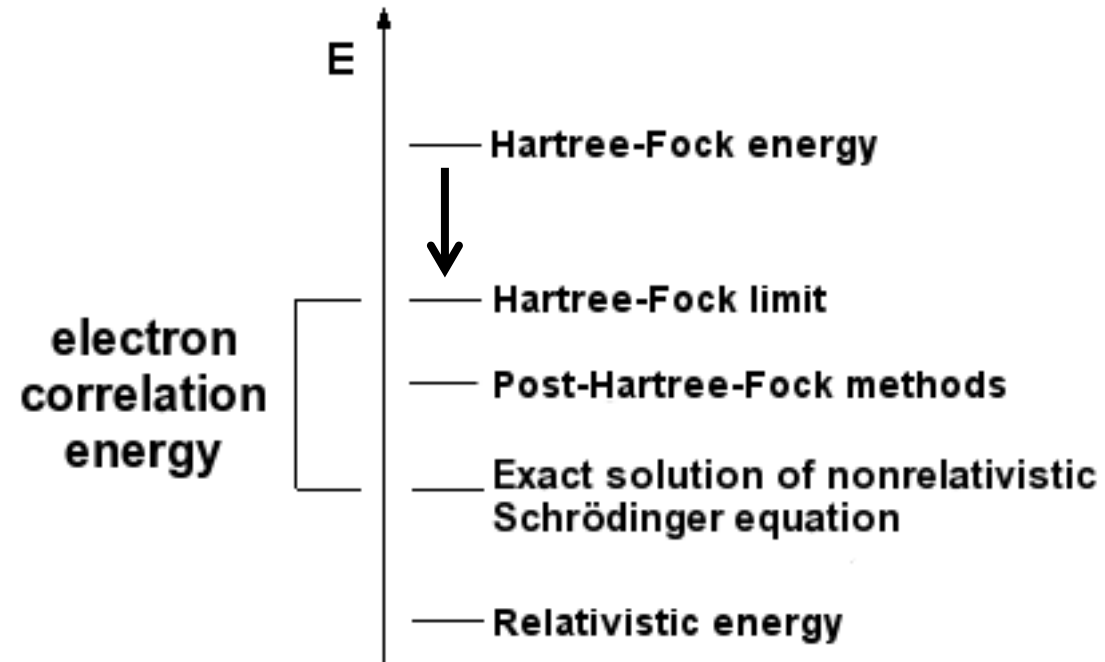
Dunning basis sets

cc-pVDZ
cc-pVTZ
cc-pVQZ
cc-pV5Z
aug-cc-pVDZ
aug-cc-pVTZ
aug-cc-pVQZ

- More highly contracted than def2
- Good for correlated methods (post-HF)
- Good choice for anions, excited states, long-range interactions using augmented version (diffuse functions)



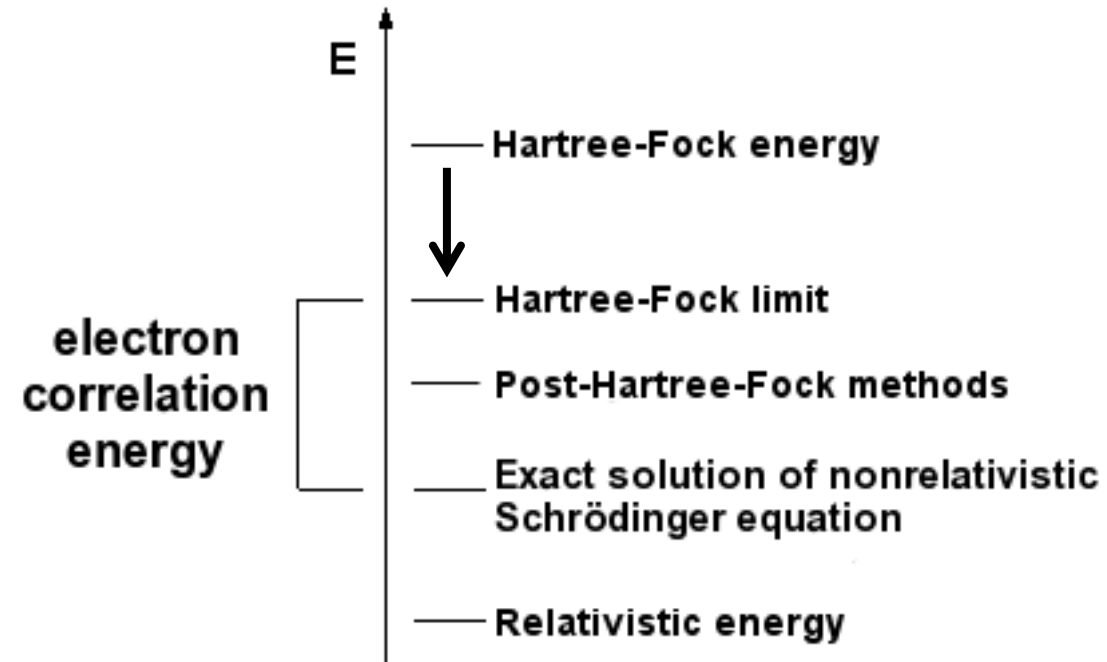
Choice of Basis Set



Using larger basis sets, the energy tends toward the *Hartree-Fock Limit* (complete basis set limit)



Choice of Basis Set



How can we recover the correlation energy?



Correlated Methods



Wavefunction Theory

Configuration interaction (full CI, CIS, CISD, etc.)

MP2 (perturbation theory)

Coupled cluster theory (CCSD, CCSD(T))

CASSCF, RASSCF, QCI, composite methods, etc.

Density Functional Theory



Density Functional Theory



Pierre Hohenberg

Hohenberg-Kohn Theorem I

“For a nondegenerate ground state of a many-electron system, the properties of the system are *uniquely determined* by the electron density.”



Walter Kohn

Hohenberg-Kohn Theorem II

“The functional that delivers the ground-state energy of the system gives the lowest energy if and only if the input density is the true ground-state density.”



Density Functional Theory



$$E = F[\rho(\mathbf{r})]$$

“The universal density functional”

$$E[\rho(\mathbf{r})] = T + V_{ne} + V_{ee} + E_{xc}$$

Electronic energy determined by:
kinetic energy
nuclear attraction
electronic repulsion
exchange and correlation



Electron interacting
with itself



Kohn-Sham DFT



Express the electron density in an *orbital basis set*

Orbitals consist of *fictitious, noninteracting* electrons

Density for noninteracting system can be solved *exactly*

Hartree-Fock: ***Approximate*** solution to ***real*** problem

Kohn-Sham: ***Exact*** solution to ***hypothetical*** problem



Exchange-Correlation Functional



Local Density Approximation: XC energy as a functional of *local* electron density, integrate over all space

$$E_{xc}^{\text{LDA}}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r}$$

Generalized Gradient Approximation: XC energy as a functional of electron density and *gradient*

$$E_{xc}^{\text{GGA}}[\rho(\mathbf{r})] = E_{xc}^{\text{LDA}}[\rho(\mathbf{r})] + \Delta E[\nabla\rho(\mathbf{r})]$$

Meta-GGA: Use higher order gradients



Hybrid Functionals



Observation:

For Hartree-Fock, we didn't know the correlation energy,
but we knew the exchange energy *exactly*

Divide XC functional into X and C functionals

$$E_{xc}[\rho(\mathbf{r})] = E_x[\rho(\mathbf{r})] + E_c[\rho(\mathbf{r})]$$

Use exchange energy from HF to obtain a more accurate approximation

$$E_x[\rho(\mathbf{r})] = aE_x[\rho(\mathbf{r})] + (1 - a)E_x^{\text{HF}}$$



Some Examples

Increasing Cost
Increasing Accuracy



Hybrid-meta-GGA: M06, M06-2x, TPSS0

Hybrid-GGA: B3LYP, PBE0, B3P86

Meta-GGA: M06-L, TPSS

GGA: PBE, BP86, B97

LDA

Which functional should I use?

Check benchmarks

Do the experiment!



Some Examples



Increasing Cost
Increasing Accuracy



Hybrid-*meta*-GGA: M06, M06-2x, TPSS0

Hybrid-GGA: B3LYP, PBE0, B3P86

***Meta*-GGA:** M06-L, TPSS

GGA: PBE, BP86, B97

LDA

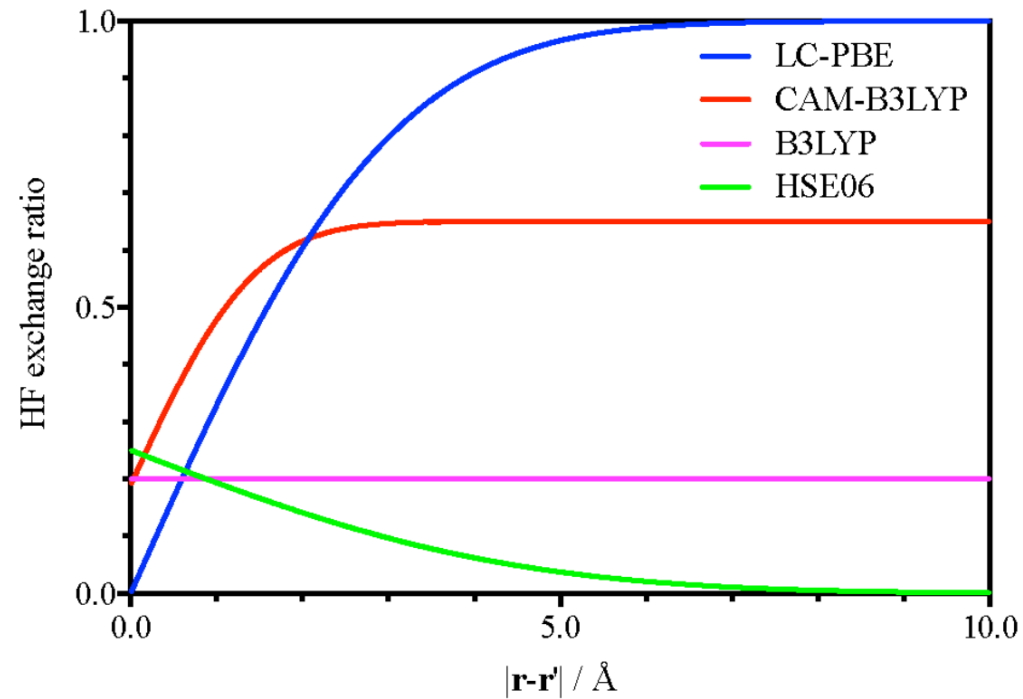
Can we improve accuracy even more?



Range-Separated Hybrids

Key Concept:

Don't use a fixed mixture of Hartree-Fock and DFT exchange,
vary exchange with distance

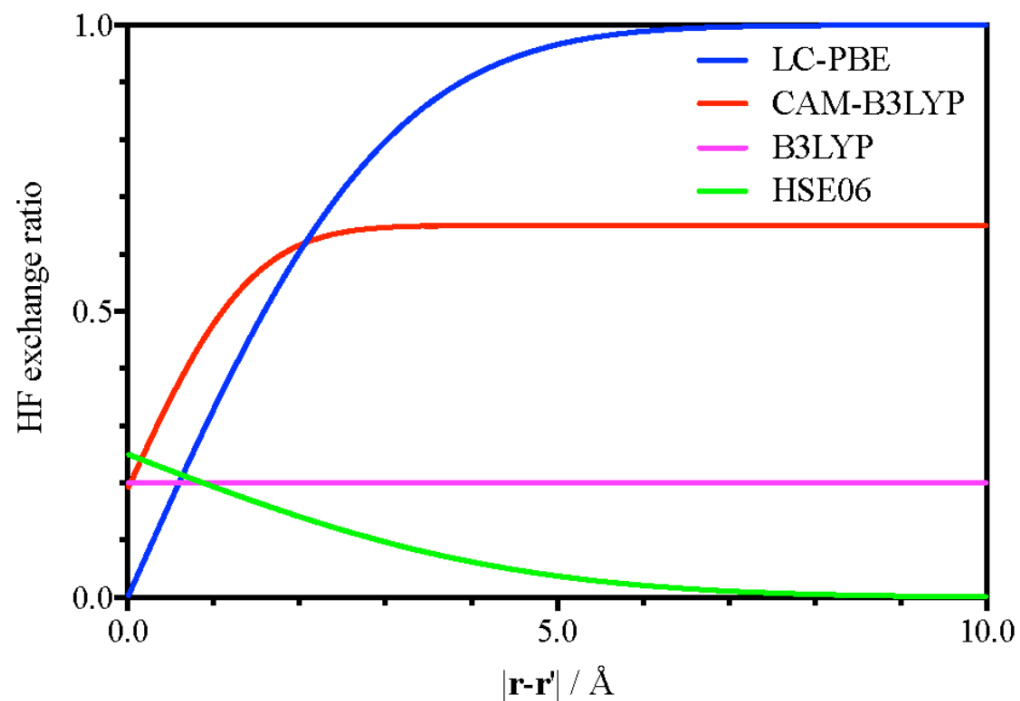




Range-Separated Hybrids

Examples:

CAM-B3LYP, ω -B97X-D, ω -B97M-V
Good for noncovalent/long-range interactions





Double Hybrids



Key Concept:

Mixing in some Hartree-Fock improved exchange energy

Can we use the same strategy to improve correlation energy?

Remember: Hartree-Fock is not correlated

Use MP2 to improve correlation energy

$$E_{xc}[\rho(\mathbf{r})] = a_x E_x[\rho(\mathbf{r})] + a_c E_c[\rho(\mathbf{r})] + (1 - a_x) E_x^{\text{HF}} + (1 - a_c) E_c^{\text{MP2}}$$

Examples:

B2-PLYP, mPW2-PLYP, B2K-PLYP, DSD-PBEP86



Practical Considerations



Geometry Optimization

Find geometry
where gradient is 0
(stationary point)

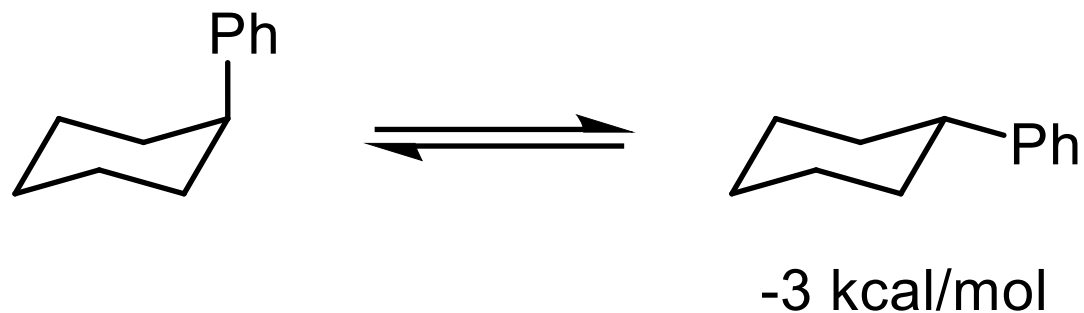
$$-\frac{\partial E}{\partial x} = \text{Force} \quad \nabla E = \begin{pmatrix} \frac{\partial E}{\partial x_1} \\ \vdots \\ \frac{\partial E}{\partial x_n} \end{pmatrix} = \text{Gradient}$$

Eigenvalues of \mathbf{H}
determine concavity
(minimum vs. saddlepoint)

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 E}{\partial x_1 \partial x_1} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial x_n} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_2 \partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial x_n \partial x_1} & \frac{\partial^2 E}{\partial x_n \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_n \partial x_n} \end{pmatrix} = \text{Hessian}$$



Practical Considerations

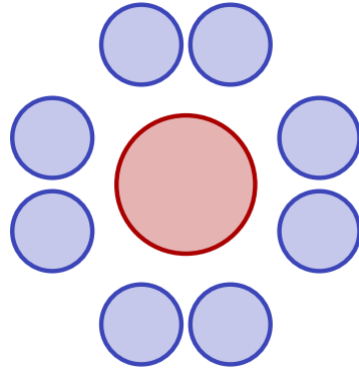


Your calculations are only as good as your geometries!

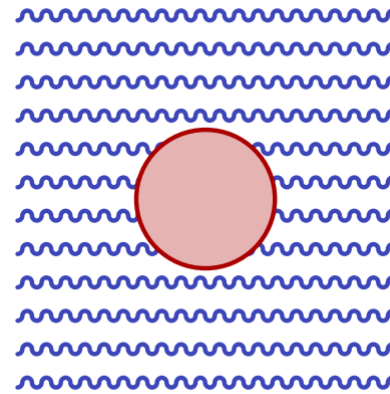
- Consider conformational effects when building a structure
- When in doubt, run the calculation for each conformer
- Always do an optimization and frequency calculation



Practical Considerations



Explicit Solvation



Implicit Solvation

We usually aren't interested only in gas-phase properties

Explicit solvation: Add solvent molecules
(expensive/inconvenient, but sometimes necessary)

Implicit solvation: Create a polarizable surface around molecule
corresponding to solvent dielectric and polarizability



Important Topics Not Covered



Spin contamination

Basis set superposition error

Semiempirical/Composite DFT Methods

Dispersion corrections (D3(0), D3(BJ), D4)

Relativistic Corrections (ZORA, Douglas-Kroll-Hess)

Excited state calculations (TD-DFT)

Optimization algorithms (RFO, quasi-Newton, etc.)