

Density Functional Theory (part II)

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Kohn-Sham Theory

- While the Hamiltonian and Ψ can be determined from ρ , when solving for the energy there is no simplification over MO theory (WFT).
- In 1965 Kohn and Sham had a key realization that things could be simplified by considering a one-electron Hamiltonian operator for non-interacting systems of electrons.

$$H = \sum_{i=1}^N h_i \quad h_i = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^M \frac{Z_k}{r_{ik}}$$

- The “Trick” that they implemented was, **take a fictitious system of non-interacting electrons where the ρ_0 is the same as the interacting system.**
- This “Trick” leads to simplifications:
 - The Atomic Number and Position of the nuclei are the same for both systems
 - Eigenfunction = product of the one-electron eigenfunctions (From Slater determinant) $\Psi = \Psi_1 \Psi_2 \dots \Psi_N \quad h_i \Psi_i = \varepsilon_i \Psi_i$
 - Eigenvalue = sum of the one-electron eigenvalues

Kohn-Sham Self-Consistent Field (SCF)

- A **major flaw** in the TFD model, is the poor representation of the T term.
- KS defined electronics energy as: ($\hat{E}_{DFT}[\rho]$ is an exact energy)

$$\hat{E}_{DFT}[\rho] = \hat{T}_{ni}[\rho] + \hat{E}_{Ne}[\rho] + \hat{J}[\rho] + \hat{V}_{xc}[\rho]$$

- The \hat{V}_{xc} term can be defined as:

$$\hat{V}_{xc}[\rho] = (\hat{T}_i[\rho] - \hat{T}_{ni}[\rho]) + (\hat{E}_{ee}[\rho] - \hat{J}[\rho])$$

- Giving the overall equation:

$$\hat{E}_{DFT}[\rho] = \hat{T}_{ni}[\rho] + \hat{E}_{Ne}[\rho] + \hat{J}[\rho] + \Delta\hat{T}[\rho] + \Delta\hat{V}_{ee}[\rho]$$

\hat{T}_{ni} : Kinetic energy of non – interacting electrons

\hat{E}_{Ne} : Nuclear – electron interaction

\hat{J} : Classical electron – electron interaction

$\Delta\hat{T}$: Correction to kinetic energy (kinetic correlation energy)

$\Delta\hat{V}_{ee}$: All non – classical corrections to electron – electron interaction

Kohn-Sham Self-Consistent Field (SCF)

- In KS theory one-electron Hamiltonian operator is defined as:

$$h_i^{KS} \chi_i = \varepsilon_i \chi_i$$

$$h_i^{KS} = -\frac{1}{2} \nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{|\tau_i - \tau_k|} + \int \frac{\rho(\tau')}{|\tau_i - \tau'|} \delta\tau' + V_{xc}$$

- Where V_{xc} :

$$V_{xc} = \frac{\delta E_{xc}}{\delta \rho}$$

- V_{xc} is a so-called **functional derivative**, which is analogous in spirit to more typical derivatives
- V_{xc} is perhaps best described as one-electron operator for which the expectation value of KS Slater determinant (χ) is E_{xc}

Kohn-Sham Self-Consistent Field (SCF)

- **Note:** because $\hat{E}_{DFT}[\rho]$ is exact energy, the χ must provide the exact density (min. must correspond to reality)
- Where χ is a **product** of the Slater-determinant eigenfunctions, for the separable **non-interacting** one-electron Hamiltonian, represented by:

$$\sum_{i=1}^N h_i^{KS} |\chi_1 \chi_2 \dots \chi_N\rangle = \sum_{i=1}^N \varepsilon_i |\chi_1 \chi_2 \dots \chi_N\rangle$$

Kohn-Sham Self-Consistent Field (SCF)

- The density of a system can be expressed in terms of orbital basis functions (χ):

$$\hat{E}_{DFT}[\rho] = \hat{T}_{ni}[\rho] + \hat{E}_{Ne}[\rho] + \hat{J}[\rho] + \hat{E}_{xc}[\rho]$$

$$\hat{E}_{DFT}[\rho] = \sum_i^N \left(\langle \chi_i | -\frac{1}{2} \nabla_i^2 | \chi_i \rangle - \langle \chi_i | \sum_k^{nuclei} \frac{Z_k}{|\tau_i - \tau_k|} | \chi_i \rangle \right) + \sum_i^N \langle \chi_i | \frac{1}{2} \int \frac{\rho(\tau')}{|\tau_i - \tau'|} \delta\tau' | \chi_i \rangle + \hat{E}_{xc}[\rho(\tau)]$$

- Where N = Number of electrons
- Density for a Slater determinantal wave function:

$$\rho \equiv \rho(\tau) = \sum_{i=1}^N |\chi_i(\tau)|^2$$

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \dots & \chi_n(1) \\ \chi_1(2) & \chi_2(2) & \dots & \chi_n(2) \\ \dots & \dots & \dots & \dots \\ \chi_1(n) & \chi_2(n) & \dots & \chi_n(n) \end{vmatrix}$$

(exact for the non-interacting system)

Kohn-Sham Self-Consistent Field (SCF)

$$\hat{E}_{DFT}[\rho] = \hat{T}_{ni}[\rho] + \hat{E}_{Ne}[\rho] + \hat{J}[\rho] + \hat{E}_{xc}[\rho]$$

- The functional dependence of E_{xc} on the electron density is expressed as:

An interaction between the electron density and an 'energy density' ε_{xc} that is dependent on electron density ρ :

$$\hat{E}_{xc}[\rho] = \int \rho(\tau)\varepsilon_{xc}[\rho(\tau)]\delta\tau$$

- The electron density ρ is a **per unit volume density**
- The 'energy' density ε_{xc} is a **per particle density**
- The ε_{xc} term is always treated as a sum of individual exchange ε_x and correlation ε_c contributions

$$\hat{E}_{xc}[\rho] = \hat{E}_x[\rho] + \hat{E}_c[\rho] = \int \rho(\tau)\varepsilon_x[\rho(\tau)]\delta\tau + \int \rho(\tau)\varepsilon_c[\rho(\tau)]\delta\tau$$

Kohn-Sham Self-Consistent Field (SCF)

- Electron density can also be express as:

$$r_s(\tau) = \left(\frac{3}{4\pi\rho(\tau)} \right)^{1/3}$$

An effective radius such that exactly one-electron would be contained within the sphere defined by that radius were it to have the same density throughout.

- Until now DFT has ignore the issue of spin
- Spin can incorporated by:

$$\zeta(\tau) = \frac{\rho^\alpha(\tau) - \rho^\beta(\tau)}{\rho(\tau)}$$

- α spin density: $\rho^\alpha(\tau) = \frac{1}{2}\rho(\tau)(\zeta + 1)$
- β spin density: $\rho^\beta(\tau) = \rho(\tau) - \rho^\alpha(\tau)$

Local Density Approximation (LDA/LSDA) – Exchange Functional

- The **exchange energy** for the uniform electron gas (ueg) can be computed exactly, and is given by:

$$\varepsilon_x[\rho] = -\frac{9\alpha}{8} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho^{1/3}(\tau) \quad \alpha_{LDA} = \frac{2}{3}$$

- For Slater ($\alpha=1$) for $X\alpha$ ($\alpha=3/4$)
- All of these models have the same 'local' dependence on the density.
- The ε_x term can be **extended to the spin-polarized** regime using: (When spin include LDA \rightarrow LSDA)

$$\varepsilon_x[\rho(\tau), \zeta] = \varepsilon_x^0[\rho(\tau)] + \{\varepsilon_x^1[\rho(\tau)] - \varepsilon_x^0[\rho(\tau)]\} \left[\frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2}{2(2^{1/3} - 1)} \right]$$

- ε_x^0 is the exchange energy density that represents electrons of opposite spin
- ε_x^1 is the exchange energy density that represents electrons of same spin
- For unpolarized system the $\zeta = 0$, so the second term in the equation becomes 0

Local Density Approximation (LDA/LSDA) – Correlation Functional

- Correlation energy density even for simple uEG has no analytical derivation.
- However, using quantum Monte Carlo techniques, Ceperley and Alder (1980) computed the **total energy** of uEGs for several different densities to very high numerical accuracy.
- The correlation energy can be determined by subtracting the **analytical exchange energy** from the **total energy**.
- Vosko, Wilk and Nusair (1980) designed local functionals of density fitting to Ceperley and Alder's results. This is given by:

$$\varepsilon_c^i(r_s) = \frac{A}{2} \left\{ \ln \frac{r_s}{r_s + b\sqrt{r_s} + c} + \frac{2b}{\sqrt{4c - b^2}} \tan^{-1} \left(\frac{\sqrt{4c - b^2}}{2\sqrt{r_s} + b} \right) - \frac{b\chi_0}{\chi_0^2 + b\chi_0 + c} \left\{ \ln \left[\frac{(\sqrt{r_s} - \chi_0)^2}{r_s + b\sqrt{r_s} + c} \right] + \frac{2(b + 2\chi_0)}{\sqrt{4c - b^2}} \tan^{-1} \left(\frac{\sqrt{4c - b^2}}{2\sqrt{r_s} + b} \right) \right\} \right\}$$

- **A, b, c, χ_0** are empirical constants (Vosko et al., *Can. J. Phys.*, **1980**. 58, 1200.)
- The two forms that have come to be most widely used tend to be **VWN** and **VWN5**

Local Density Approximation (LDA/LSDA)

- LSDA calculations employ a combination of **Slater exchange** and the **VWN correlation energy** expression.
- Sometimes referred to as SVWN method.
- Solution of E_{xc} integrals typically not possible analytically
- Evaluation of integrals involving exchange and correlation energy densities in DFT is done numerically on a grid.

Generalized Gradient Approximation (GGA)

- In a molecular system, the electron density is typically rather far from spatially uniform, which limits the LDA approach.
- One way to improve the correlation functional is to make it depend not only on the **local value**, but also the gradient **of the density** (the extent to which the density is locally changing)
- Originally referred to as ‘non-local’ DFT
- GGA = **Local term** + **Gradient correction**:

$$\varepsilon_{x/c}^{GGA}[\rho(\tau)] = \varepsilon_{x/c}^{LDA}[\rho(\tau)] + \Delta\varepsilon_{x/c} \left[\frac{|\nabla\rho(\tau)|}{\rho^{4/3}(\tau)} \right]$$

Generalized Gradient Approximation (GGA) – Exchange Functional

- The first widely popular GGA exchange functional was developed by Becke (B)
- B adopts a mathematical form that has correct asymptotic behavior at long range for energy density.
- B also incorporates a single empirical parameter, the value of which was optimized by fitting to the exactly known exchange energies of six noble gas atoms (He – Rn)
- Other GGA exchange functionals: CAM, FT97, O, PW, *m*PW, and X
- X = a combination of B and PW exchange functionals (Found to give an improved performance over either B and PW)
- Alternative GGA exchange functionals have been developed based on rational function expansion of the reduced gradient.
- These functionals, which contain no empirically optimized parameters include B86, LG, P, PBE, and *m*PBE.

Generalized Gradient Approximation (GGA) – Correlation Functional

- Corrections to the correlation energy density in:

$$\varepsilon_{x/c}^{GGA}[\rho(\tau)] = \varepsilon_{x/c}^{LDA}[\rho(\tau)] + \Delta\varepsilon_{x/c} \left[\frac{|\nabla\rho(\tau)|}{\rho^{4/3}(\tau)} \right]$$

- Include B88, P86, and PW91
- These functionals contain a different expression than VWN correlation expression for the LDA correlation energy density and contains no empirical parameters
- Another popular GGA correlation functional, LYP, doesn't correct the VWN correlation expression, but instead computes the correlation energy as a whole.
- The LYP correlation functional includes four empirical parameter fit to the helium atom, but is the only correlation functional discussed that provides an exact cancellation of the SIE in one electron system.
- A pure functional is the combination of an exchange functional component and a correlation functional component.

Meta-GGA

- The next logical step to **improve** the GGA functional might be to take account of the **second derivative of the density** (∇^2)
- Becke and Roussel were the first to propose an **exchange** functional (BR) with a dependence on the second derivative of the density.
- Proynov, Salahub, and coworkers applied the same idea to a **correlation** functional (Lap)
- Calculations for MGGA functional pose some technical challenge, but give somewhat improved performance.
- An alternate MGGA formalism that is more numerically stable is to include in the exchange correlation potential a dependency on the **kinetic energy density** $\tau(r)$. Defined as:

$$\tau(r) = \sum_i^{\text{occupied}} \frac{1}{2} |\nabla \Psi_i(r)|^2$$

Adiabatic Connection Method (Hybrid)

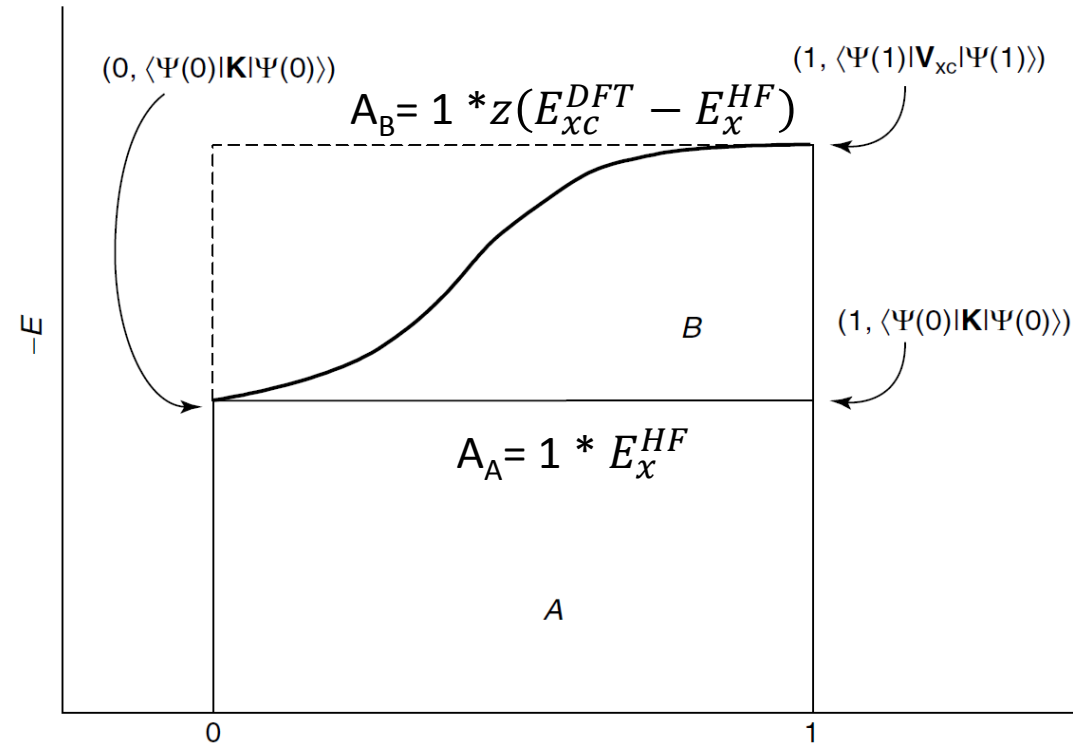
- Little is known about V and Ψ as a function of λ .
- The expectation value is the exact exchange for the non-interacting system ($E_x^{HF} = \langle \Psi | K | \Psi \rangle$)
- The resulting equation is called the Adiabatic Connection Method (ACM):

$$E_{xc} = \int_0^1 \langle \Psi(\lambda) | V_{xc}(\lambda) | \Psi(\lambda) \rangle \delta(\lambda)$$

- The area under the curve can be represented by:

$$E_{xc} = E_x^{HF} + z(E_{xc}^{DFT} - E_x^{HF})$$

- Where z (some fraction) of the area corresponding to the rectangle



Adiabatic Connection Method (Hybrid)

$$E_{xc} = E_x^{HF} + z(E_{xc}^{DFT} - E_x^{HF}) \quad E_{xc} = (1 - a)E_{xc}^{DFT} + aE_x^{HF}$$

- B3PW91 model is defined as:

$$E_{xc}^{B3PW91} = (1 - a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^B + E_c^{LSDA} + c\Delta E_c^{PW91}$$

- B3LYP model is defined as:

$$E_{xc}^{B3LYP} = (1 - a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^B + (1 - c)E_c^{LSDA} + cE_c^{LYP}$$

- Further information can be found:

Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

Method Comparison for DFT

Mean (unsigned errors in kcal/mol)		
Methods	Bond Energies	Barrier heights
Hartree-Fock Theory	31	9
LSDA	16	18
GGA: BLYP (1988)	1.5	8
Hybrid: B3LYP (1993)	0.9	4

Slater-Type Orbitals

$$\Psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi)$$

- Slater Type Orbitals represent the radial distribution of electron density very well.
- In molecules, one often has to evaluate numerical integrals of the product of 4 different STOs on 4 different nuclei (aka four centered integrals).
- This is very time consuming for STOs

$$\Psi_{\zeta nlm}(r, \theta, \varphi) = NY_{lm}(\theta, \varphi)r^{n-1}e^{-\zeta r}$$

$R_{nl}(r)$ = Is the radial function

$Y_{lm}(\theta, \varphi)$ = Is the spherical harmonic function

N = Is a normalization constant

r = distance of electron from nucleus

ζ = Determines how far from the nucleus the orbital extends.

Gaussian-Type Orbitals

- The integrals can be evaluated much more quickly for “Gaussian” functions (GTOs)

$$\Psi_{\zeta nlm}(r, \theta, \varphi) = NY_{lm}(\theta, \varphi)r^{2n-2-l}e^{-\zeta r^2}$$

- Compared to the multi-centered integral associated with STOs, GTOs only have single center integrals

- STOs can be approximated by a fixed sum of GTOs

$$S(r, \theta, \varphi) \approx \sum a_i G_i(r, \theta, \varphi)$$

- For example an STO may be approximated as a sum of 3 GTOs

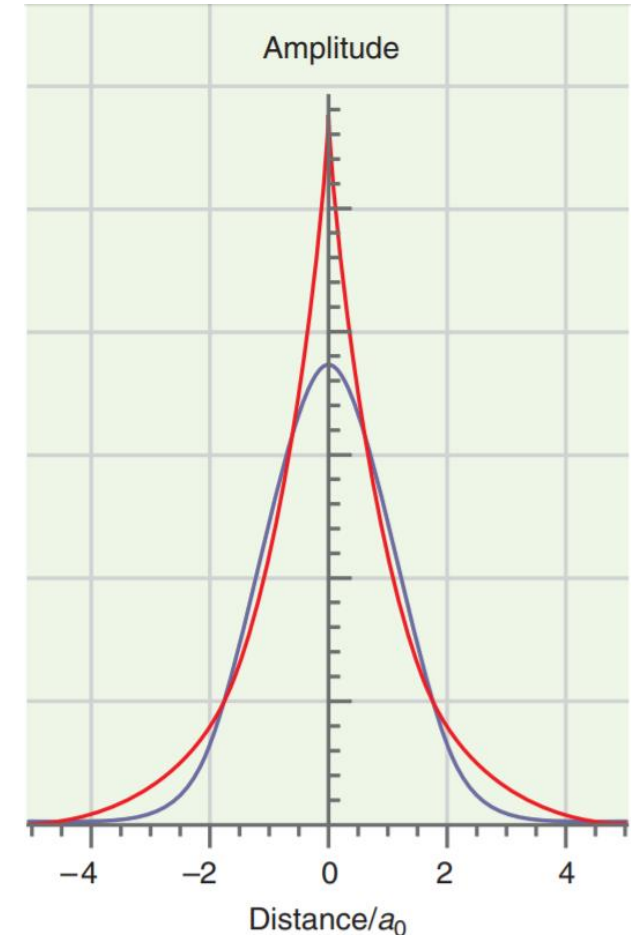
$$S(r, \theta, \varphi) \approx a_1 G_1(r, \theta, \varphi) + a_2 G_2(r, \theta, \varphi) + a_3 G_3(r, \theta, \varphi)$$

- It requires more GTOs to replicate an STO with large zeta (close to nucleus) than one with a smaller zeta (further from nucleus)
- The problem is that GTOs do not represent the radial dependence of electron density well at all

STOs vs GTOs

- The r^2 dependence in the exponential term makes the GTOs inferior to the STOs in two aspects:
 - At the nucleus the GTOs has a slope of 0, in contrast to the STOs which has a cusp. (discontinuous derivative)
 - The GTOs have problem representing the proper behavior near the nucleus
- Another problem is the GTOs fall off too rapidly far from the nucleus compared to STOs

$$S_{1s} = Ae^{-\zeta r} \qquad G_{1s} = Ae^{-\zeta r^2}$$



Basis Sets

- Within the Linear Combination of Atomic Orbital (LCAO) framework, a Molecular Orbital (ϕ_i) is taken to be a linear combination of “basis functions” (χ_j), which are usually STOs (composed of the sum of GTOs).

$$\phi_i = \sum C_{ij}\chi_j$$

- The number and type of basis functions (χ_j) used to describe the electrons on each atom is determined by the “Basis Set”.
- There are various levels of basis sets, depending upon how many basis functions are used to characterize a given electron in an atom in the molecule.

Basis set

- Combining the full set of basis functions (primitive GTOs) into a smaller set of functions by forming fixed linear combinations is known as basis set contractions (resulting functions are called contracted GTOs)

$$\chi(CGTO) = \sum_i^k a_i \chi_i(PGTO)$$

Basis Sets

- Minimal basis set contains the min. number of STOs necessary to contain the electrons in an atom. For example:
 - H atom: Has 1s AO, represented by one basis function
 - C atoms: Has 5 AO (1s, 2s, 3 2p), represented by five basis functions
- Double zeta (DZ) (Dunning): Uses two basis functions (different zeta) to represent each AO
 - H atom: Has 1s AO, represented by two basis functions
 - C atom: Has 5 AO, represented by ten basis functions
- Triple zeta (TZ): Uses three basis functions (different zeta) to represent each AO
- Quadruple zeta (QZ): Uses four basis functions (different zeta) to represent each AO
- And so on...

Basis Sets

- **Split valence:** One basis function for core AOs, and more basis functions for valence AOs
- Inner shell (core) electrons do not participate significantly in bonding.
- Therefore, a common variation of the multiple zeta basis set is to use two (or more) different STOs only in the valence shell, and a single STO for core electrons.
- For example **6-31G** is: (Pople basis set)
 - Core electrons are characterized by a single STO, composed of a fixed combination of six GTOs.
 - Two STOs with different values of zeta are used for valence:
 - The “inner” STO (higher zeta) is composed of three GTOs
 - The “outer” STO (lower zeta) is composed of one GTO
- Triply split valence basis set, for example **6-311G**:
 - Core electrons are characterized by a single STO, composed of a fixed combination of six GTOs.
 - Three STOs with different values of zeta are used for valence:
 - The “inner” STO (higher zeta) is composed of three GTOs
 - The “middle” STO is composed of one GTO
 - The “outer” STO (lower zeta) is composed of one GTO

Basis Sets

- Polarization Functions:
 - Often, the electron density in a bond is distorted from cylindrical symmetry. (e.g. $\text{H}_2\text{C}=\text{CH}_2$)
 - To allow for this distortion, polarization functions are often added to the basis set.
 - They are **STOs** usually composed of **single GTO** with the angular momentum quantum number greater than that required to describe the electron in the atom.
 - **H atom**: polarization function is composed of three 2p orbitals.
 - **C atom**: polarizations function is composed of five 3d orbitals.
- Examples of polarization functions:
 - 6-31G(d): **one** set of **d-orbitals** is added to p-block elements.
 - 6-31G(d,p): **one** set of **d-orbitals** is added to p-block elements, and **one** set of **p-orbitals** is added to hydrogen/helium.
 - 6-311G(3df,2pd): **Three** sets of **d-orbitals** and **one** set of **f-orbitals** are added to p-block elements, and **two** sets of **p-orbital** and **one** set of **d-orbitals** is added to the hydrogen/helium.

Basis Sets

- **Diffuse functions** are useful for Molecules:
 - with a negative charge
 - in excited electronic states
 - involved in hydrogen bonding
- Have a significant electron density at distances **further** from the nuclei than most ground state neutral molecules.
- To account for this, “diffuse” functions are sometimes added to the basis set.
- For H atom this is a single ns orbitals with a **very small value of zeta** (large extension away from the nucleus)
- For atoms other than H, this is an ns orbital and three np orbitals with a small value of zeta.
- **Examples** of diffuse functions:
 - 6-31+G: An s and 3p diffuse orbitals are added to all p-block elements
 - 6-31++G: An s and 3p diffuse orbitals are added to all p-block elements, while an s diffuse orbital is added to both hydrogen/helium

Effective Core Potential (ECP)

- Elements from the third row or higher in the periodic table contains large numbers of core electrons.
- These core electron are generally **unimportant** to chemical bonding/properties.
- However, it is necessary to use large number of basis functions to expand the corresponding orbitals, in order to accommodate the valence electrons (chemically important)
- Core electrons are modeled by a suitable potential function, and only the valence electrons are treated explicitly.
- Two common ECPs are:
 - LANL2DZ
 - Stuttgart

References

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- Engel, T. Quantum Chemistry & Spectroscopy, 3rd Ed. Pearson, Glenview, IL, United States of America 507.
- Notes from Dr. Cisneros (Chem 5660) & Dr. Schwartz (Chem 5210)
- Presentation “Introduction to Density Functional Theory” by Dr. Cuevas

Thank you!

