Basis Sets and Pseudopotentials

Slater-Type Orbitals (STO's)

$$\phi_{abc}^{STO}(x,y,z) = Nx^a y^b z^c e^{-\zeta r}$$

- N is a normalization constant
- a, b, and c determine the angular momentum, i.e. L=a+b+c
- ζ is the orbital exponent. It determines the size of the orbital.
- STO exhibits the correct short- and long-range behavior.
- Resembles H-like orbitals for 1s
- **Difficult to integrate for polyatomics**

Gaussian-Type Orbitals (GTO's)

$$\phi_{abc}^{GTO}(x,y,z) = Nx^a y^b z^c e^{-\zeta r^2}$$

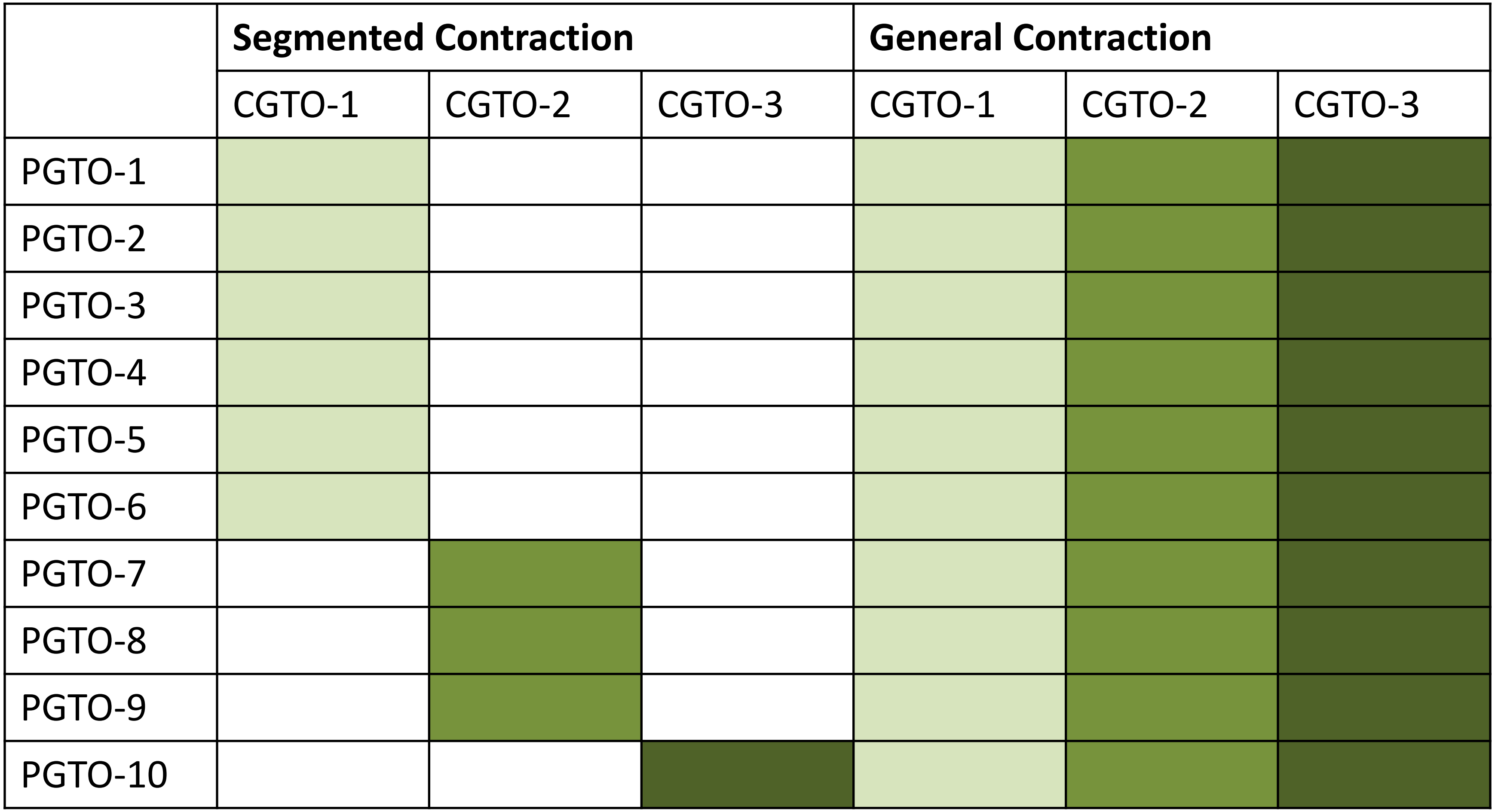
- N is a normalization constant
- a, b, and c determine the angular momentum, i.e. L=a+b+c
- ζ is the orbital exponent. It determines the size of the orbital.
- **Smooth curve near r=0 instead of a cusp.**
- **Tail drops off faster a than Slater orbital.**
- **Easy to integrate.**

Contracted Basis Sets

$$\chi(\mathrm{CGTO}) = \sum_{i=a}^{b} \alpha_i \chi_i(\mathrm{PGTO})$$

- P=primitive, C=contracted
- Reduces the number of basis functions
- The contraction coefficients, α_i, are constant
- Can be a segmented contraction or a general contraction

Contracted Basis Sets



	Segmented Contraction			**General Contraction**		
	CGTO-1	CGTO-2	CGTO-3	CGTO-1	CGTO-2	CGTO-3
PGTO-1	░			░	▒	▓
PGTO-2	░			░	▒	▓
PGTO-3	░			░	▒	▓
PGTO-4	░			░	▒	▓
PGTO-5	░			░	▒	▓
PGTO-6	░			░	▒	▓
PGTO-7		▒		░	▒	▓
PGTO-8		▒		░	▒	▓
PGTO-9		▒		░	▒	▓
PGTO-10			▓	░	▒	▓

Jensen, Figure 5.3, p. 202

STO-NG: STO approximated by linear combination of N Gaussians

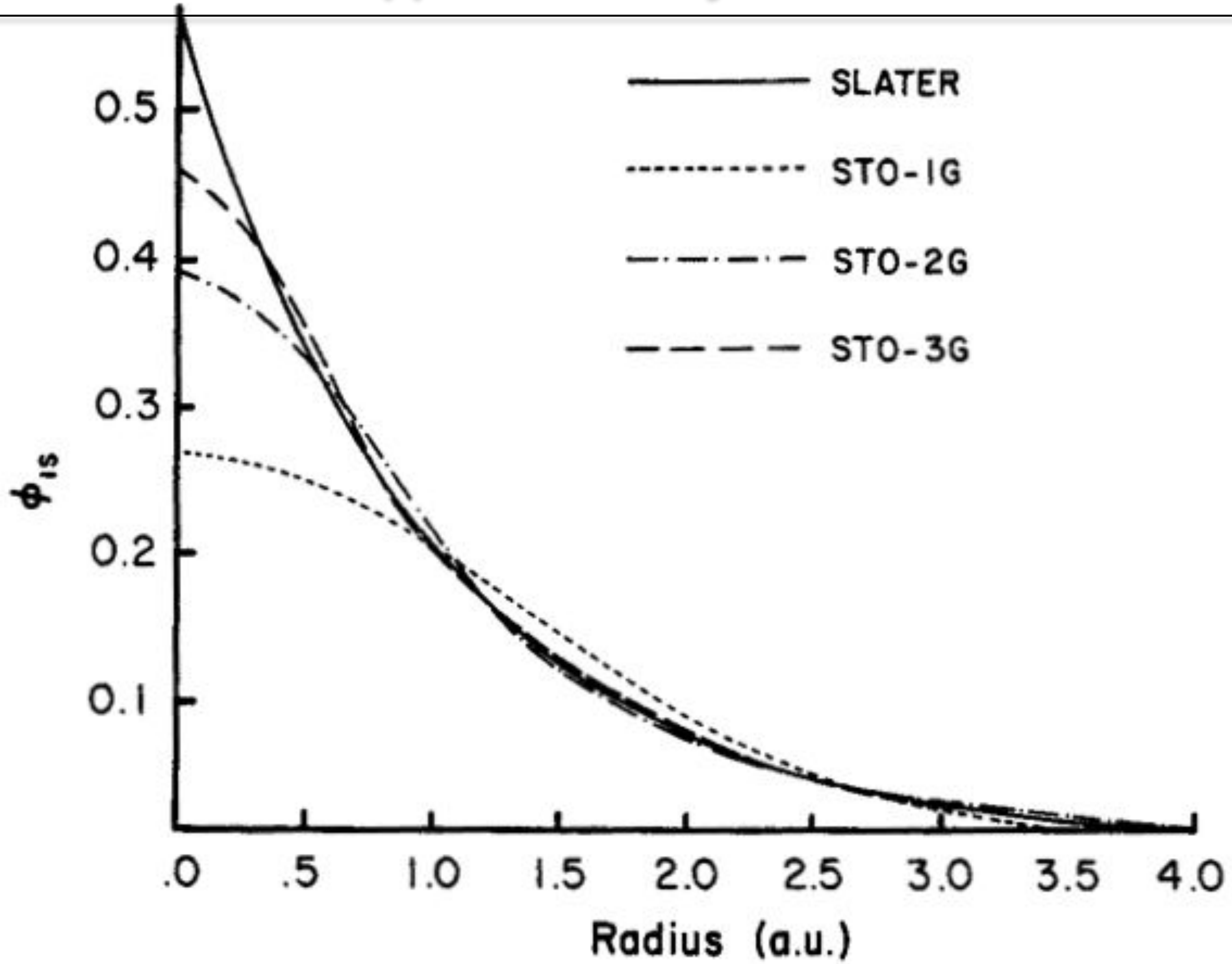


Figure 3.3 Comparison of the quality of the least-squares fit of a 1*s* Slater function ($\zeta = 1.0$) obtained at the STO-1G, STO-2G, and STO-3G levels.

Figure from Szabo and Ostlund, Modern Quantum Chemistry.

Even-tempered Basis Sets

$$\phi_{abc}(x,y,z) = Nx^a y^b z^c e^{-\zeta r^2}$$

$$\zeta_i = \alpha\beta_i$$

- Same functional form as the Gaussian functions used earlier

- The exponent, ζ, is fitted to two parameters with different α and β for s, p, d, etc. functions.

- Successive exponents are related by a geometric series
  - log(ζ) are evenly spaced

Reudenberg, K., *et Al.*, *Energy, Structure and Reactivity, Proceedings of the 1972 Boulder Conference*; Wiley: New York, 1973.
Reeves, C. M. *J. Chem Phys.* **1963**, *39*, 1.

Well-tempered Basis Sets

$$\phi_{abc}(x,y,z) = Nx^a y^b z^c e^{-\zeta r^2}$$

$$\zeta_i = \alpha\beta^{k-1}[1+\gamma(\tfrac{k}{K})^{\delta}], \quad k = 1,2,\ldots,K$$

- α, β, γ, and δ are parameters optimized to minimize the SCF energy
- Exponents are shared for s, p, d, etc. functions

Huzinaga, S. *et Al.*, *Can. J. Chem.* **1985**, *63*, 1812.

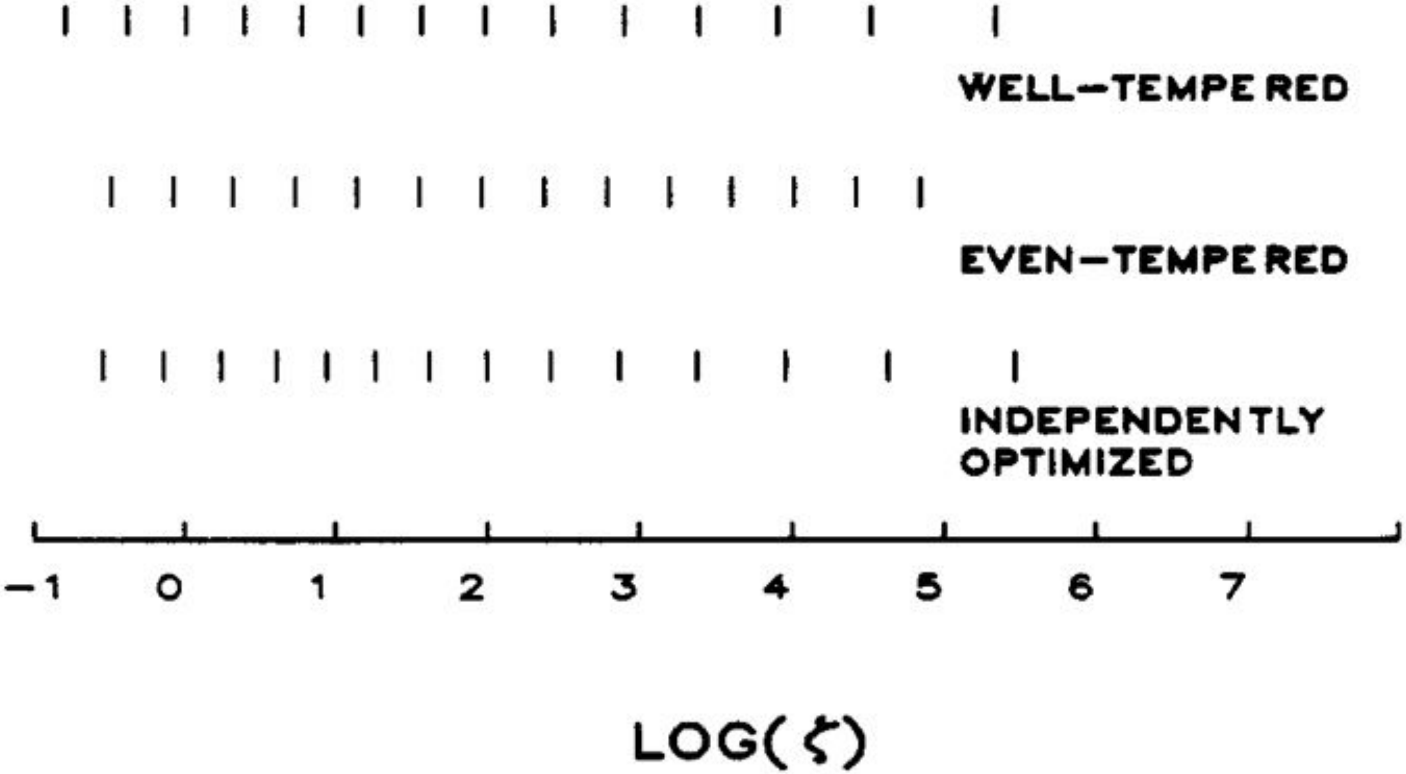


Figure 1. The distribution of s-symmetry gaussian exponents in three energy-optimized (14s,9p) neon atom basis sets.

Davidson, E. R.; Feller, D. *Chem. Rev.* **1986**, *86*, 681-696.

Plane Wave Basis Sets

- Used to model infinite systems (e.g. metals, crystals, etc.)
- In infinite systems, molecular orbitals become bands
- Electrons in bands can be described by a basis set of plane waves of the form

$$\chi_k(r) = e^{ik \cdot r}$$

- The wave vector **k** in a plane wave function is similar to the orbital exponent in a Gaussian function
- Basis set size is related to the size of the unit cell rather than the number of atoms

Polarization Functions

- Similar exponent as valence function
- Higher angular momentum (l+1)
- Uncontracted Gaussian (coefficient=1)
- Introduces flexibility in the wave function by making it directional
- Important for modeling chemical bonds

Diffuse Functions

- Smaller exponent than valence functions (larger spatial extent)
- Same angular momentum as valence functions
- Uncontracted Gaussian (coefficient=1)
- Useful for modeling anions, excited states and weak (e.g., van der Waals) interactions

Cartesian vs. Spherical

Cartesians:	Sphericals:
s – 1 function	s – 1 function
p – 3 functions	p – 3 functions
d – 6 functions	d – 5 functions
f – 10 functions	f – 7 functions

Look at the d functions:
In chemistry, there should be 5 d functions (usually chosen to be , $d_{x^2-y^2}$ d_{z^2}, d_{xy}, d_{xz} and d_{yz}. These are “pure angular momentum” functions.

But it is easier to write a program to use Cartesian functions (, d_{x^2}, d_{y^2}, d_{z^2} d_{xy}, d_{xz} and d_{yz}.

Cartesian vs. Spherical

Suppose we calculated the energy of HCl using a cc-pVDZ basis set using Cartesians then again using sphericals.

Which calculation produces the lower energy? Why?

Pople Basis Sets

- Optimized using Hartree-Fock
- Names have the form

  k-nlm++G** or k-nlmG(…)
- k is the number of contracted Gaussians used for core orbitals
- nl indicate a split valence
- nlm indicate a triple split valence
- + indicates diffuse functions on heavy atoms
- ++ indicates diffuse functions on heavy atoms and hydrogens

Pople Basis Sets

Examples:

6-31G Three contracted Gaussians for the core with the valence represented by three contracted Gaussians and one primitive Gaussian

6-31G* Same basis set with a polarizing function added

6-31G(d) Same as 6-31G*

6-31G** Polarizing functions added to hydrogen and heavy atoms

6-31G(d,p) Same as 6-31G**

6-31++G 6-31G basis set with diffuse functions on hydrogen and heavy atoms

The ** notation is confusing and not used for larger basis sets:

6-311++G(3df, 2pd)

Dunning Correlatoin Consistent Basis Sets

- Optimized using a correlated method (CIS, CISD, etc.)
- Names have the form

  aug-cc-pVnZ-dk
- “aug” denotes diffuse functions (optional)
- “cc” means “correlation consistent”
- “p” indicates polarization functions
- “VnZ” means “valence n zeta” where n is the number of functions used to describe a valence orbital
- “dk” indicates that the basis set was optimized for relativistic calculations
- Very useful for correlated calculations, poor for HF
- Size of basis increases rapidly with n

Dunning Basis Sets

Examples:

cc-pVDZ	Double zeta with polarization
aug-cc-pVTZ	Triple zeta with polarization and diffuse functions
cc-pV5Z-dk	Quintuple zeta with polarization optimized for relativistic effects

Extrapolate to complete basis set limit

Most useful for electron correlation methods

$P(l_{max}) = P(CBS) + A(l_{max})^{-3}$

$P(n) = P(CBS) + A(n)^{-3}$

n refers to cc basis set level: for for DZ, 3 for TZ, etc.

Best to use TZP and better

http://molecularmodelingbasics.blogspot.dk/2012/06/complete-basis-set-limit-extrapolation.html

TCA, 99, 265 (1998)

Basis Set Superposition Error

- Occurs when a basis function centered at one nucleus contributes the the electron density around another nucleus

- Artificially lowers the total energy

- Frequently occurs when using an unnecessarily large basis set (e.g. diffuse functions for a cation)

- Can be corrected for using the counterpoise correction.

  - **Counterpoise usually overcorrects**

  - Better to use a larger basis set

Counterpoise Correction

$$\Delta E_{CP} = E(A)_{ab} + E(B)_{ab} - E(A)_{a} - E(B)_{b}$$

- $E(A)_{ab}$ is the energy of fragment A with the basis functions for A+B
- $E(A)_{a}$ is the energy of fragment A with the basis functions centered on fragment A
- $E(B)_{ab}$ and $E(B)_{b}$ are similarly defined

Additional Information

EMSL Basis Set Exchange:

https://bse.pnl.gov/bse/portal

Further reading:

Davidson, E. R.; Feller, D. *Chem. Rev.* **1986**, *86*, 681-696.

Jensen, F. “Introduction to Computational Chemistry”, 2nd ed., Wiley, **2009**, Chapter 5.

Effective Core Potentials (ECPs) and Model Core Potentials (MCPs)

Frozen Core Approximation

All electron Fock operator:

$$F = h^{kinetic} - \sum_{A}^{Nuclei} \frac{Z_A}{r_A} + \sum_{j}^{occ} (J_j - K_j)$$

Partition the core (atomic) orbitals and the valence orbitals:

$$F = h^{kinetic} - \sum_{Z}^{Nuclei} \frac{Z_A}{r_A} + \sum_{A}^{Nuclei} \sum_{c}^{core} (J_c^A - K_c^A) + \sum_{v}^{valence} (J_v - K_v)$$

Introduce a modified nuclear charge ($Z_A^* = Z_A - Z_{core}$):

$$F = h^{kinetic} - \sum_{A}^{Nuclei} \frac{Z_A^*}{r_A} + \sum_{v}^{valence} (J_v - K_v) + \sum_{A}^{Nuclei} \left(- \frac{Z_A^{core}}{r_A} + \sum_{c}^{core} J_c^A \right) - \sum_{A}^{Nuclei} \sum_{c}^{core} K_c^A$$

$V_{Coulomb}$ $V_{Exchange}$

Approximation made: atomic core orbitals are not allowed to change upon molecular formation; all other orbitals stay orthogonal to these AOs

Pseudopotentials - ECPs

Effective core potentials (ECPs) are pseudopotentials that replace core electrons by a potential fit to all-electron calculations. Scalar relativisitc effects (e.g. mass-velocity and Darwin) are included via a fit to relativistic orbitals.

Two schools of though:

1. Shape consistent ECPs
   (e.g. LANLDZ RECP, etc.)

2. Energy consistent ECPs
   (e.g. Stüttgart LC/SC RECP, etc.)

Shape Consistent ECPs

- Nodeless pseudo-orbitals that resemble the valence orbitals in the bonding region

$$\psi_v(\vec{r}) \rightarrow \tilde{\psi}_v(\vec{r}) = \begin{cases} \psi_v(\vec{r}) & (r \geq r_c) \\ f_v(\vec{r}) & (r < r_c) \end{cases}$$

Original orbital in the outer region

Smooth polynomial expansion in the inner region

- The fit is usually done to either the large component of the Dirac wave function or to a 3rd order Douglas-Kroll wave function

- Creating a normalized shape consistent orbital requires mixing in virtual orbitals

- Usually gives accurate bond lengths and structures

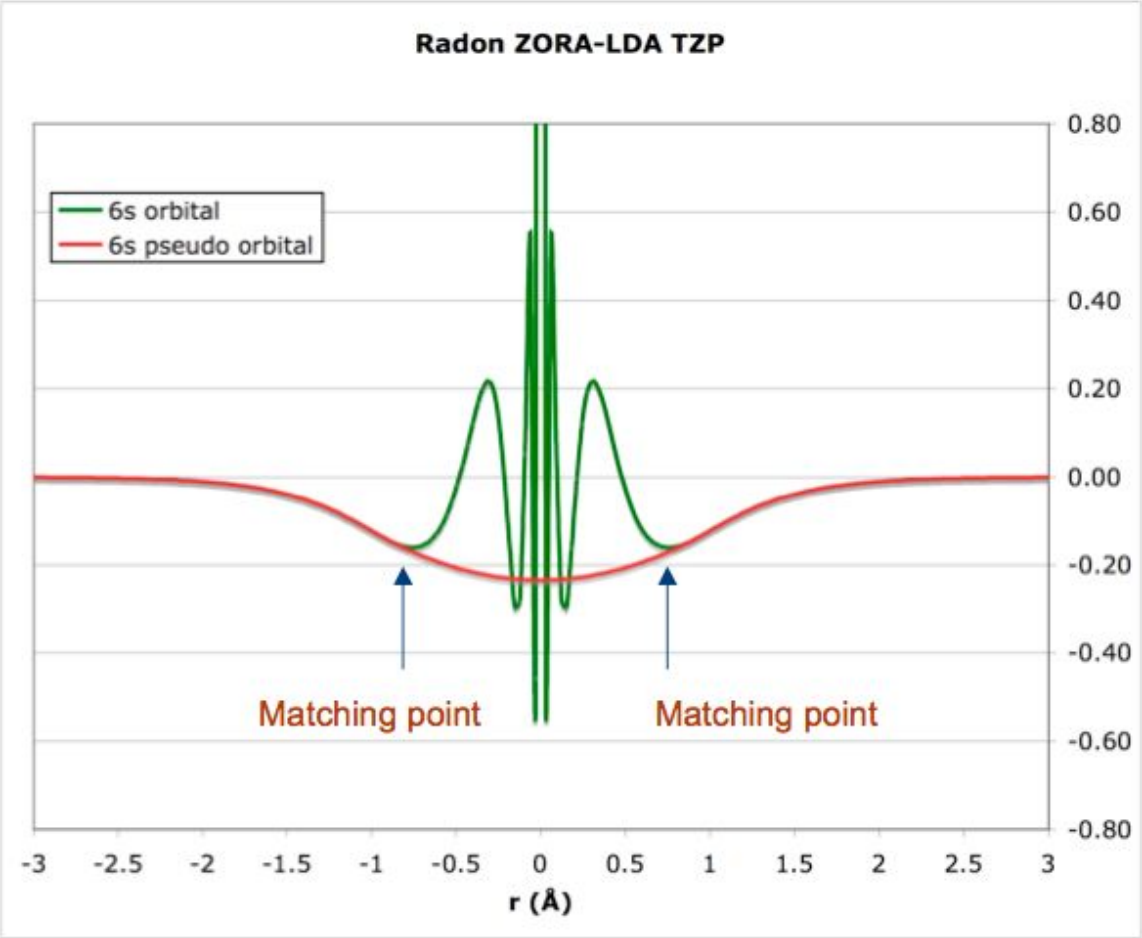
Energy Consistent ECPs

- Approach that tries to reproduce the low-energy atomic spectrum (via correlated calculations)

$$\min\left(\sum_{I}^{\substack{Low-lying\\levels}} w_I\left(E_I^{PP}-E_I^{\mathrm{Re}ference}\right)^2\right)$$

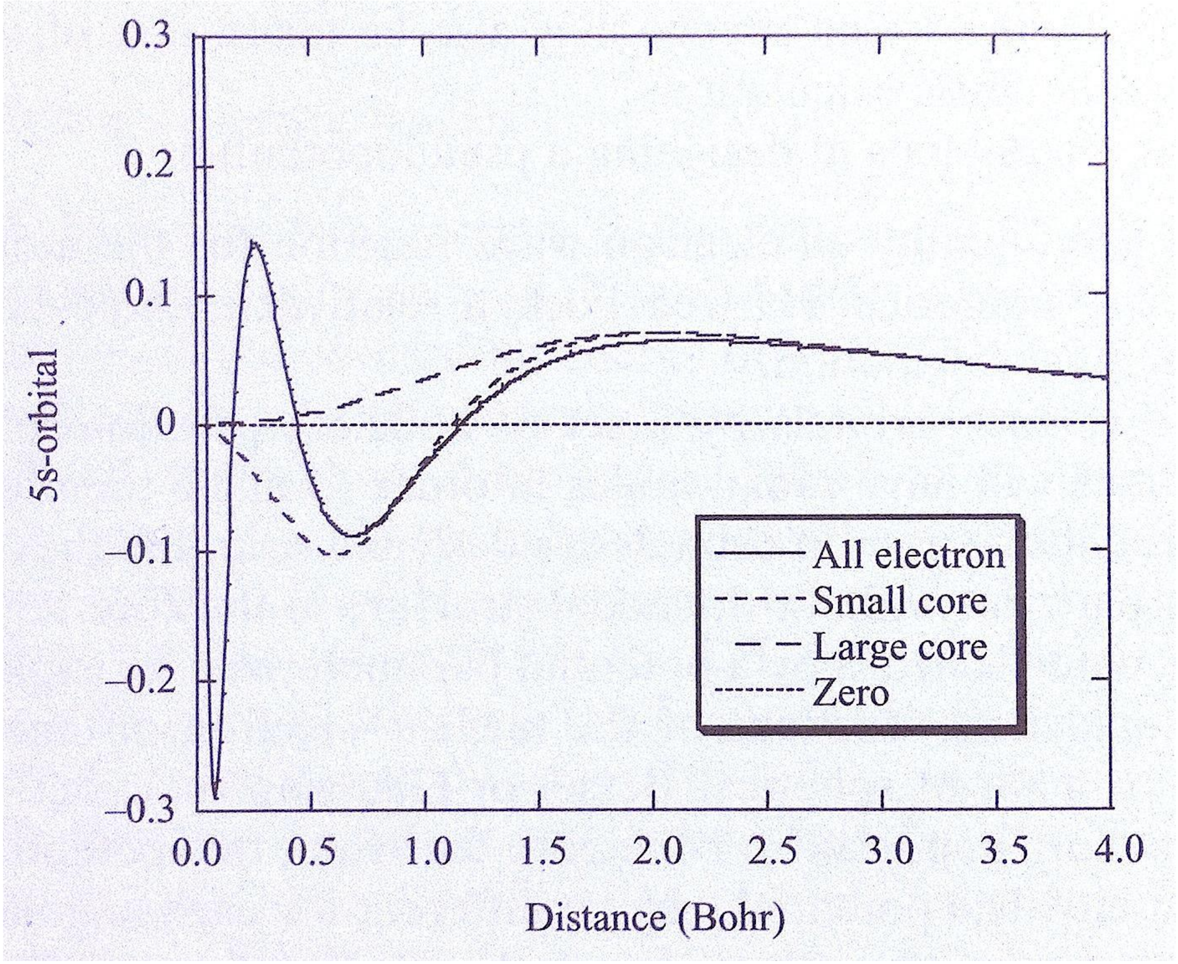
- Usually fit to 3rd order Douglas-Kroll
- Difference in correlation energy due to the nodeless valence orbitals is included in the fit
- Small cores are still sometimes necessary to obtain reliable results (e.g. actinides)
- Cheap core description allows for a good valence basis set (e.g. TZVP)
- Provides accurate results for many elements and bonding situations

Pseudo-orbitals



Visscher, L., “Relativisitic Electronic Structure Theory”, 2006 Winter School, Helkinki, Finland.

Large and Small Core ECPs



Jensen, Figure 5.7, p. 224.

Pseudopotentials - MCPs

- Model Core Potentials (MCP) provide a computationally feasible treatment of heavy elements.
- MCPs can be made to include scalar relativistic effects
  - Mass-velocity terms
  - Darwin terms
- Spin orbit effects are neglected.
  - Inclusion of spin-orbit as a perturbation has been proposed
- MCPs for elements up to and including the lanthanides are as computationally demanding as large core ECPs.

MCP Formulation

All-electron (AE) Hamiltonian:

$$\hat{H}(1,2,\ldots,N)=\sum_{i=1}^{N}h_i^{AE}+\sum_{i>j}^{N}\frac{1}{r_{ij}}+\sum_{L>M}^{N_{atom}}\frac{Z_L Z_M}{R_{LM}}$$

MCP Hamiltonian:

$$\hat{H}\left(1,2,\ldots,N_v\right)=\sum_{i=1}^{N_v}h_i^{MCP}+\sum_{i>j}^{N_v}\frac{1}{r_{ij}}+\sum_{L>M}^{N_{atom}}\frac{\left(Z_L-N_{L,Core}\right)\left(Z_M-N_{M,Core}\right)}{R_{LM}}$$

- First term is the 1 electron MCP Hamiltonian
- Second term is electron-electron repulsion (valence only)
- Third term is an effective nuclear repulsion

Huzinaga, S.; Klobukowski, M.; Sakai, Y. *J. Phys. Chem.* **1982**, *88*, 21.
Mori, H; Eisaku, M *Group Meeting*, Nov. 8, **2006**.

1-electron Hamiltonian

All-electron (AE) Hamiltonian:

$$\hat{H}(1,2,\cdots,N) = \sum_{i=1}^{N} h_i^{AE} + \sum_{i>j}^{N} \frac{1}{r_{ij}} + \sum_{L>M}^{N_{atom}} \frac{Z_L Z_M}{R_{LM}}$$

MCP Hamiltonian:

$$\hat{H}(1,2,\cdots,N_v) = \sum_{i=1}^{N_v} h_i^{MCP} + \sum_{i>j}^{N_v} \frac{1}{r_{ij}} + \sum_{L>M}^{N_{atom}} \frac{(Z_L - N_{L,Core})(Z_M - N_{M,Core})}{R_{LM}}$$

- First term is the 1 electron MCP Hamiltonian
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Huzinaga, S.; Klobukowski, M.; Sakai, Y. *J. Phys. Chem.* **1982**, *88*, 21.
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MCP Nuclear Attraction

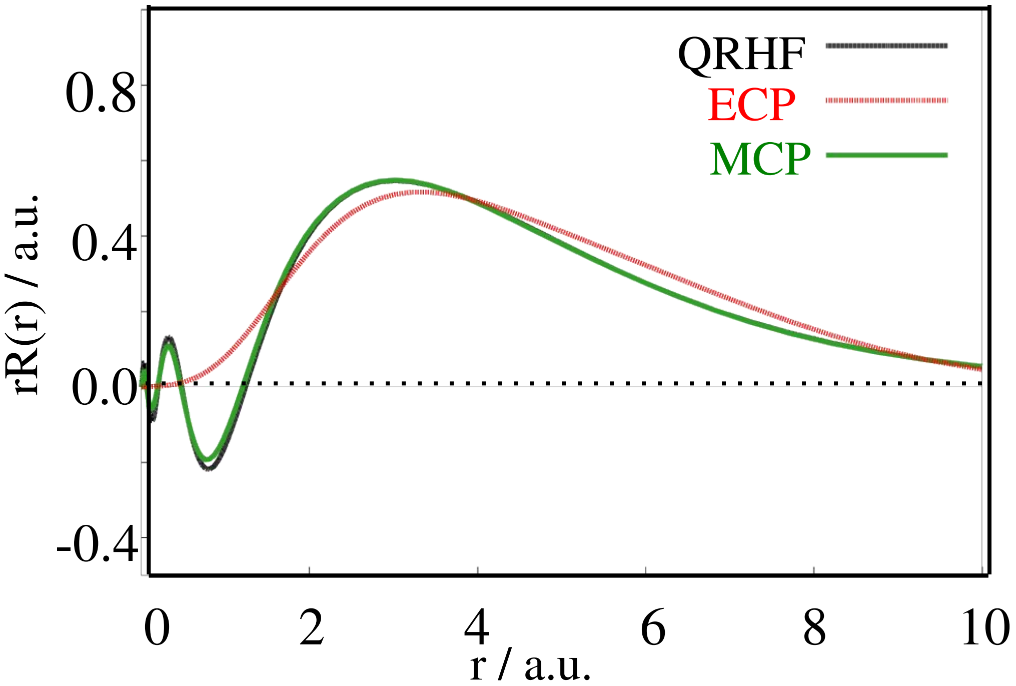
$$V_K^{MCP}\left(\mathbf{r}_i\right) = -\frac{Z_K - N_{K,core}}{r_{iK}}\left[1 + \sum_{I}^{3} A_I \exp\left(-\alpha_I r_{iK}^2\right) + \sum_{J}^{3} B_J r_{iK} \exp\left(-\beta_J r_{iK}^2\right)\right]$$

- A_I, α_I, B_J, and β_J are fitted MCP parameters
- MCP parameters are fitted to 3rd order Douglas-Kroll orbitals

Huzinaga, S.; Klobukowski, M.; Sakai, Y. *J. Phys. Chem.* **1982**, *88*, 21.
Mori, H; Eisaku, M *Group Meeting*, Nov. 8, **2006**.

MCP vs. ECP

■ 6s Orbital of Au atom



- ECPs “smooth out” the core, eliminating the radial nodal structure
- MCPs retain the correct radial nodal structure

Mori, H; Eisaku, M *Group Meeting*, Nov. 8, 2006.