Correlation Consistent Basis Sets

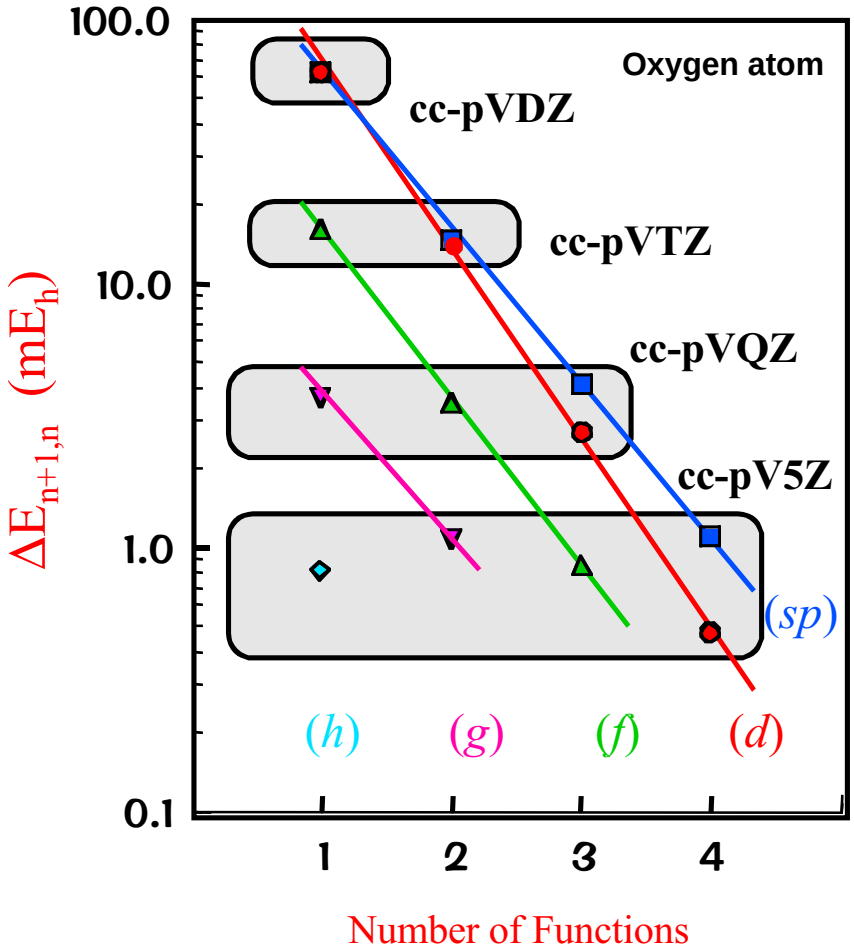
Basis Function Groupings

Contributions of basis functions to the correlation energy for the first row atoms fall into distinct groups with

$$\Delta E_{1,0}(sp) \approx \Delta E_{1,0}(d)$$
$$\Delta E_{2,1}(sp) \approx \Delta E_{2,1}(d) \approx \Delta E_{1,0}(f)$$
$$\Delta E_{3,2}(sp) \approx \Delta E_{3,2}(d) \approx \Delta E_{2,1}(f) \approx \Delta E_{1,0}(g)$$

These groupings form the foundation for the construction of correlation consistent basis sets:

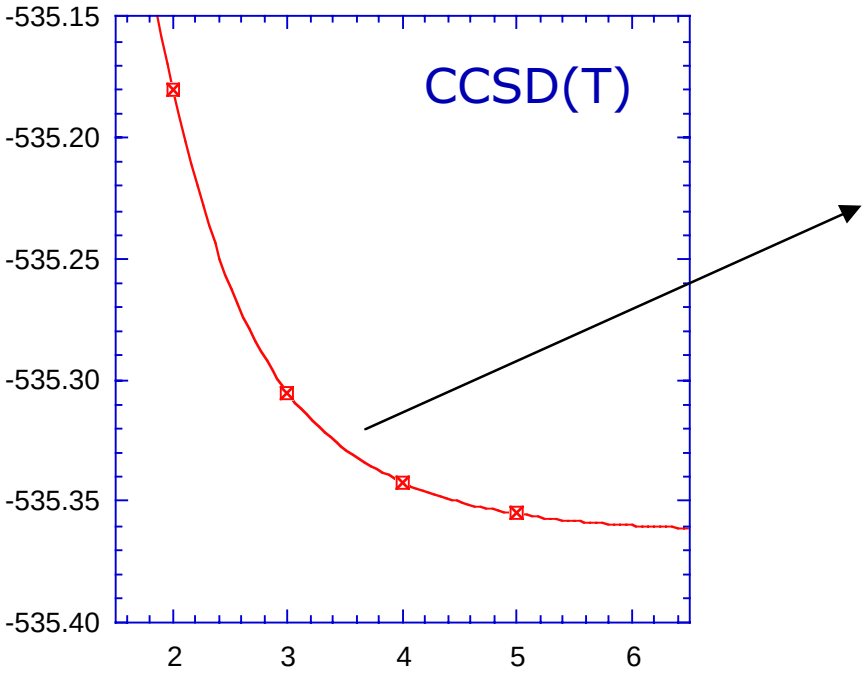
cc-pVDZ: HF Orbitals + $(1s1p1d)$
cc-pVTZ: HF Orbitals + $(2s2p2d1f)$
cc-pVQZ: HF Orbitals + $(3s3p3d2f1g)$
…



Approaching the Complete Basis Set Limit

Exploit the regular convergence of the correlation consistent basis sets

Example: the O(^{3}P)+HCl TS



aug-cc-pVnZ

Common extrapolation formulae

$$E(n) = E_{CBS} + Be^{-Cn}$$

$$E(n) = E_{CBS} + Be^{-(n-1)} + Ce^{-(n-1)^2}$$

$$E(n) = E_{CBS} + \frac{B}{\left(\ell_{\max} + \frac{1}{2}\right)^4} + \frac{C}{\left(\ell_{\max} + \frac{1}{2}\right)^6}$$

$$E(n) = E_{CBS} + \frac{B}{\left(\ell_{\max} + \frac{1}{2}\right)^C}$$

Note: $\ell_{\max} = n$