Effective Core Potential (ECP) Basis Sets

Svante Hedström, Batista Lab, Yale University

Name	ECP on atoms	ζ (zeta) type	Polariz.	Corresp. Pople	Notes
SDDall	Li and heavier	All double-ζ	None	6-31G	Hardly useful
LANL2MB	Na and heavier	Minimal basis	None	STO-3G	VERY small basis
LANL2DZ	Na and heavier	Valence double-ζ	None	6-31G	
SDD	K and heavier	All double-ζ	None	6-31G	
Def2SV	Rb and heavier	Valence double-ζ	Little	6-31G(d)	A.k.a. Def2SV(P)
Def2SVP	Rb and heavier	Valence double-ζ	Medium	6-31G(d,p)	
Def2TZV	Rb and heavier	Valence triple-ζ	None	6-311G	Hardly useful
Def2TZVP	Rb and heavier	Valence triple-ζ	More	6-311G(2df,p)	
Def2TZVPP	Rb and heavier	Valence triple-ζ	Lots	6-311G(3df,pd)	

Tips and suggestions

- If only one basis set (with ECP) is used for all atoms, it can be specified in the route section, e.g. *# b3lyp/def2svp* . To use more than one basis, *genecp* or equivalently *gen pseudo=read* must be specified in the route section, followed by the basis and ECP cards after the molecule specification. Example of basis and ECP card:

  H C N O 0
  6-31g(d,p)
  ****
  Au 0
  SDD
  ****

  Au 0
  SDD

- ECP bases are useful for two main reasons:
  - reducing computational cost on systems with many metal centers, e.g. metal or metal oxide clusters or slabs.
  - circumventing having to describe relativistic effects in deep core electrons.
- In metal complexes with only a few metal centers, using ECPs gives a very negligible speedup. Using LANL2x or SDDx for these is generally a bad idea for publication-grade calculations, not because they use an ECP but because the non-ECP part is so small, e.g. having no polarization functions which are important since frontier orbitals of such systems often involve the metal basis functions, and these orbitals are the most important for redox reactions and excitations.
- For ECP and all-electron bases alike, using a smaller basis for geometry optimization (e.g. Def2SV) and then a larger for single point orbital and total energies (e.g. Def2TZVP), is a good way of obtaining good accuracy at a smaller computational cost.
- None of these ECP bases include diffuse functions which are important for describing localized anions. In systems where oxygen or smaller moieties such as nitro groups bear formal negative charges, it is a good to use e.g. 6-31+G(d,p) for those corresponding atom types, and Def2SVP on remaining atom types.