Basis Set

The Hydrogen Atom Eigenfunctions

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

$$R_{10}(r) = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

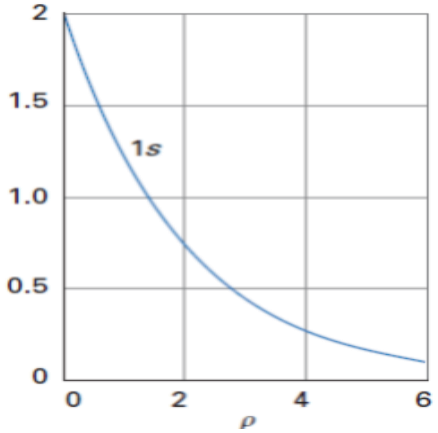
$$R_{20}(r) = \frac{1}{\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2}\left(1-\frac{Zr}{2a}\right)e^{-Zr/2a}$$

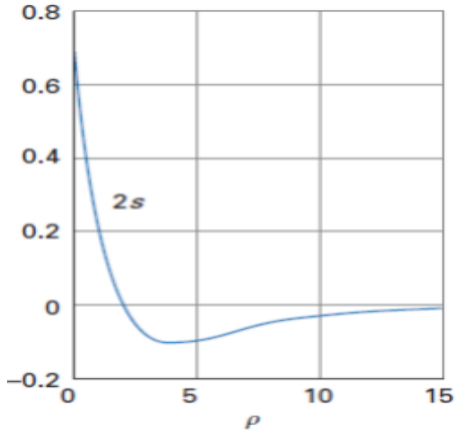
$$R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}$$

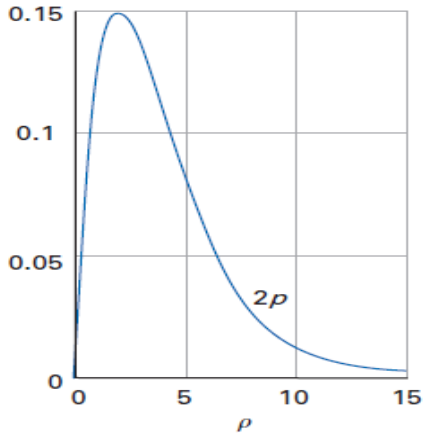
$$R_{30}(r) = \frac{2}{3\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2}\left(1-\frac{2Zr}{3a}+\frac{2Z^2r^2}{27a^2}\right)e^{-Zr/3a}$$

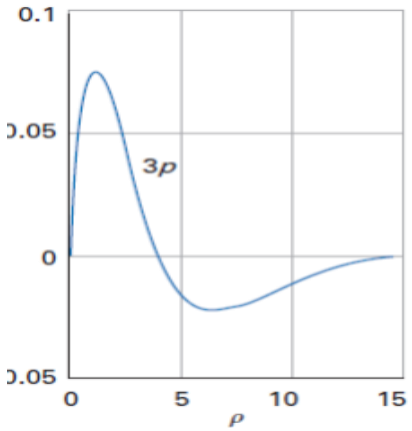
$$R_{31}(r) = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}-\frac{Z^2r^2}{6a^2}\right)e^{-Zr/3a}$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a}$$









Basis functions

Should

- have analytical form
- form a ‘complete set’ with less number of functions
- be easily orthogonalizable
- allow fast integral evaluation

Choice of basis functions

Hydrogenic functions

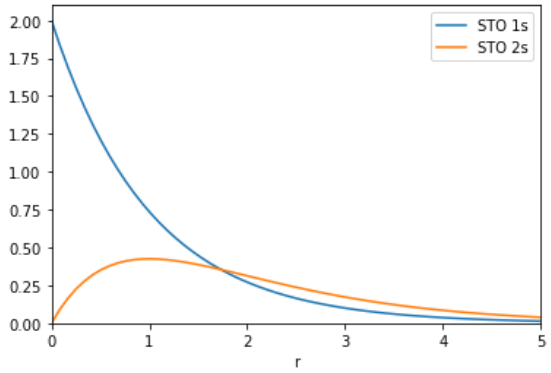
$$\Psi_{nlm} = \left(\frac{2Z}{n}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n(n+1)!}} \left(\frac{2Zr}{n}\right)^{l} L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right) \exp\left(-\frac{Zr}{n}\right) Y_{lm}(\theta,\phi)$$

$$\langle \hat{r} \rangle = \frac{3n^2 - l(l+1)}{2Z}$$

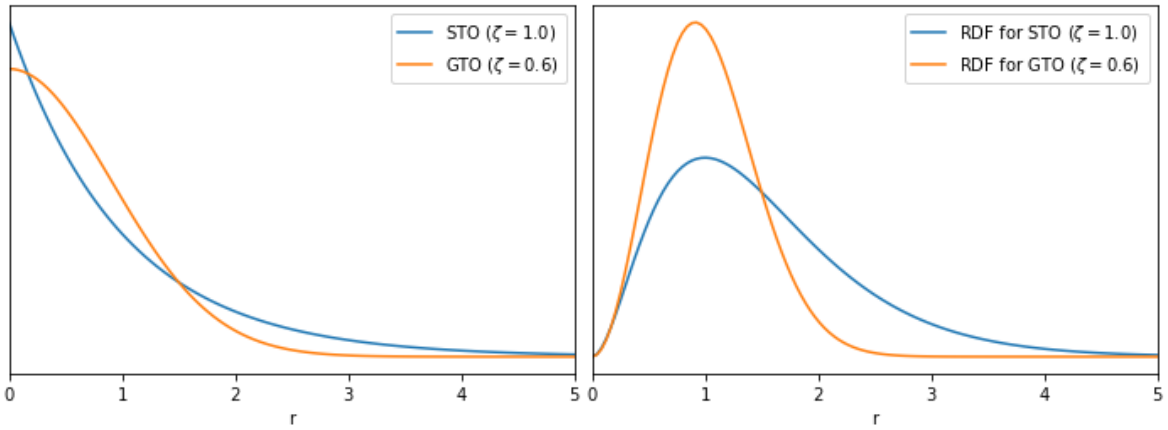
Slater Type Orbitals

$$\Psi_{nlm}^{\mathrm{STO}} = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1} \exp\left(-\zeta r\right) Y_{lm}(\theta,\phi)$$

$$\langle \hat{r} \rangle = \frac{2n+1}{2\zeta}$$



Gaussian-type Orbitals (GTOs)

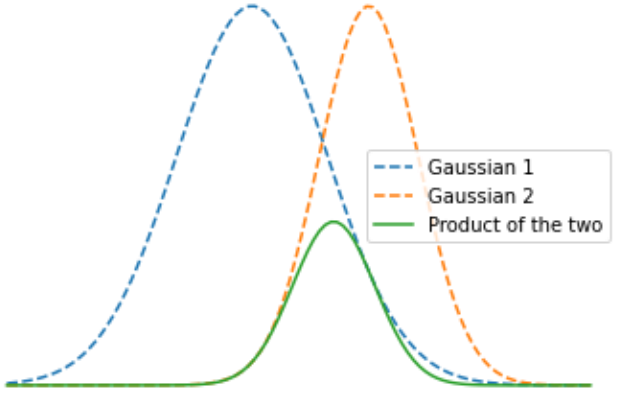


$$\Psi_{nlm}^{\mathrm{GTO}} = \mathcal{N} r^{2n-2-l} \exp\left(-\zeta r^2\right) Y_{lm}(\theta, \phi)$$

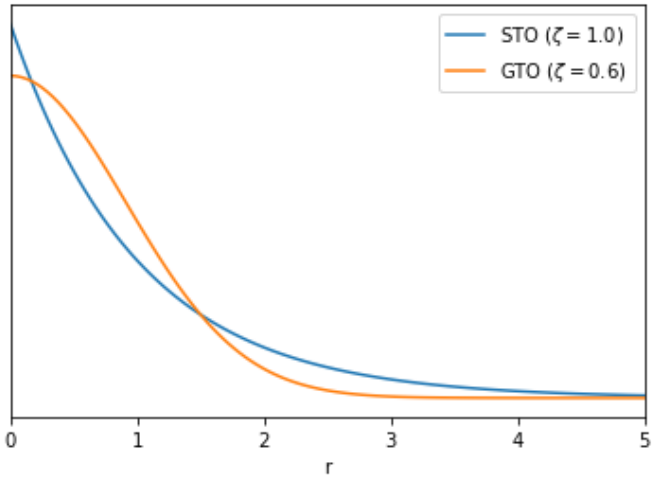
$$\Psi_{nlm}^{\mathrm{GTO}} = \mathcal{N} x^i y^j z^k \exp\left(-\zeta r^2\right), \qquad i + j + k = l$$

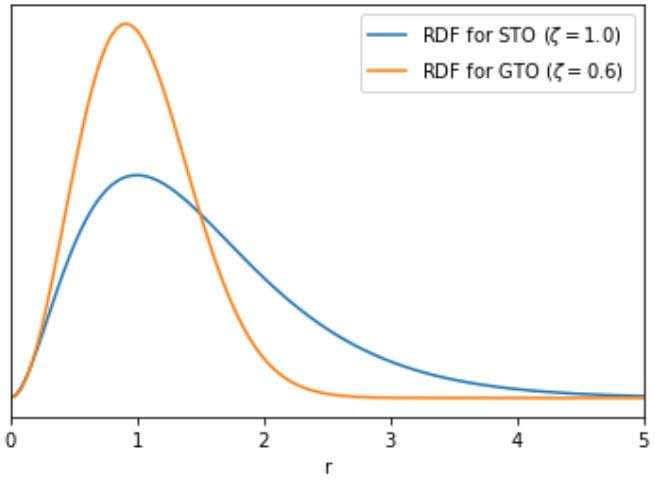
Product of two Gaussians is a Gaussian

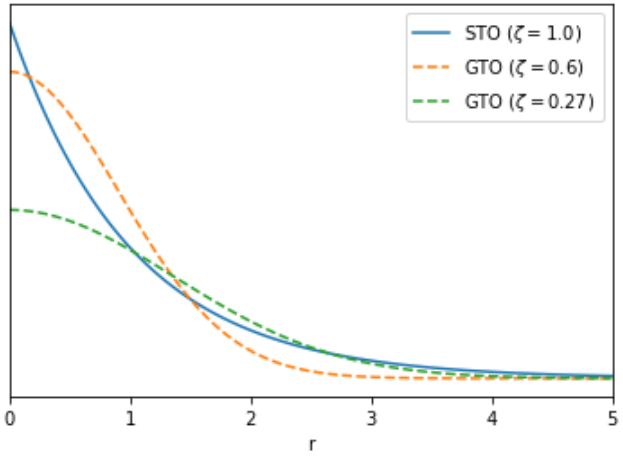
$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda} \left((\mu\lambda|\nu\sigma) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right)$$

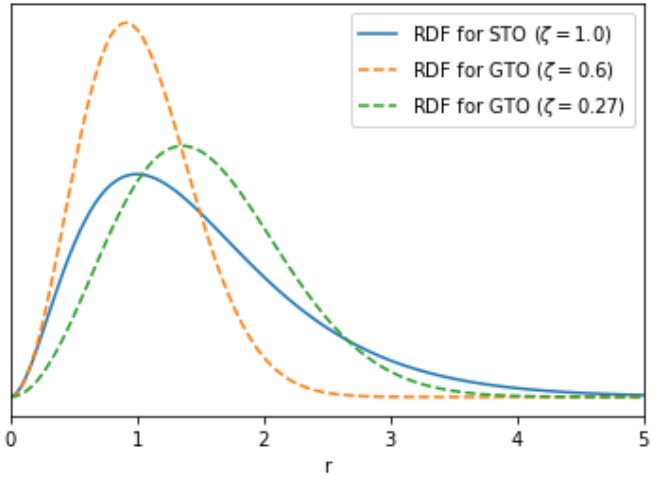


Gaussian-type Orbitals (GTOs)









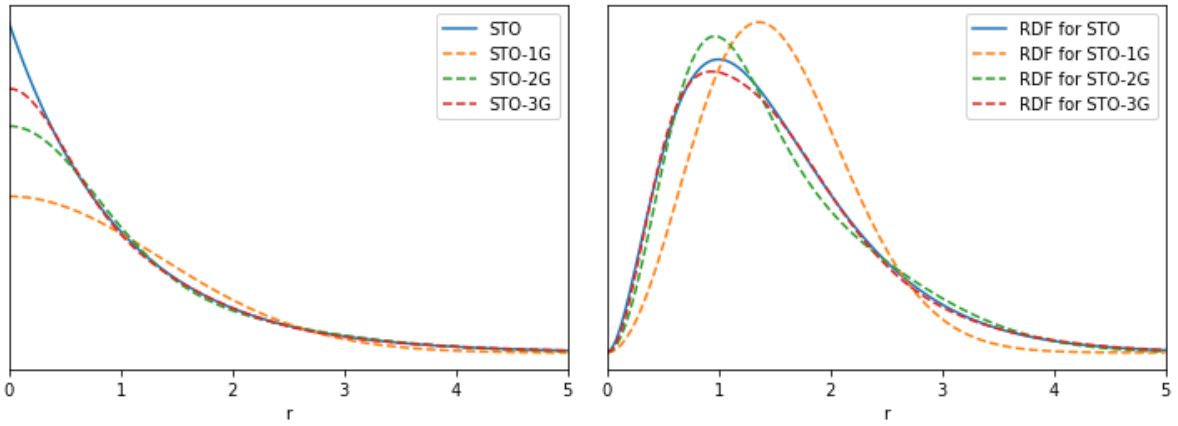
Radial Distribution Function (RDF)

$$= 4\pi r^2 |\psi(r)|^2$$

Contracted Gaussian Type Functions

$$\Psi^{\mathrm{cGTO}} = \mathcal{N} \sum_{i}^{n} c_i \Psi^{\mathrm{GTO}}_{\mathrm{primitive}}$$

$$\Psi^{\mathrm{cGTO}} = \mathcal{N} \sum_{i}^{n} c_i x^i y^j z^k \exp\left(-\zeta_i r^2\right)$$



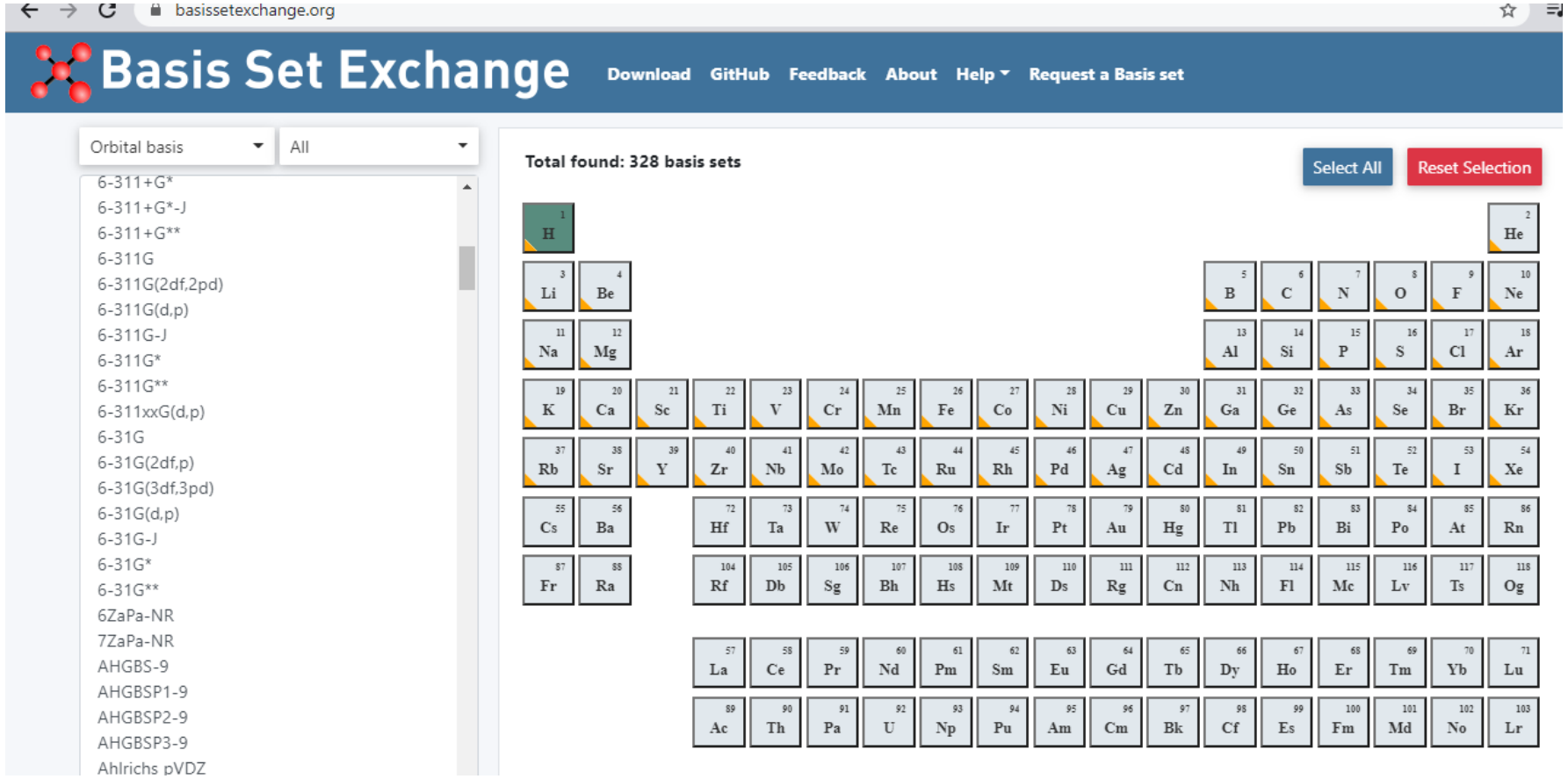
name	ζ	c_i
STO-1G	0.270	1.0
STO-2G	0.151	0.67
	0.851	0.43
STO-3G	0.109	0.44
	0.405	0.53
	2.227	0.15

$$\Psi^{cGTF}_{1\mathrm{G}}(\zeta = 1.0) = \Psi^{GTO}_{1\mathrm{G}}(\zeta = 0.27)$$

$$\Psi^{cGTF}_{2\mathrm{G}}(\zeta = 1.0) = 0.67\ \Psi^{GTO}_{2\mathrm{G}}(\zeta = 0.151) + 0.43\ \Psi^{GTO}_{2\mathrm{G}}(\zeta = 0.851)$$

$$\Psi^{cGTF}_{3\mathrm{G}}(\zeta = 1.0) = 0.44\ \Psi^{GTO}_{3\mathrm{G}}(\zeta = 0.109) + 0.53\ \Psi^{GTO}_{3\mathrm{G}}(\zeta = 0.405) + 0.15\ \Psi^{GTO}_{3\mathrm{G}}(\zeta = 2.227)$$

Library of basis functions



https://www.basissetexchange.org/

Contracted Gaussian Functions

STO-3G for Carbon

C S

71.61683735	0.1543289673
13.04509632	0.5353281423
3.530512160	0.4446345422

C SP

2.941249355	-0.0999672291	0.1559162750
0.683483096	0.3995128261	0.6076837186
0.222289915	0.7001154689	0.3919573931
ζ_i	c_i	c_i

$$\psi_{1s}^{\mathrm{STO}} = 0.15e^{-71.61r^2} + 0.53e^{-13.04r^2} + 0.44e^{-3.53r^2}$$

$$\psi_{2s}^{\mathrm{STO}} = -0.09e^{-2.94r^2} + 0.39e^{-0.68r^2} + 0.70e^{-0.22r^2}$$

$$\psi_{2p}^{\mathrm{STO}} = 0.15e^{-2.94r^2} + 0.60e^{-0.68r^2} + 0.39e^{-0.22r^2}$$

STOs: 1s, 2s, 2p [2s,1p] # 5 functions

GTOs: 1s(3), 2s(3), 2p(3) (6s,3p)

Contraction Scheme: (6s,3p) -> [2s,1p]

Single zeta – Double zeta – Triple zeta …

Split-Valence Basis

3-21G basis for Nitrogen

#BASIS SET: (6s,3p) -> [3s,2p]

N	S		
	242.7660000	0.0598657005	
	36.48510000	0.3529550030	
	7.814490000	0.7065130060	
N	SP		
	5.425220000	-0.4133000774	0.2379720162
	1.149150000	1.2224417267	0.8589530586
N	SP		
	0.2832050000	1.0000000000	1.0000000000
	ζ_i	c_i	c_i

l/m/n GTOs to describe the 1st/2nd/3rd STO of valence orbital

K GTOs to describe **1** STO of core orbital

K–lmnG

core-valence separation

# of digits = # of STOs for each valence orbital

Split-Valence Basis

6-31G for Carbon

#BASIS SET: (10s,4p) -> [3s,2p]

C S

3047.524880	0.1834737132E-02
457.3695180	0.1403732281E-01
103.9486850	0.6884262226E-01
29.21015530	0.2321844432E+00
9.286662960	0.4679413484E+00
3.163926960	0.3623119853E+00

core

C SP

7.868272350	-0.1193324198E+00	0.6899906659E-01
1.881288540	-0.1608541517E+00	0.3164239610E+00
0.544249258	0.1143456438E+01	0.7443082909E+00

cGTF 1

C SP

0.1687144782	0.1000000000E+01	0.1000000000E+01
ζ_i	c_i	c_i

cGTF 2

valence

	1s	2s	2p	#K
#STOs	1	2	2	9
#GTOs	6	3+1	3+1	

Further improvements

- Polarization functions
  - Basis function with angular momentum *l* is mixed with basis function of angular momentum *l*+1

K–lmnG*

- Diffuse functions
  - Small zeta exponent of same *l*
  - Necessary for anions, electronegative atoms, Rydberg states, weakly bound complexes

K–lmn+G

- Correlation Consistent
  - Basis sets are optimized using correlated wavefunctions (not HF wavefunctions)

cc–pVDZ

- Effective Core Potentials (ECP)
  - For heavy elements core electrons are treated as ECP with relativistic corrections

LANL2DZ

- Plane wave basis
  - For periodic materials – valence electrons are modelled as free electrons

Recommended Basis*

- For most applications on structure, bonding etc, use 6-311G** (same as 6-311G(d,p) ; Split-valence, triple-zeta function with polarization for heavy atom and for H) works well. If you have anions, use 6-311+G**. Use LANL2DZ ECP if you have metals.

- For spectroscopic applications, use cc-pVTZ (correlation-consistent polarized valence triple zeta). With anions, use aug-ccpVTZ (augmented cc-pVTZ).

- With hybrid/meta-hybrid DFT functionals, use def2-TZVP.

* with a pinch of salt