

- Which of the following basis sets are valence-double-zeta basis sets?

(a) STO-3G	(g) 6-31G	(m) 6-311G**
(b) 3-21G	(h) 6-31++G	(n) 6-311++G**
(c) 3-21+G	(i) 6-31G**	(o) cc-pVDZ
(d) 3-21+G*	(j) 6-31++G**	(p) aug-cc-pVDZ
(e) 3-21G*	(k) 6-311G	(q) cc-pVTZ
(f) 6-31G	(l) 6-311++G	(r) aug-cc-pVTZ
- Suppose you want to do a computational study of the “cis-effect” for disubstituted ethylenes. To do this, you would need to find an acceptable computational protocol for cis-trans isomerization in disubstituted ethylenes. In this problem, you will estimate the Heat of Reaction ( $\Delta H_{\text{iso}}$ ) and the Gibbs Free Energy of reaction ( $\Delta G_{\text{iso}}$ ) for the isomerization of **cis-difluoroethylene** to **trans-difluoroethylene** in various ways to identify a good model for further studies. To do this:
  - compute  $\Delta H_{\text{iso}}$  and  $\Delta G_{\text{iso}}$  for cis-DFE  $\rightarrow$  trans-DFE using the G2MP2 and G3MP2B3 **multilevel methods** (see [https://en.wikipedia.org/wiki/Quantum\\_chemistry\\_composite\\_methods](https://en.wikipedia.org/wiki/Quantum_chemistry_composite_methods))
  - Compute  $\Delta H_{\text{iso}}$  and  $\Delta G_{\text{iso}}$  by DFT using functionals appropriate for organic chemistry. e.g., M06L, M06, M062X, M06HF. Do DFT calculations for both 3-21G and 6-31G basis sets.
    - What is a multilevel method ?
    - Based on your results, what would you recommend as the best method to use for further studies of the cis-effect in disubstituted ethylenes? [*In practice, you would have to look at many more reactions (probably 5-10 reactions) in order to make a definitive choice for the best functional.*]
- Using MP2 /6-31G(d) calculate (1) the ground state and (2) first 5 excited states of **methylene cyclopropene**. (keywords: # RCIS(NStates=5)/6-31+G(D) Density=All Test)
  - Compare your results to experiment [1,2] and other theory [3]. How well does it agree ? How does the electronic excitation calculation interpret the experimental spectrum ?
  - How well do your ground state orbital energies compare to the photoelectron spectroscopy results ?
  - Plot all the orbitals for which there is a photoelectron band below 20 eV binding energy, and discuss their bonding character.
  - How might you go beyond Koopman’s Theorem ? (describe the method but do not do the calculation)
    - excited states: SW Staley & TD Norden, J Am Chem Soc 106 (1984) 3699
    - PES: SW Staley and TD Norden, J Am Chem Soc 111 (1989) 445
    - theory: M. Merehfin,, R, Gonzfilez-Luqu & B. O. Roos, Theor Chim Acta 94 (1996) 143