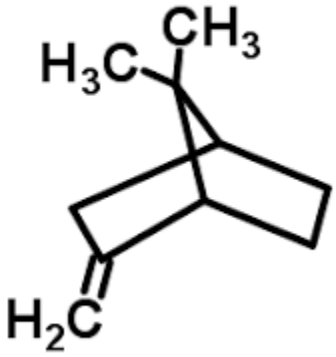
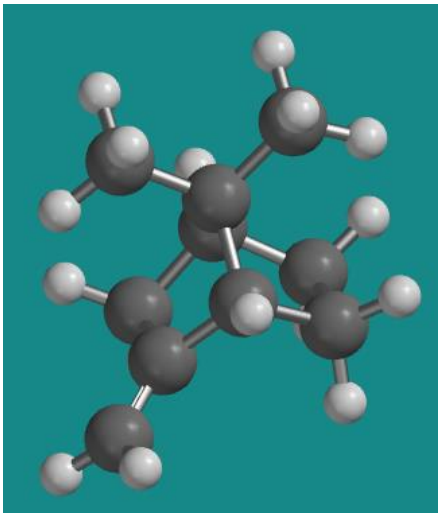
Computational Chemistry

Mid-term November, 16, 2021

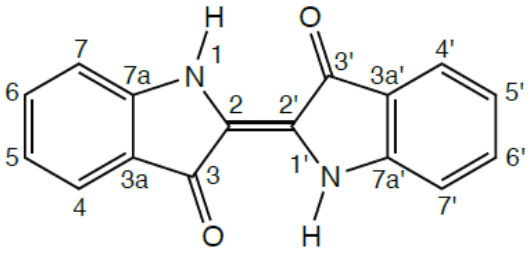
1. Plot the following molecules using Spartan (30%)

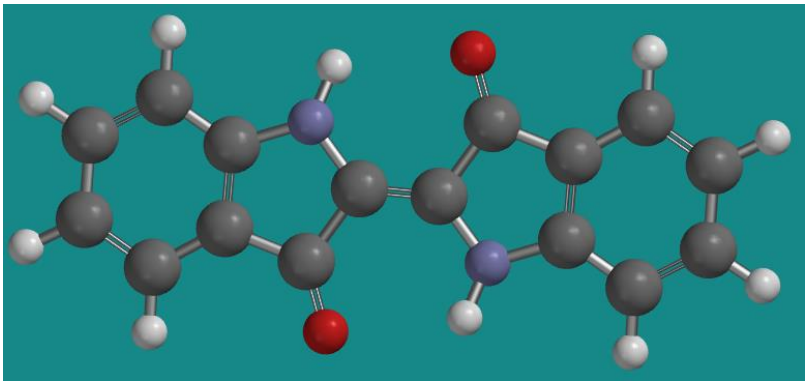
(a) 7,7-dimethyl-2-methylene



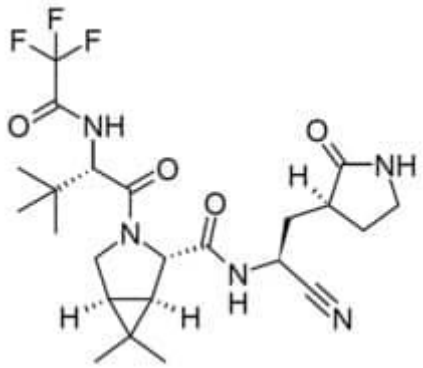


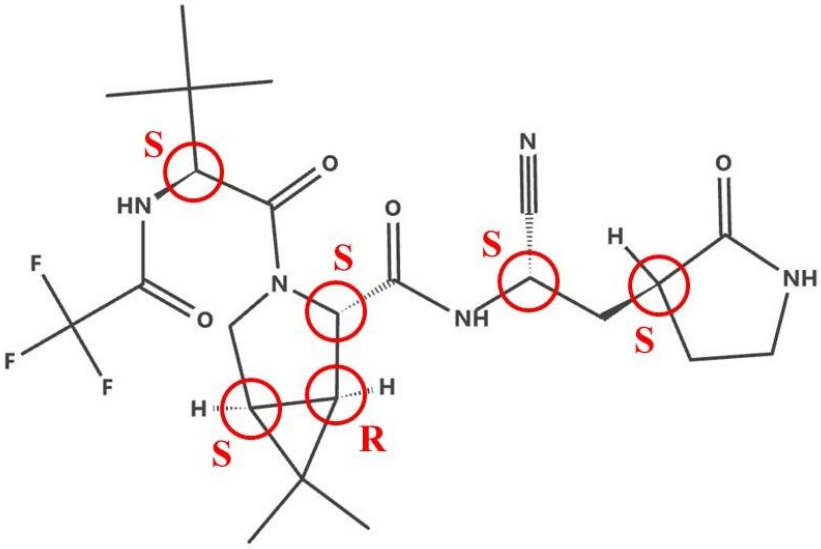
(b) Indigo

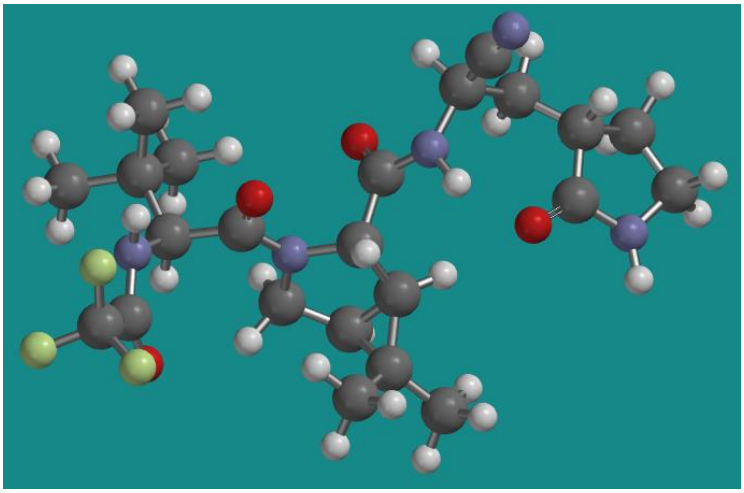




(c) PAXLOVID







2. Compare the accuracy of your calculation on IPs and EAs with various methods and basis sets. Why do some of the calculated EAs have very large errors? How to overcome the difficulty? (20%)

1) For the computational data of ionization energy, these data are close to experimental values by MP2 or B3LYP theory. However, for the computational data

of electron affinities of helium and neon, these data have large error no matter what common basis sets I use; on the other hand, for the computational data of electron affinities of other atoms, there have less error if I use the common basis set which has more diffuse functions.

2) It is too hard to predict the energies and distribution of unoccupied orbitals of noble gases. In addition, the valance shells and core shells of noble gases are filled up by electrons, it is difficult to add another electron to noble gas.

3) I add the diffuse functions to common basis set which can improve accuracy of computation. No matter what the theory I use in the same common basis set, these data still have large error.

※ the URL links of the computational data of ionization energy and electron affinity:
http://cculecture.ccu.edu.tw/~cpc608260005/hw3.htm
http://cculecture.ccu.edu.tw/~cpc608260005/hw4.htm
http://cculecture.ccu.edu.tw/~cpc608260005/hw5.htm

3. What are GTOs? How many basis functions will be used in a calculation of a CH_3OH molecule with the 6-31+G(d,p) basis set (6D)? How many occupied and unoccupied orbitals are obtained after a HF calculation? (20%)

1) GTOs are the abbreviation of Gaussian-type orbitals, they cost less computational resources than Slater-type orbitals (STOs). In the function of GTOs, *i*, *j*, and *k* are zero or positive integer; Z means orbital exponent, N means normalization constant of GTOs. When $i + j + k = 0$, the GTO belongs to *s*-type GTO; when $i + j + k = 1$, the GTO belongs to *p*-type GTO; when $i + j + k = 2$, the GTO belongs to *d*-type GTO, and so on. The following is the function of GTOs:

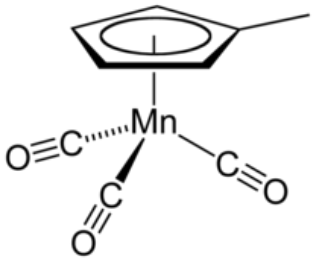
$$f_{\mathrm{GTO}} = \mathrm{N}x^i y^j z^k e^{-Zr^2}$$

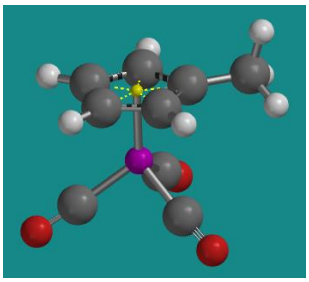
2) 58 basis functions (Carbon: 1s+2s+2p+s*+p*+d*= 19 basis functions; Oxygen: 1s+2s+2p+s*+p*+d*= 19 basis functions; Hydrogen: 1s • 2+p*=5 basis functions)

3) 9 occupied orbitals (18 electrons); 49 unoccupied orbitals

Label	Energy (eV)	Sym. Lab.	Label	Energy (eV)	Sym. Lab.
LUMO{+48}	133.13	A'	LUMO{+19}	35.11	A'
LUMO{+47}	125.62	A'	LUMO{+18}	34.43	A'
LUMO{+46}	107.69	A'	LUMO{+17}	30.94	A"
LUMO{+45}	103.70	A"	LUMO{+16}	30.82	A'
LUMO{+44}	102.87	A'	LUMO{+15}	24.34	A'
LUMO{+43}	98.02	A'	LUMO{+14}	23.53	A"
LUMO{+42}	91.37	A'	LUMO{+13}	22.96	A'
LUMO{+41}	87.63	A"	LUMO{+12}	12.62	A'
LUMO{+40}	87.33	A'	LUMO{+11}	12.11	A'
LUMO{+39}	83.12	A'	LUMO{+10}	11.05	A'
LUMO{+38}	82.65	A"	LUMO{+9}	9.59	A"
LUMO{+37}	80.07	A'	LUMO{+8}	9.58	A'
LUMO{+36}	78.08	A"	LUMO{+7}	9.20	A'
LUMO{+35}	74.62	A'	LUMO{+6}	8.38	A"
LUMO{+34}	73.69	A'	LUMO{+5}	7.76	A'
LUMO{+33}	65.62	A'	LUMO{+4}	6.82	A'
LUMO{+32}	65.49	A"	LUMO{+3}	3.15	A"
LUMO{+31}	64.51	A'	LUMO{+2}	3.09	A'
LUMO{+30}	63.65	A"	LUMO{+1}	2.60	A'
LUMO{+29}	61.44	A"	LUMO	2.16	A'
LUMO{+28}	57.70	A'	HOMO	-12.23	A"
LUMO{+27}	50.88	A"	HOMO{-1}	-13.66	A'
LUMO{+26}	50.07	A'	HOMO{-2}	-16.37	A'
LUMO{+25}	46.64	A'	HOMO{-3}	-17.02	A"
LUMO{+24}	44.53	A"	HOMO{-4}	-19.06	A'
LUMO{+23}	41.23	A'	HOMO{-5}	-25.39	A'
LUMO{+22}	39.73	A"	HOMO{-6}	-37.26	A'
LUMO{+21}	38.66	A'	HOMO{-7}	-306.74	A'
LUMO{+20}	38.15	A'	HOMO{-8}	-559.71	A'

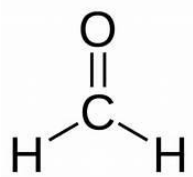
4. Build the following (MeCp)Mn(CO)$_3$ structure and estimate the Mn–C, C–O bond lengths and C–Mn–C bond angle at B3LYP/6-31G(d) level? (20%)



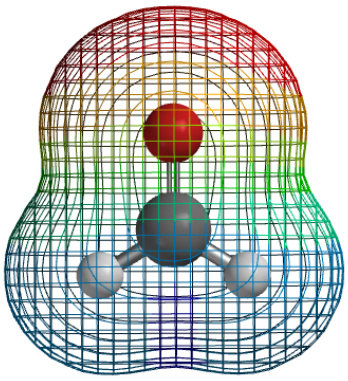
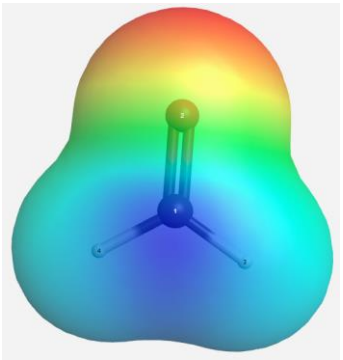


Mn–C = 1.791 Å
C≡O = 1.158 Å
C–Mn–C = 93.8 degrees

5. Calculate the structure, vibrational frequencies, zero-point energy, total atomization energy (TAE), and electrostatic map of formaldehyde at MP2/6-31+G(d,p) level. (30%)



C=O = 1.224 Å
C–H = 1.099 Å
H–C–H = 116.5 degrees
Frequencies (cm^{-1}) = 1211,1282,1570,1760,3040,3123
Zero-Point Energy (kcal/mol) = 17.1
TAE (kcal/mol) = 360.4

Atom/molecule	Unpaired electrons	Multiplicity	Born–Oppenheimer energy（Hartree）
Formaldehyde	0	1	-114.19263
Carbon	2	3	-37.73661
Oxygen	2	3	-0.49823
Hydrogen	1	2	-74.88529