Computational Chemistry and Materials Modeling

Discussion of Labs 1 and 2 on Computational Chemistry of Molecules

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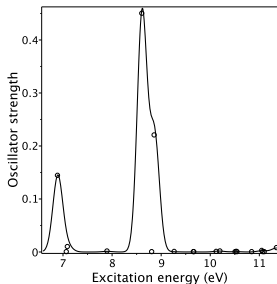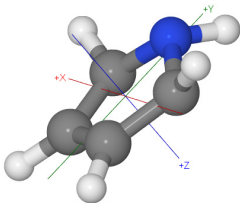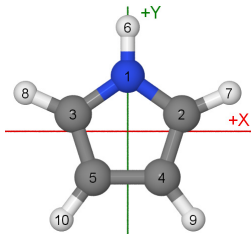
Questions to discuss

1. Why modeling of electronic properties of small molecules is nontrivial?
2. What MOs should be considered frontier?
3. Why EA is often negative for small molecules?
4. Analysis of MOs in terms of simple QM models.
5. What is special about acenes compared to graphene flakes?
6. When canonical MOs are not very useful compared to LMOs.
7. Functionalization of π-conjugated molecules.
8. Other interesting discussions by students about their Labs 1-2.
9. Discuss protonation and deprotonation.

Questions to discuss

Why modeling of electronic properties of small molecules is nontrivial?

Large band gap $\implies$ large energies to consider $\implies$ non-valence states + high-energy conformers + chemical reactions.

Example: pyrrole with B3LYP/6-31G* – anion and excitations + deprotonation and protonation at N atom should be considered

Questions to discuss: continuation

Pyrrole with large basis set (c3a=aug-cc-pVTZ or p3pppaa=6-311++G**)

1) Anion is planar. To get it in 6-31G* exchange α-MO #19 and 21
2) Excited states [JCP 140, 034317 (2014)]:
Interpretation: A2=$\pi \to \sigma^*$, B1=$\pi' \to \sigma^*$, A2(3pz)=$\pi \to Y$,
B1(3py)=$\pi \to X$, B2=$\pi \to \pi^*$, A1=$\pi' \to \pi^*$, $\pi' \to Z$, $\pi \to ZX$, $\pi \to \pi'^*$

	A2	B1	A2(3pz)	B1(3py)	B2	A1
Neville2014	5.06	5.86	5.87	6.00	6.24	6.01
MR-CASPT2	5.22	5.87	5.97	5.87	5.97	5.82
EOM-CCSD	5.18	5.84	5.88	5.97	6.02	6.55
CCSD	5.17	5.88	5.91	6.04	6.01	6.55
exp	5.22	6.43	--	5.85	5.90	--
CAM-B3LYPc3a	5.17	6.11	5.93	5.89	6.18	6.72
CAM-B3LYPp3ppaa	5.20	6.14	6.01	5.94	6.28	6.74
CAM-B3LYPp2p	7.07	7.90	--	--	6.89	7.10
B3LYPp2p	6.50	7.35	--	--	6.76	6.78
B3LYp3ppaa	4.77	5.62	5.56	5.53	6.09	6.42

Questions to discuss

Strictly speaking, any MO accessible in phenomena of interest.

In practice:

- Any MO in close proximity to band gap: at least from kT to width of vibrational broadening (tenths of eV).
- Any MO of different type than HOMO. Example of pyrrole: LUMO (NHσ^*), LUMO+1-4 (σ-symmetry Rydberg states), LUMO+5,6 (π^* intermixed with π-symmetry Rydberg states).
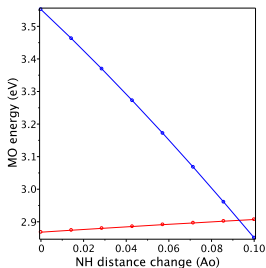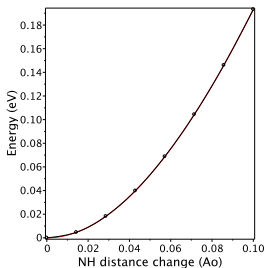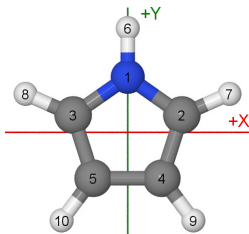
Example of LUMO and LUMO+1 of pyrrole molecule crossing at NH bond elongation (CAM-B3LYP/6-31G*)
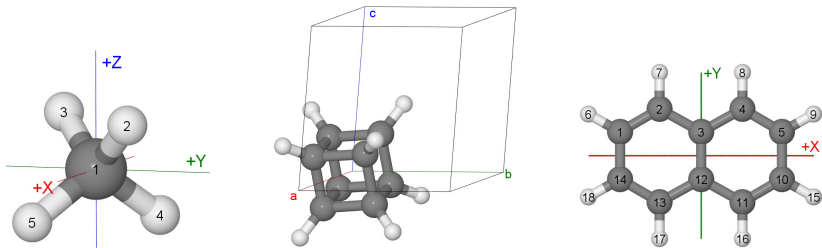
Questions to discuss
Why EA is often negative for small molecules?

- Because small closed-shell molecules have no room for extra electrons.

- Can also be an artifact of small basis set.

Questions to discuss

Analysis of MOs of molecules in terms of simple QM models

- Small molecules spherical-shaped molecules – spherical potential box or simply in terms of spherical harmonics: 1S, 1P, 1D, 2S, 3S etc. Examples: methane, cubane.

- Cubic-shaped molecules – cubic potential box. Examples: cubane.

- Rectangular-shaped molecules – rectangular potential box. Examples: acenes (naphthalene).

Questions to discuss: continuation

Cubane MOs in terms of spherical polynomials and cubic box eigenfunctions

```
  1  1S       9:-25.46  A1G  111   .018 C8S, .018 C7S, .018 C6S, .018 C5S, .018 C4S, .01...
  2  1Py     10:-19.53  T1U  121   .020 C8S, .020 C7S, .020 C6S, .020 C5S, .020 C4S, .02...
  3   z      11:-19.53  T1U  112   .020 C8S, .020 C7S, .020 C6S, .020 C5S, .020 C4S, .02...
  4   x      12:-19.53  T1U  211   .020 C8S, .020 C7S, .020 C6S, .020 C5S, .020 C4S, .02...
  5  1Dxy    13:-15.06  T2G  221   .020 C8S, .020 C7S, .020 C6S, .020 C5S, .020 C4S, .02...
  6   zx     14:-15.06  T2G  212   .020 C8S, .020 C7S, .020 C6S, .020 C5S, .020 C4S, .02...
  7   yz     15:-15.06  T2G  122   .020 C8S, .020 C7S, .020 C6S, .020 C5S, .020 C4S, .02...
  8  2S      16:-14.31  A1G *311  .0089 H16S, .0089 H15S, .0089 H14S, .0089 H13S, .0089...
  9  1Fxyz   17:-12.53  A2U  222   .025 C8S, .025 C7S, .025 C6S, .025 C5S, .025 C4S, .02...
 10  1Dxy'   18:-11.54  EG  *311   .026 C8Y, .026 C7Y, .026 C6Y, .026 C5Y, .026 C4Y, .02...
 11  1Dzx'   19:-11.54  EG  *311   .028 C8Z, .028 C7Z, .028 C6Z, .028 C5Z, .028 C4Z, .02...
 12  1Fy3    20:-11.42  T1U *321   .016 C8Z, .016 C7Z, .016 C6Z, .016 C5Z, .016 C4Z, .01...
 13   x3     21:-11.42  T1U *321   .016 C8Z, .016 C7Z, .016 C6Z, .016 C5Z, .016 C4Z, .01...
 14   z3     22:-11.42  T1U *321   .016 C8Y, .016 C7Y, .016 C6Y, .016 C5Y, .016 C4Y, .01...
 15  1Fxyz'  23: -7.24  T2U *321   .027 C8Z, .027 C7Z, .027 C6Z, .027 C5Z, .027 C4Z, .02...
 16   zxy'   24: -7.24  T2U *321   .027 C8Y, .027 C7Y, .027 C6Y, .027 C5Y, .027 C4Y, .02...
 17   yzx'   25: -7.24  T2U *321   .027 C8X, .027 C7X, .027 C6X, .027 C5X, .027 C4X, .02...
 18  1Gzxy2  26: -6.99  T2G  232   .048 C8Y, .048 C7Y, .048 C6Y, .048 C5Y, .048 C4Y, .04...
 19   xyz2   27: -6.99  T2G  223   .048 C8Z, .048 C7Z, .048 C6Z, .048 C5Z, .048 C4Z, .04...
 20   yzx2   28: -6.99  T2G  322   .048 C8X, .048 C7X, .048 C6X, .048 C5X, .048 C4X, .04...
----------------------------------------------------------------------------------
 21  2Pz     29:  2.16  T1U  114   .33 C8S, .33 C7S, .33 C6S, .33 C5S, .33 C4S, .33 C3S,...
 22   x      30:  2.16  T1U  411   .33 C8S, .33 C7S, .33 C6S, .33 C5S, .33 C4S, .33 C3S,...
 23   y      31:  2.16  T1U  141   .33 C8S, .33 C7S, .33 C6S, .33 C5S, .33 C4S, .33 C3S,...
 24  3S      32:  2.45  A1G ?333   .41 H16S, .41 H15S, .41 H14S, .41 H13S, .41 H12S, .41...
 25  3Py     33:  4.50  T1U ?323   .60 H16S, .60 H15S, .60 H14S, .60 H13S, .60 H12S, .60...
 26   x      34:  4.50  T1U ?233   .60 H16S, .60 H15S, .60 H14S, .60 H13S, .60 H12S, .60...
 27   z      35:  4.50  T1U ?332   .60 H16S, .60 H15S, .60 H14S, .60 H13S, .60 H12S, .60...
cubic box hybrids
 5.95X 0.00   -12.46         311   mo [-0.577 8  0.612 10  0.540 11]
 5.95Y 0.00   -12.46         131   mo [-0.577 8 -0.774 10  0.260 11]
 5.95Z 0.00   -12.46         113   mo [ 0.577 8 -0.162 10  0.800 11]
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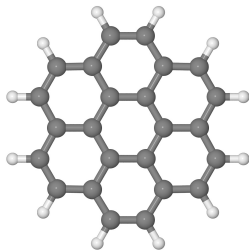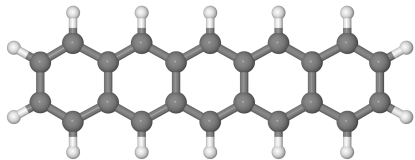
Questions to discuss

What is special about acenes compared to graphene flakes?

	na	gap	cgap	ogap	sgap
B3LYP/6-31G*					
layer6	12	6.80	11.31	5.54	5.08
layer16	26	3.85	7.03	3.72	2.44
layer24	36	4.04	6.82	3.23	2.89
layer54	72	2.82	4.85	2.24	2.02
CAM-B3LYP/6-31G*					
benzene	12	9.66	11.42	5.68	4.57
naphthalene	18	7.45	8.84	4.75	3.37
anthracene	24	6.02	7.14	3.70	2.33
tetracene	30	5.06	5.99	2.93	1.65
pentacene	36	4.37	5.16	2.39	1.17
hexacene	42	3.87	4.55	2.00	0.82

Questions to discuss

When canonical MOs are not very useful compared to LMOs

Example: PETN molecule

```
LMOs:        S      PZ    Palong  Pperp
          -22.04  -14.46  -14.46  -14.46
  -9.35    0.55    0.17   -0.30    0.07  LP(sig)
  -9.65   -0.00   -0.00   -0.07   -0.28  pi
  -9.99    0.00    0.00    0.05    0.19  pi
 -10.23    0.46    0.10   -0.64    0.15
 -12.44   -0.72   -0.80    0.24   -0.06
 -13.52    0.00   -0.00   -0.25   -1.02
 -15.27    0.34    0.39   -0.37    0.09
 -16.36   -0.00    0.00    0.06    0.26
 -16.54   -0.11    0.34    0.26   -0.06
 -17.44    1.04    1.43   -1.07    0.26
 -20.08   -1.32   -1.08    2.08   -0.50
 -29.66   -0.82   -0.47    1.63   -0.39
 -30.66    0.09    0.02   -0.14    0.03
 -35.54   -0.12    0.05    0.30   -0.07
LMOs(vacant):
  -2.39   no strong couplings
   0.58   -0.41 to neighbor
   3.00    0.55,-0.47,-0.47 to neighbors
   3.13   -1.01 to neighbor
   3.69   -0.57,-0.38,-0.38 to neighbors
   5.45    0.17 to neighbor
   6.47    0.31 to 5.45
   9.91   no strong couplings
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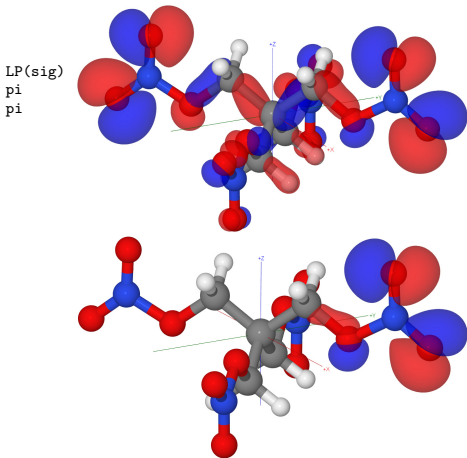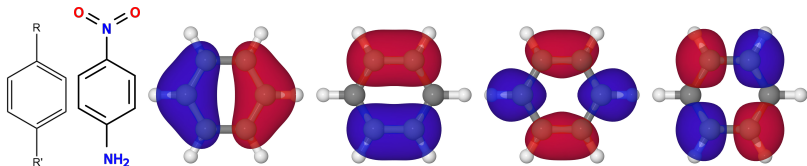
Questions to discuss

Functionalization of π-conjugated molecules

Question: What can we say about electronic properties of the functionalized molecule relative to properties of benzene molecule?

- Its frontier MOs is a perturbation of benzene HOMO/LUMO.

- The most perturbed are HOMO$^{(0)}$/LUMO$^{(0)}$ with nonzero density at bridging carbons – they will be HOMO/LUMO.

- The largest changes are for push-pull functionalization. In this case electronic density distribution is sensitive to density functional.

- Why NH2 is π-donor whereas NO2 is π-acceptor (and also N is more electronegative than C)?

- Why Br attached to benzene draws more electronic density than Cl, and Cl draws more than F?