TÜBİTAK

ODTÜ
METU

EURO^2

Electronic structure calculations by Gaussian 16

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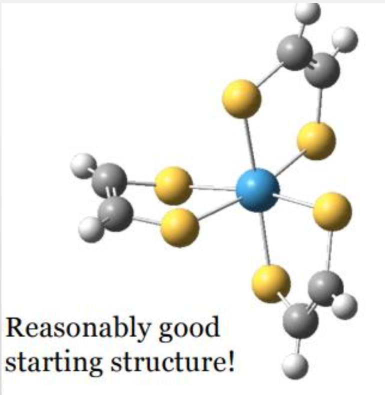
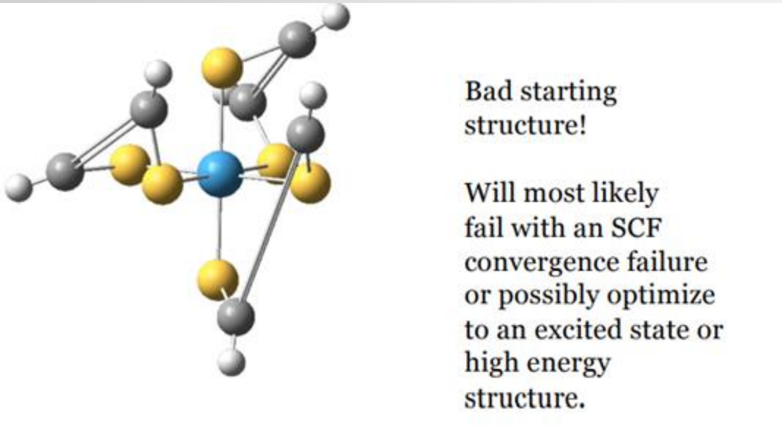
OPTIMIZATION

initial structure is important



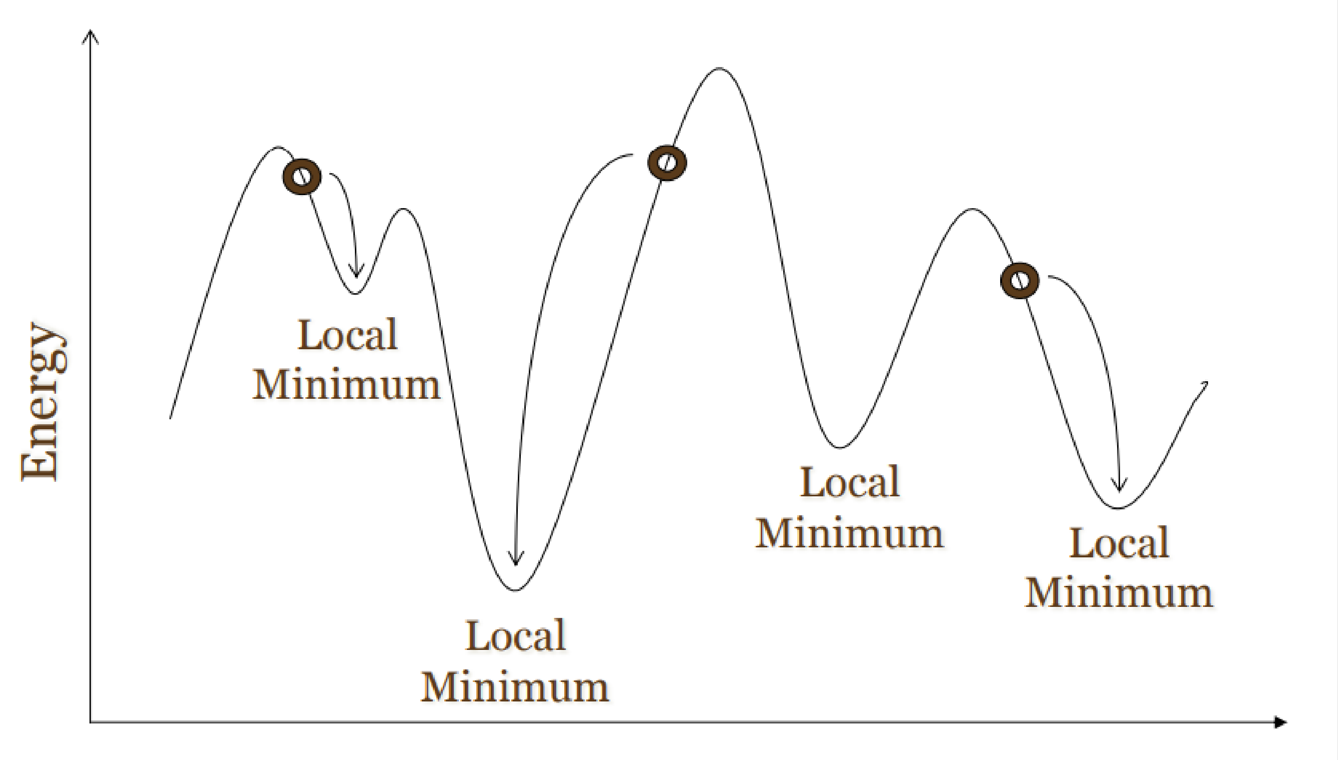
Reasonably good starting structure!



Bad starting structure!

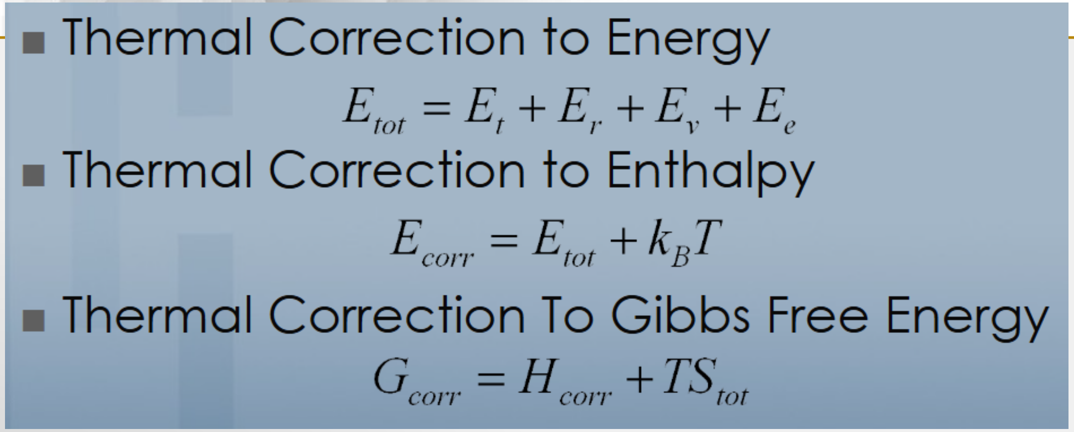
Will most likely fail with an SCF convergence failure or possibly optimize to an excited state or high energy structure.

Avoid Local Minima



https://hprc.tamu.edu/files/training/2020/Summer/Intro_QM_Lect1.pdf

FREQ



- Thermal Correction to Energy

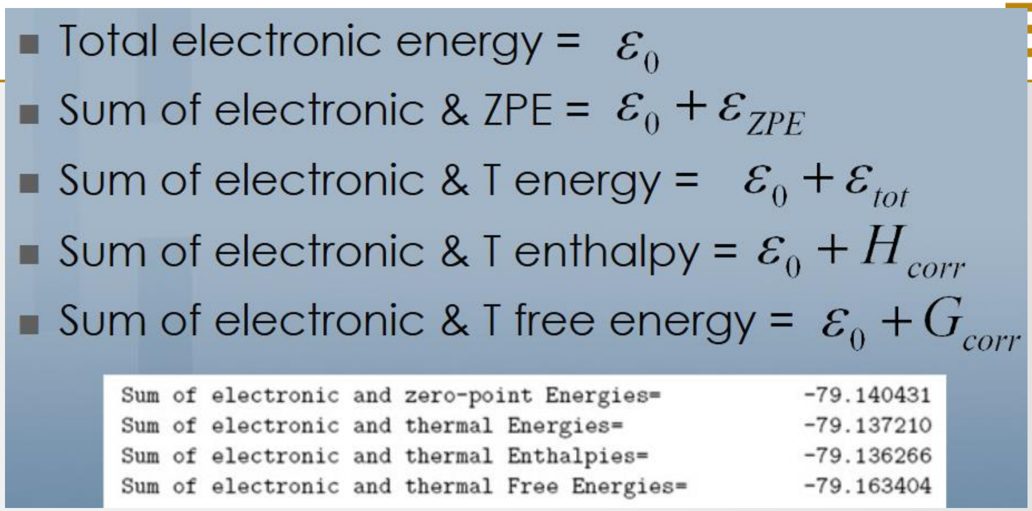
$$E_{tot} = E_t + E_r + E_v + E_e$$

- Thermal Correction to Enthalpy

$$E_{corr} = E_{tot} + k_B T$$

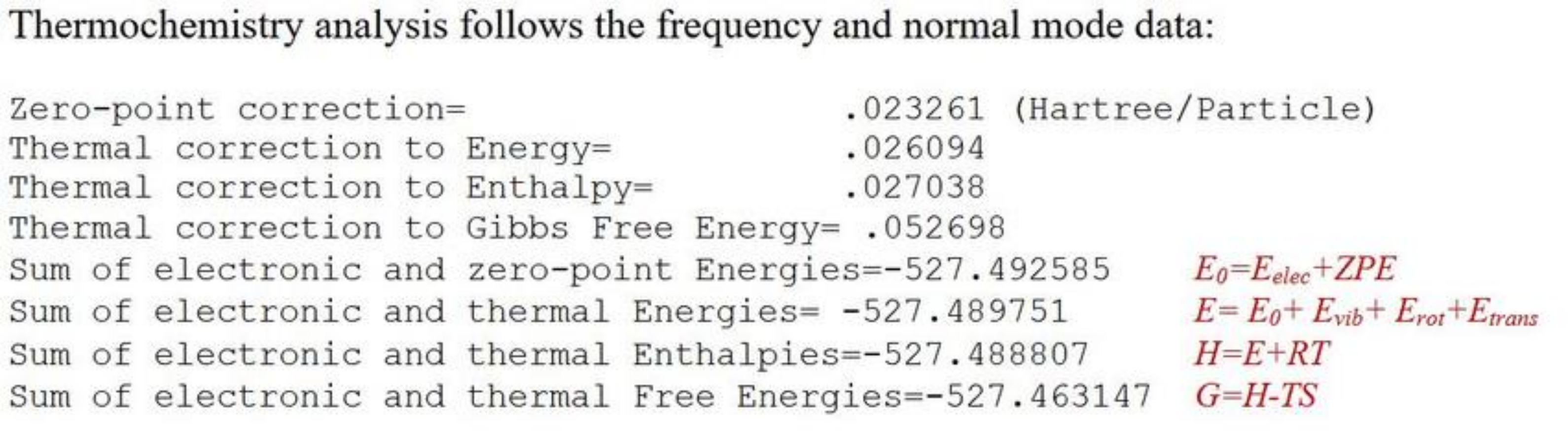
- Thermal Correction To Gibbs Free Energy

$$G_{corr} = H_{corr} + TS_{tot}$$



- Total electronic energy = ε_0
- Sum of electronic & ZPE = $\varepsilon_0 + \varepsilon_{ZPE}$
- Sum of electronic & T energy = $\varepsilon_0 + \varepsilon_{tot}$
- Sum of electronic & T enthalpy = $\varepsilon_0 + H_{corr}$
- Sum of electronic & T free energy = $\varepsilon_0 + G_{corr}$

```
Sum of electronic and zero-point Energies=          -79.140431
Sum of electronic and thermal Energies=             -79.137210
Sum of electronic and thermal Enthalpies=           -79.136266
Sum of electronic and thermal Free Energies=        -79.163404
```



Thermochemistry analysis follows the frequency and normal mode data:

```
Zero-point correction=                           .023261 (Hartree/Particle)
Thermal correction to Energy=                    .026094
Thermal correction to Enthalpy=                  .027038
Thermal correction to Gibbs Free Energy=  .052698
Sum of electronic and zero-point Energies=-527.492585
Sum of electronic and thermal Energies= -527.489751
Sum of electronic and thermal Enthalpies=-527.488807
Sum of electronic and thermal Free Energies=-527.463147
```

$E_0 = E_{elec} + ZPE$

$E = E_0 + E_{vib} + E_{rot} + E_{trans}$

$H = E + RT$

$G = H - TS$

Caitlin Williams
https://www.researchgate.net/post/How-to-calculate-solvation-energy-using-Gaussian-09

- Selection of Theory Level Determines Accuracy
  - HF, MP2, MP3, DFT (B3LYP, BP86, vb.), CCSD (T), vb.

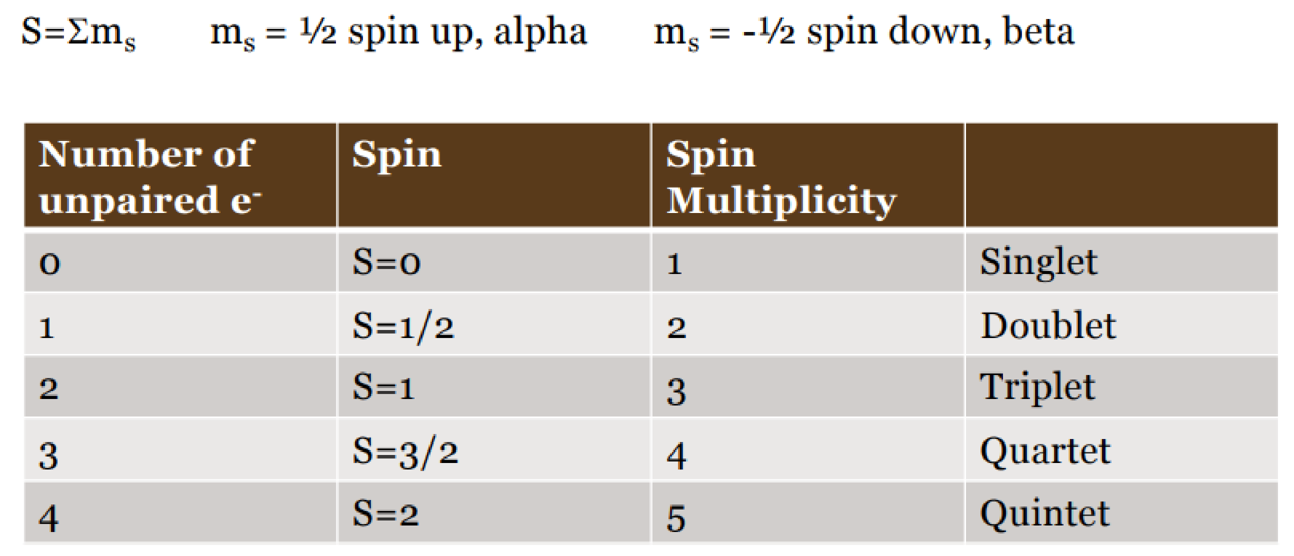
Selection of basis set

- 6-31G(d), SDD, LANL2DZ, vb.

Calibration

- Against experiments
- Against high level calculations (CCSD(T), MRCI, vb.)

Be careful about charge and multiplicity



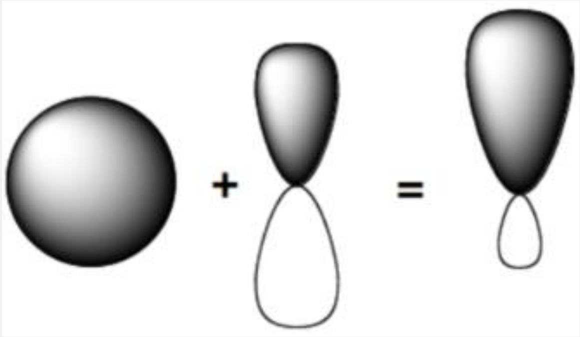
$S=\Sigma m_s$ $m_s = \frac{1}{2}$ spin up, alpha $m_s = -\frac{1}{2}$ spin down, beta

Number of unpaired e$^-$	Spin	Spin Multiplicity	
0	S=0	1	Singlet
1	S=1/2	2	Doublet
2	S=1	3	Triplet
3	S=3/2	4	Quartet
4	S=2	5	Quintet

- Using other visualization and analysis softwares: Multiwfn, Gaussum, VMD

Polarization Functions

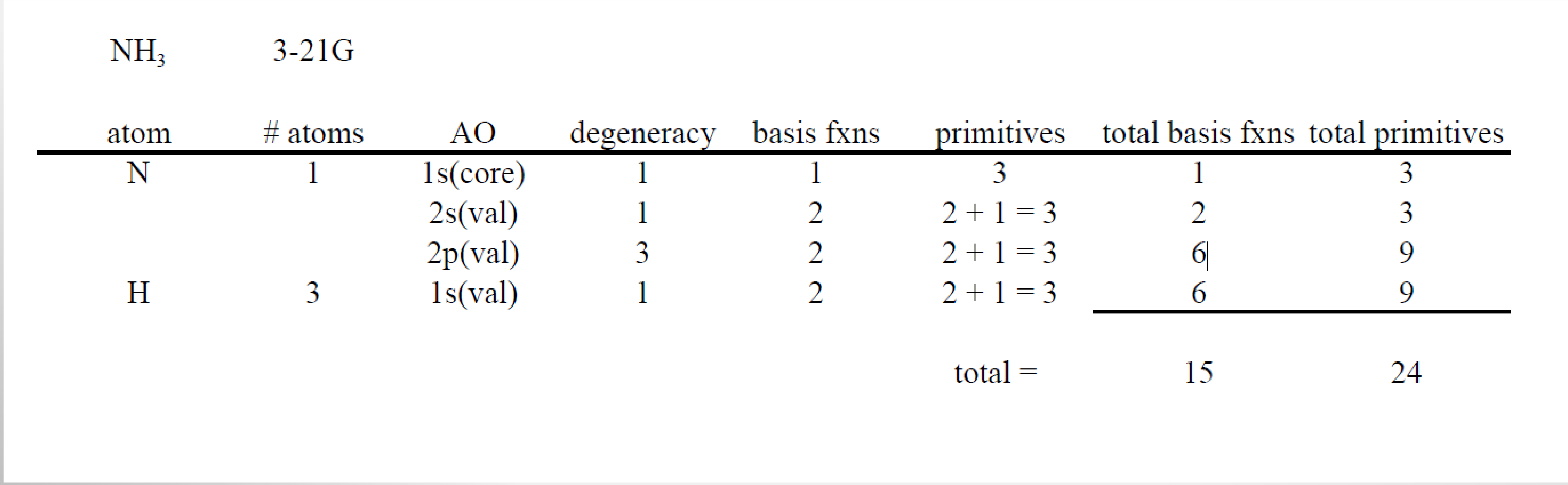
- Polarization functions have higher angular momentum
- They allow for anisotropic variations that occur in bonding and help model the inter-electronic cusp.



- Examples include **6-31G(*d*)** or **6-31G*** which include *d* functions on the *heavy* atoms and **6-31G(*d,p*)** or **6-31G**** which include *d* functions on heavy atoms and *p* functions on hydrogen atoms.

Diffuse Functions

- Diffuse basis functions are additional functions with small exponents, and are therefore large
- They allow for accurate modelling of systems with weakly bound electrons, such as
  - ✓ Anions
  - ✓ Excited states
- A set of diffuse functions usually includes a diffuse *s* orbital and a set of diffuse *p* orbitals with the same exponent
- Examples in include 6-31+G which has diffuse functions on the heavy atoms and 6-31++G which has diffuse functions on hydrogen atoms as well.



NH_3 3-21G

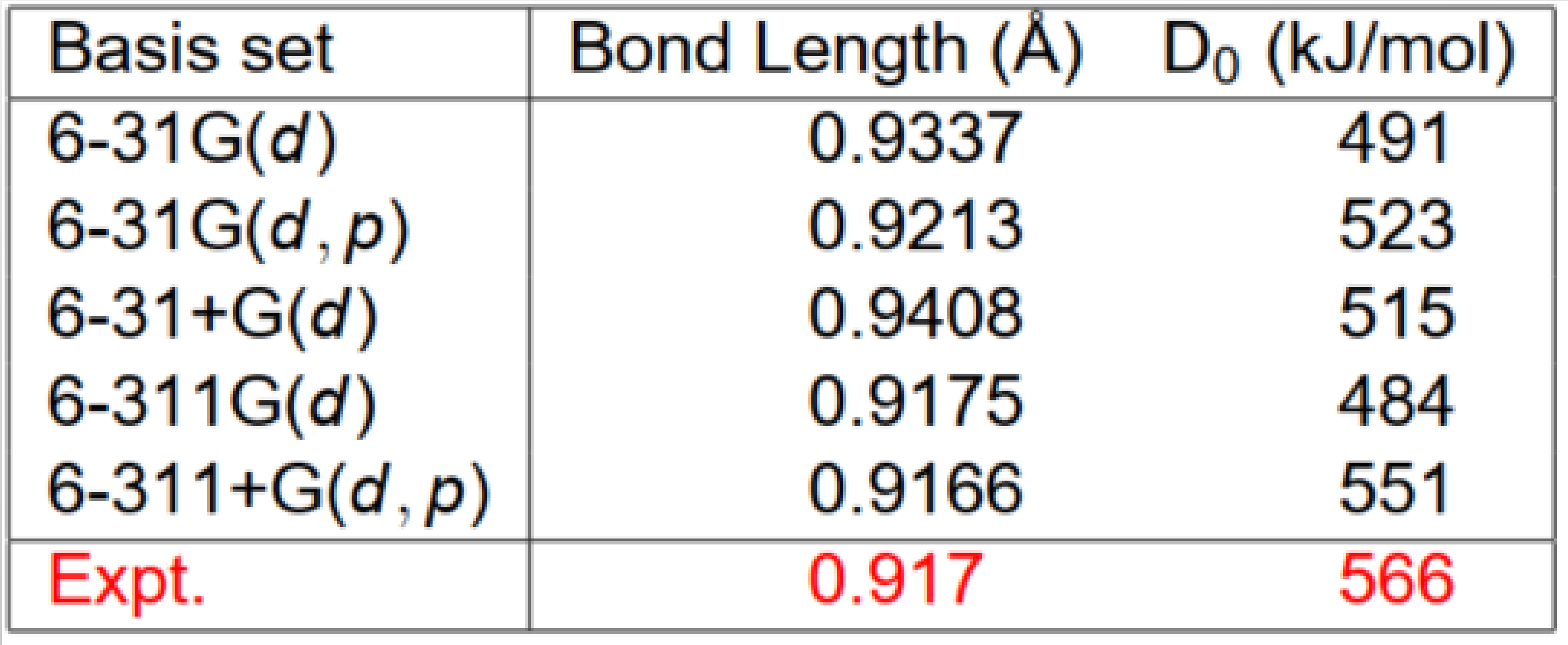
atom	# atoms	AO	degeneracy	basis fxns	primitives	total basis fxns	total primitives
N	1	1s(core)	1	1	3	1	3
		2s(val)	1	2	2 + 1 = 3	2	3
		2p(val)	3	2	2 + 1 = 3	6	9
H	3	1s(val)	1	2	2 + 1 = 3	6	9
					total =	15	24

Basis Set Families

Baz Set Type	**Pople**	**Ahlrichs**	**Duning Huzinga**
Double ζ	6-31G	Def2-SVP	cc-pVDZ
Triple ζ	6-311G	def2-TZVP	cc-pVTZ
Quadruple ζ		Def2-QZVP	cc-pVQZ

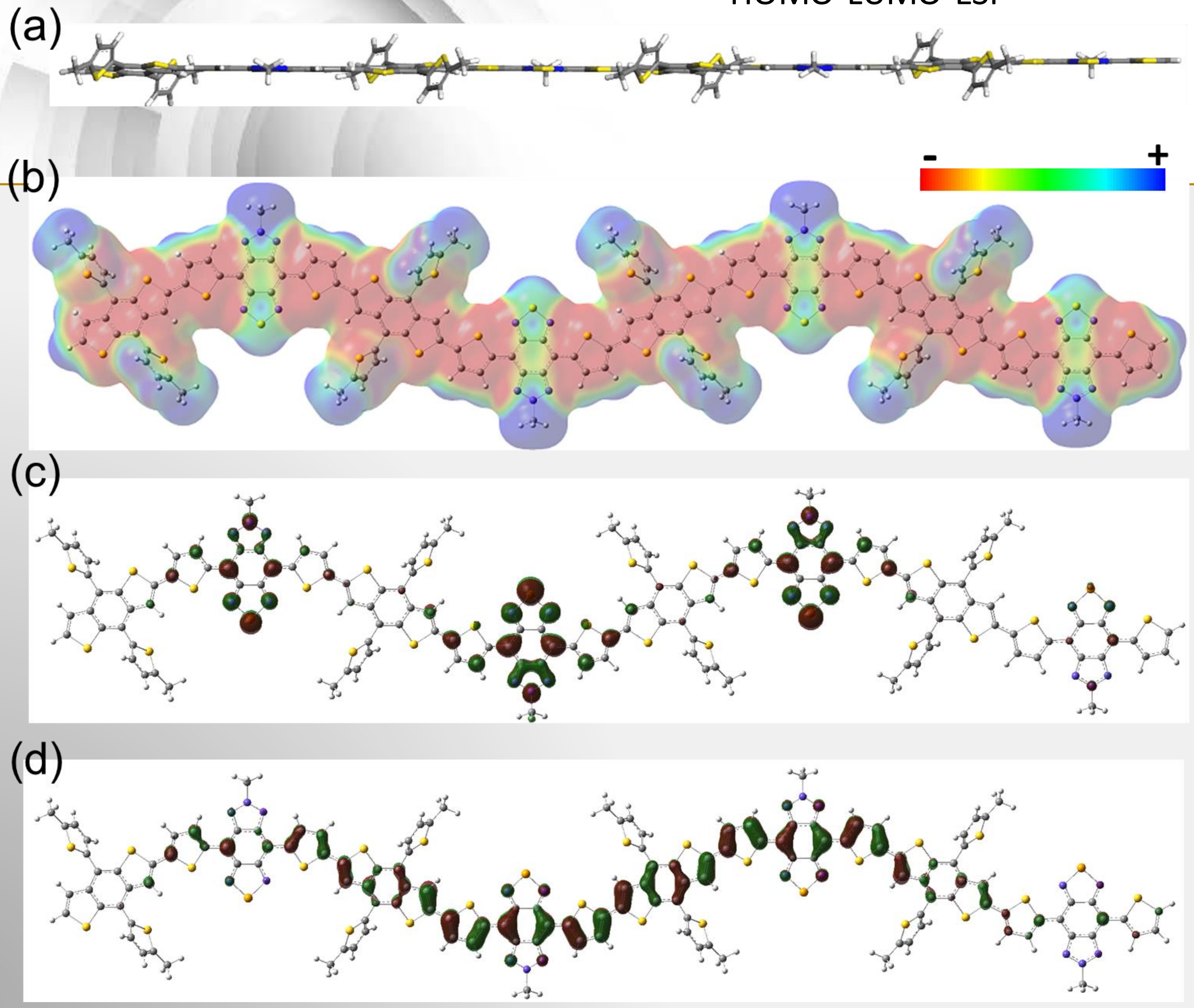
Accuracy vs Basis Set

- Bond Distance in HF molecule



Basis set	Bond Length (Å)	D_0 (kJ/mol)
6-31G(*d*)	0.9337	491
6-31G(*d*, *p*)	0.9213	523
6-31+G(*d*)	0.9408	515
6-311G(*d*)	0.9175	484
6-311+G(*d*, *p*)	0.9166	551
Expt.	0.917	566

HOMO-LUMO-ESP



lkan EA, Goker S,Sarigul H, Yıldırım E, Udum YA, Toppare L. The impact of [1,2,5]chalcogenazolo[3,4-f]-benzo[1,2,3]triazole structure on the optoelectronic properties of conjugated polymers. J Polym Sci. 2020;58:956–968. https://doi.org/10.1002/pol.20190275968

Önemli web Siteleri

- https://cccbdb.nist.gov/vibscalejustx.asp
- https://www.basissetexchange.org/
- http://www.theochem.uni-stuttgart.de/pseudopotentials/index.en.html
- Correlation Consistent Basis Sets

http://tyr0.chem.wsu.edu/~kipeters/basis.html

- http://sobereva.com/multiwfn/

HF - Hartree Fock (uses RHF for singlets and UHF for others)
RHF - restricted Hartree Fock
UHF - unrestricted Hartree Fock
ROHF - spin-restricted open-shell Hartree Fock
CASSCF - complete active space
DFT- Density Functional Theory (Yoğunluk Fonksiyoneli Teorisi)
MP2 - Moller-Plesset second order correlation energy correction
MP3 - Moller-Plesset third order correlation energy correction
MP4 - same as MP4SDTQ
MP4DQ - Moller-Plesset fourth order correlation energy correction with double and quadruple substitutions.
MP4SDQ - Moller-Plesset fourth order correlation energy correction with single, double and quadruple substitutions.
MP4SDTQ - Moller-Plesset fourth order correlation energy correction with single, double, triple and quadruple substitutions.
CI - same as
CIS - configuration interaction with single excitations
CID - configuration interaction with double excitations
CISD - configuration interaction with single and double excitations
QCISD - quadratic configuration interaction with single and double excitations
QCISD(T) - quadratic configuration interaction with single and double excitations and triples contribution to the energy
CC: Couples Cluster
….

HF<DFT<MP2<CISD<MP4(SDQ)~CCSD<MP4<CCSD(T)

Hartree-Fock and Post-HF (Post-SCF)

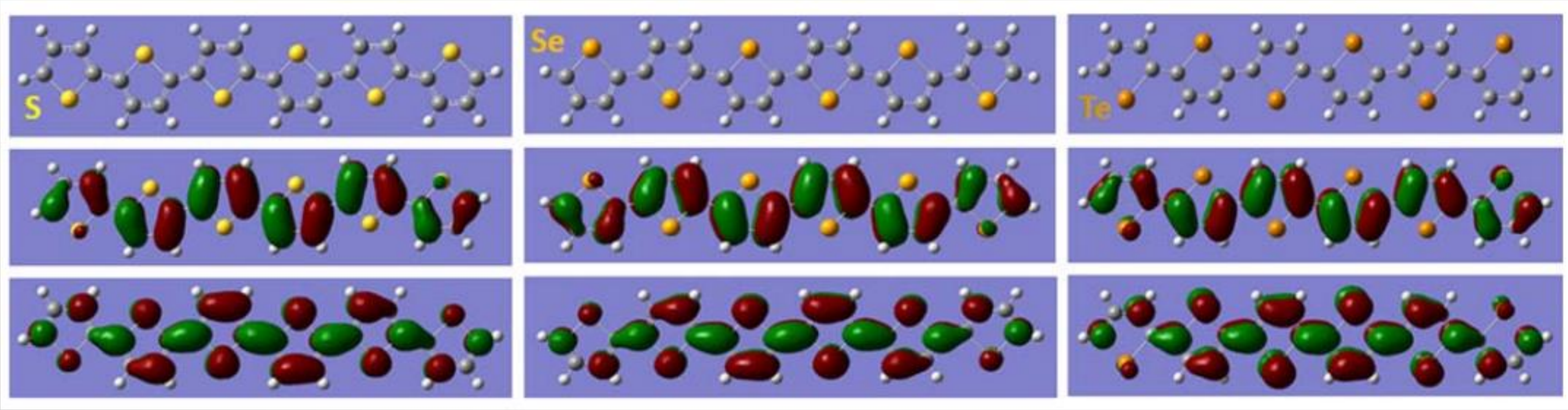
$H + F \rightarrow HF$

Method	ΔE_{bond} (kcal mol^{-1})
HF/STO-3G	73.9
HF/6-311++G(3df,3pd)	97.9
MP2/6-311++G(3df,3pd)	144.9
MP3/6-311++G(3df,3pd)	137.9
MP4/6-311++G(3df,3pd)	141.8
QCISD/6-311++G(3df,3pd)	138.8
QCISD(T) /6-311++G(3df,3pd)	140.6
Experimental	141.2

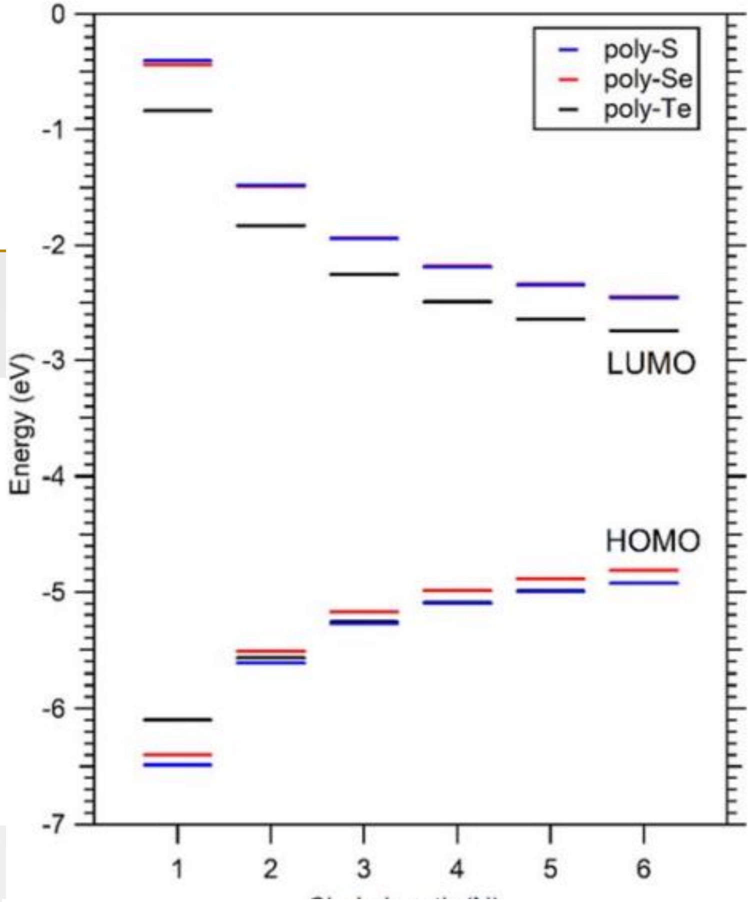
Cost of Calculation

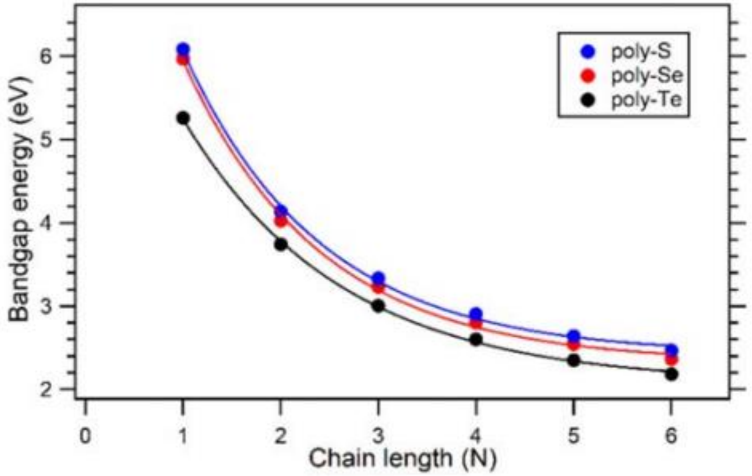
Level of Theory	Scaling
HF	N^3 iterative
Density Functional Theory	N^3 iterative
MP2	N^5 non-iterative
MP3, MP4(SDQ)	N^6 non-iterative
CISD, CCSD, QCISD	N^6 iterative
MP4(SDTQ)	N^7 non-iterative
MP5	N^8 non-iterative
CISDT, CCSDT, QCISDT	N^8 iterative
MP6	N^9 non-iterative
MP7	N^{10} non-iterative
CISDTQ, CCSDTQ, QCISDTQ	N^{10} iterative

N: number of basis function



Optimized geometries of hexamers of thiophene, selenophene, and tellurophene





Eur. J. Phys. 44 (2023) 025401

Significant Enhancement in the Seebeck Coefficient and Thermoelectric Power Factor of PEDOT:PSS by Surface Energy Filtering

Motivation: Seebeck coefficient (S) of conducting polymers are much lower than their inorganic counterparts. In this work, we find that both the S and the power factor of acid and base treated PEDOT:PSS can be enhanced by coating a layer of Rhodamine 101 zwitterion.

Results: Increasing conjugation length not only decreases band gap and increasing charge carrier density but also enhancing π-π stacking of the chains. Charge carriers are forced to be distributed nonhomogeneously along the PEDOT chain by the electric field induced by Rh101 at the interface. This creates electrostatic traps and defects that decrease conjugation length.

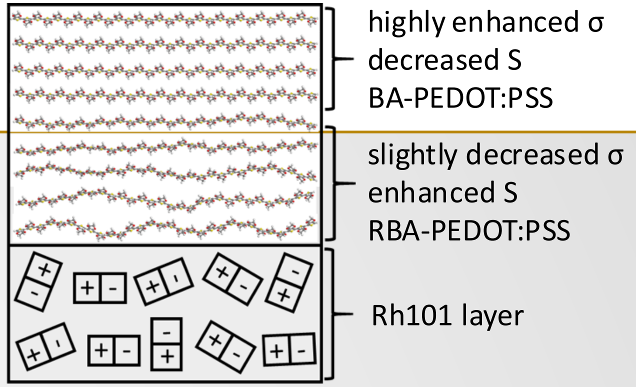
Rh101 disrupts π-conjugation of the chains by decreasing overlap of orbitals between neighboring π-bonds and planarity that resulted in the increasing band gap and reduced π–π interactions leads to lower amount of nanoscale aggregations of PEDOT chains.

Conclusion: Slight decrease in σ and enhancement in S lead to PF as high as 401.2 μW m^{-1} K^{-2} which is ascribed to the surface energy filtering and interfacial dipole moment induced by Rhodamine 101 at the surface of PEDOT:PSS films.

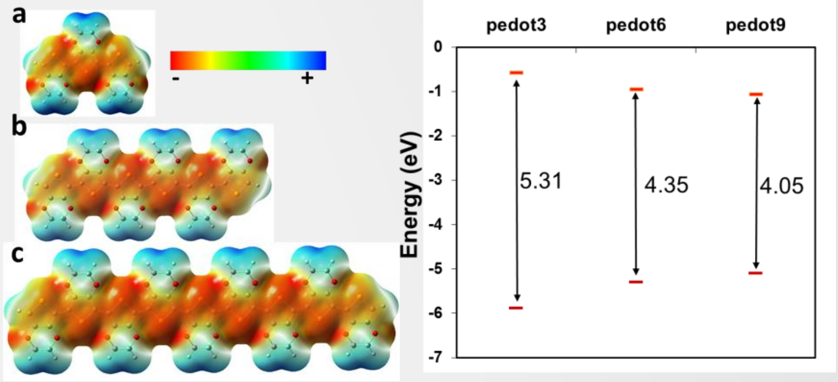
TE properties and work function of samples (*Ouyang Group, NUS*).

Sample	S (μV K^{-1})	σ (S cm^{-1})	PF (μW m^{-1} K^{-2})
A-PEDOR:PSS	14.0	3057	59.9
RA-PEDOR:PSS	34.5	2294	273.0
BA-PEDOT:PSS	38.0	2089	301.7
RBA-PEDOT:PSS	47.2	1801	401.2

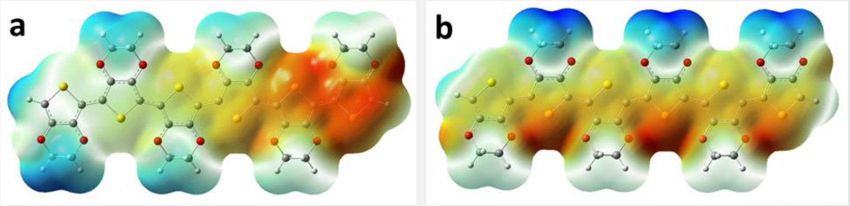
R: rhodamine interface, A: acid treatment, B: base treatment



Self-organisation of PEDOT chains at the Rh 101 interface



Electrostatic potential surface (ESP) for increasing conjugation length, a) $PEDOT_3$, b) $PEDOT_6$, c) $PEDOT_9$. Band gap for these structures.

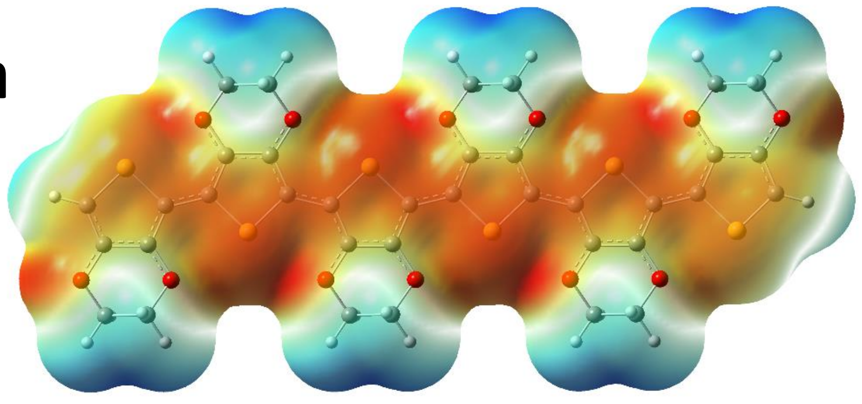


ESP for $PEDOT_6$ under the electric field at a) X- and b) Y-direction.

J. Mater. Chem. A, 2020, **8**, 13600-13609

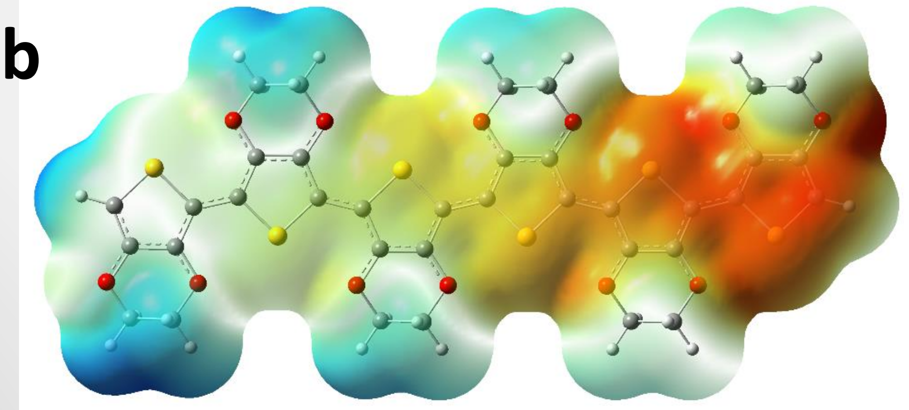
Field command in G16

a



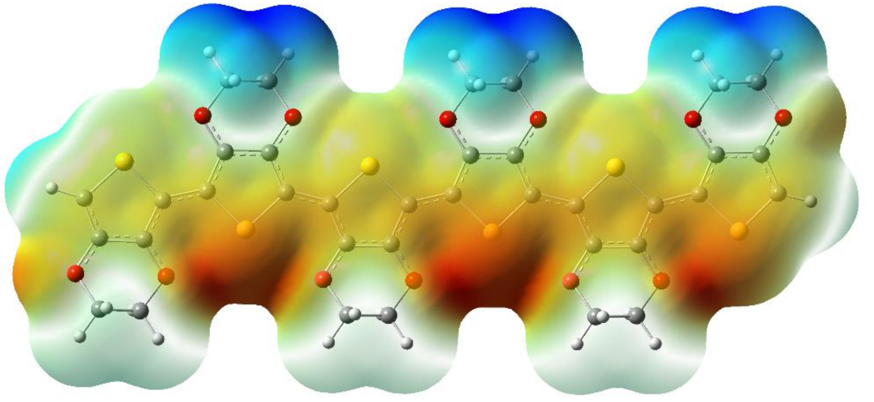
No dipole moment

b



X direction of 0.005 au

c



Y direction of 0.005 au

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