

# Molecular properties of monoxides, hydrides, and oxyhydrides of superheavy elements

**Artem Kotov**, Yu. S. Kozhedub, D. A. Glazov, V. M. Shabaev  
SPbU, Russia

V. Pershina, GSI, Germany  
M. Iliaš, Matej Bel University, Slovakia

supported by Ministry of Science and Higher Education of the Russian Federation Grant  
Calculations are carried out at LIT JINR

April 26 2023

# Introduction

|   | 1                                 | 2                                 | 3                                | 4                                      | 5                                | 6                                    | 7                                     | 8                                   | 9                                 | 10                                  | 11                                 | 12                                | 13                                  | 14                                     | 15<br>Pnictogens                       | 16<br>Chalcogens                         | 17<br>Halogens                            | 18                                  |
|---|-----------------------------------|-----------------------------------|----------------------------------|--|----------------------------------|--------------------------------------|---------------------------------------|-------------------------------------|-----------------------------------|-------------------------------------|------------------------------------|-----------------------------------|-------------------------------------|--|--|--|---|-------------------------------------|
| 1 | 1<br><b>H</b><br>Hydrogen<br>-1 1 | 2<br><b>He</b><br>Helium          |                                  |  |                                  |                                      |                                       |                                     |                                   |                                     |                                    |                                   |                                     |  |  |  |   |                                     |
| 2 | 3<br><b>Li</b><br>Lithium<br>1    | 4<br><b>Be</b><br>Beryllium<br>2  |                                  |  |                                  |                                      |                                       |                                     |                                   |                                     |                                    |                                   | 5<br><b>B</b><br>Boron<br>3         | 6<br><b>C</b><br>Carbon<br>-4 4        | 7<br><b>N</b><br>Nitrogen<br>-3 3 5    | 8<br><b>O</b><br>Oxygen<br>-2            | 9<br><b>F</b><br>Fluorine<br>-1           | 10<br><b>Ne</b><br>Neon             |
| 3 | 11<br><b>Na</b><br>Sodium<br>1    | 12<br><b>Mg</b><br>Magnesium<br>2 |                                  |  |                                  |                                      |                                       |                                     |                                   |                                     |                                    |                                   | 13<br><b>Al</b><br>Aluminium<br>3   | 14<br><b>Si</b><br>Silicon<br>-4 4     | 15<br><b>P</b><br>Phosphorus<br>-3 3 5 | 16<br><b>S</b><br>Sulfur<br>-2 2 4 6     | 17<br><b>Cl</b><br>Chlorine<br>-1 1 3 5 7 | 18<br><b>Ar</b><br>Argon            |
| 4 | 19<br><b>K</b><br>Potassium<br>1  | 20<br><b>Ca</b><br>Calcium<br>2   | 21<br><b>Sc</b><br>Scandium<br>3 | 22<br><b>Ti</b><br>Titanium<br>4       | 23<br><b>V</b><br>Vanadium<br>5  | 24<br><b>Cr</b><br>Chromium<br>3 6   | 25<br><b>Mn</b><br>Manganese<br>2 4 7 | 26<br><b>Fe</b><br>Iron<br>2 3      | 27<br><b>Co</b><br>Cobalt<br>2 3  | 28<br><b>Ni</b><br>Nickel<br>2      | 29<br><b>Cu</b><br>Copper<br>2     | 30<br><b>Zn</b><br>Zinc<br>2      | 31<br><b>Ga</b><br>Gallium<br>3     | 32<br><b>Ge</b><br>Germanium<br>-4 2 4 | 33<br><b>As</b><br>Arsenic<br>-3 3 5   | 34<br><b>Se</b><br>Selenium<br>-2 2 4 6  | 35<br><b>Br</b><br>Bromine<br>-1 1 3 5    | 36<br><b>Kr</b><br>Krypton<br>2     |
| 5 | 37<br><b>Rb</b><br>Rubidium<br>1  | 38<br><b>Sr</b><br>Strontium<br>2 | 39<br><b>Y</b><br>Yttrium<br>3   | 40<br><b>Zr</b><br>Zirconium<br>4      | 41<br><b>Nb</b><br>Niobium<br>5  | 42<br><b>Mo</b><br>Molybdenum<br>4 6 | 43<br><b>Tc</b><br>Technetium<br>4 7  | 44<br><b>Ru</b><br>Ruthenium<br>3 4 | 45<br><b>Rh</b><br>Rhodium<br>3 7 | 46<br><b>Pd</b><br>Palladium<br>2 4 | 47<br><b>Ag</b><br>Silver<br>1     | 48<br><b>Cd</b><br>Cadmium<br>2   | 49<br><b>In</b><br>Indium<br>3      | 50<br><b>Sn</b><br>Tin<br>-4 2 4       | 51<br><b>Sb</b><br>Antimony<br>-3 3 5  | 52<br><b>Te</b><br>Tellurium<br>-2 2 4 6 | 53<br><b>I</b><br>Iodine<br>-1 1 3 5 7    | 54<br><b>Xe</b><br>Xenon<br>2 4 6   |
| 6 | 55<br><b>Cs</b><br>Caesium<br>1   | 56<br><b>Ba</b><br>Barium<br>2    | 57-71                            | 72<br><b>Hf</b><br>Hafnium<br>4        | 73<br><b>Ta</b><br>Tantalum<br>5 | 74<br><b>W</b><br>Tungsten<br>4 6    | 75<br><b>Re</b><br>Rhenium<br>4       | 76<br><b>Os</b><br>Osmium<br>4      | 77<br><b>Ir</b><br>Iridium<br>3 4 | 78<br><b>Pt</b><br>Platinum<br>2 4  | 79<br><b>Au</b><br>Gold<br>3       | 80<br><b>Hg</b><br>Mercury<br>1 2 | 81<br><b>Tl</b><br>Thallium<br>1 3  | 82<br><b>Pb</b><br>Lead<br>-2 4        | 83<br><b>Bi</b><br>Bismuth<br>3        | 84<br><b>Po</b><br>Polonium<br>-2 2 4    | 85<br><b>At</b><br>Astatine<br>-1 1       | 86<br><b>Rn</b><br>Radon<br>2       |
| 7 | 87<br><b>Fr</b><br>Francium<br>1  | 88<br><b>Ra</b><br>Radium<br>2    | 89-103                           | 104<br><b>Rf</b><br>Rutherfordium<br>4 | 105<br><b>Db</b><br>Dubnium<br>5 | 106<br><b>Sg</b><br>Seaborgium<br>6  | 107<br><b>Bh</b><br>Bohrium<br>7      | 108<br><b>Hs</b><br>Hassium<br>8    | 109<br><b>Mt</b><br>Meitnerium    | 110<br><b>Ds</b><br>Darmstadtium    | 111<br><b>Rg</b><br>Roentgenium    | 112<br><b>Cn</b><br>Copernicium   | 113<br><b>Nh</b><br>Nihonium        | 114<br><b>Fl</b><br>Flerovium          | 115<br><b>Mc</b><br>Moscovium          | 116<br><b>Lv</b><br>Livermorium          | 117<br><b>Ts</b><br>Tennessine            | 118<br><b>Og</b><br>Oganesson       |
|   |                                   |                                   | 6                                | 57<br><b>La</b><br>Lanthanum<br>3      | 58<br><b>Ce</b><br>Cerium<br>3 4 | 59<br><b>Pr</b><br>Praseodymium<br>3 | 60<br><b>Nd</b><br>Neodymium<br>3     | 61<br><b>Pm</b><br>Promethium<br>3  | 62<br><b>Sm</b><br>Samarium<br>3  | 63<br><b>Eu</b><br>Europium<br>2 3  | 64<br><b>Gd</b><br>Gadolinium<br>3 | 65<br><b>Tb</b><br>Terbium<br>3   | 66<br><b>Dy</b><br>Dysprosium<br>3  | 67<br><b>Ho</b><br>Holmium<br>3        | 68<br><b>Er</b><br>Erbium<br>3         | 69<br><b>Tm</b><br>Thulium<br>3          | 70<br><b>Yb</b><br>Ytterbium<br>3         | 71<br><b>Lu</b><br>Lutetium<br>3    |
|   |                                   |                                   | 7                                | 89<br><b>Ac</b><br>Actinium<br>3       | 90<br><b>Th</b><br>Thorium<br>4  | 91<br><b>Pa</b><br>Protactinium<br>5 | 92<br><b>U</b><br>Uranium<br>6        | 93<br><b>Np</b><br>Neptunium<br>5   | 94<br><b>Pu</b><br>Plutonium<br>4 | 95<br><b>Am</b><br>Americium<br>3   | 96<br><b>Cm</b><br>Curium<br>3     | 97<br><b>Bk</b><br>Berkelium<br>3 | 98<br><b>Cf</b><br>Californium<br>3 | 99<br><b>Es</b><br>Einsteinium<br>3    | 100<br><b>Fm</b><br>Fermium<br>3       | 101<br><b>Md</b><br>Mendelevium<br>3     | 102<br><b>No</b><br>Nobelium<br>2         | 103<br><b>Lr</b><br>Lawrencium<br>3 |

# Chemical properties

- Formation energies of MO, MO<sub>2</sub>, M(OH)
- Molecular properties of MO, MH, MOH:
  - geometry, R
  - Ionization potential, IP
  - dipole moment,  $\mu$
  - polarizability,  $\alpha$
  - dissociation energy
- Adsorption properties of MO, MH, MOH:
  - Teflon
  - Quartz
  - Gold
- DFT: ADF BAND
- $E_{\text{ads}}(\mu, \alpha, IP_{\text{mol}}, IP_{\text{surf}}, \epsilon, \chi)$

# Formation of HgO, CnO и F1O

- Hg

- $\text{Hg} + \text{O}_2 = \text{HgO} + \text{O} \Rightarrow E = 5.322 \text{ eV}$
- $\text{Hg} + \text{O}_2 = \text{HgOO} \Rightarrow E = 0.014 \text{ eV}$
- **$\text{Hg} + \text{O} = \text{HgO} \Rightarrow E = -0.618 \text{ eV}$**

- Cn

- $\text{Cn} + \text{O}_2 = \text{CnOO} \Rightarrow E = 0.005 \text{ eV}$
- **$\text{Cn} + \text{O} = \text{CnO} \Rightarrow E = -0.733 \text{ eV}$**

- F1

- $\text{F1} + \text{O}_2 = \text{F1O} + \text{O} \Rightarrow E = 3.993 \text{ eV}$
- $\text{F1} + \text{O}_2 = \text{F1OO} \Rightarrow E = -0.044 \text{ eV}$
- $\text{F1} + \text{O}_2 = \text{OF1O} \Rightarrow E = -0.003 \text{ eV}$
- **$\text{F1} + \text{O} = \text{F1O} \Rightarrow E = -1.947 \text{ eV}$**
- $\text{F1} + \text{O}_3 = \text{F1O} + \text{O}_2 \Rightarrow E = -0.348 \text{ eV}$

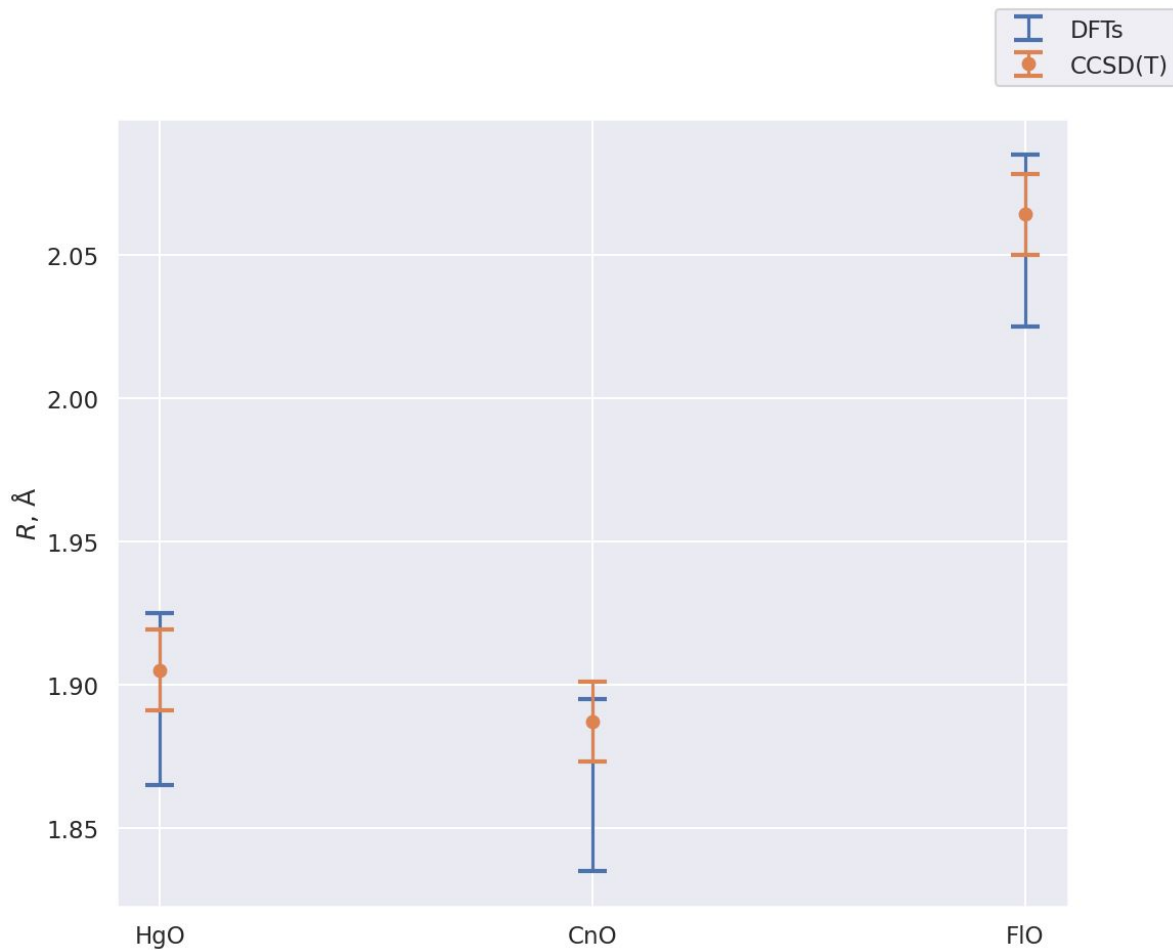
V. Pershina и M. Iliaš, TASCA 2022

# Coupled-cluster approach

$$\Psi_{CC} = (1 + T_1 + \frac{1}{2}T_1^2 + T_2 + \frac{1}{3!}T_1^3 + T_1T_2 + T_3 + \dots)\Phi$$

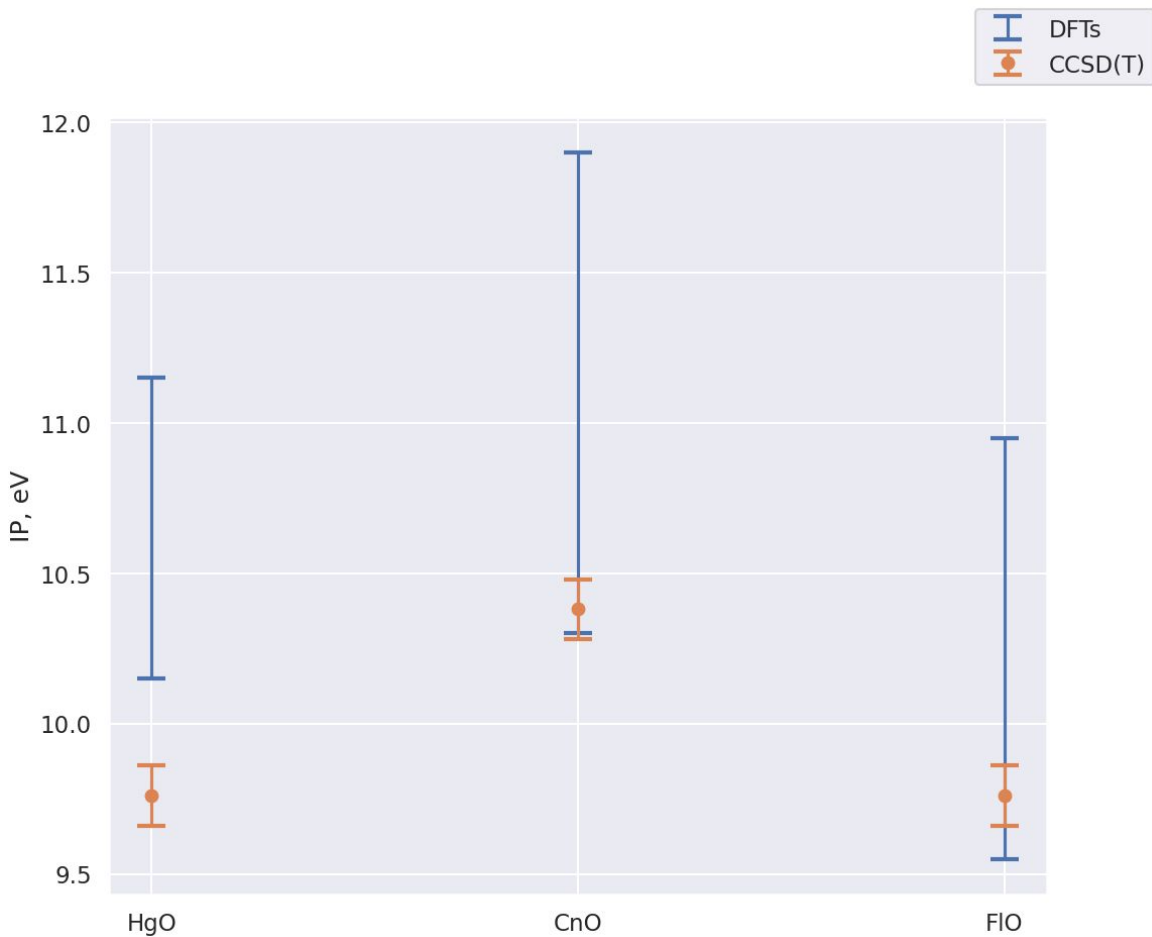
- Approximations:
  - eXact 2-Component vs. Dirac-Coulomb Hamiltonians
  - relativistic effects
- Quality of the basis functions
  - completeness
  - diffuse functions
  - higher orbital momentum
- Size of the correlation space
  - number of electrons and virtual orbitals accounted in the CC procedure
- Order of excitations
  - fully accounted Single and Double
  - Triples via perturbation theory (T)
  - and beyond: A. V. Oleynichenko, A. Zaitsevskii, E. Eliav, Towards High Performance Relativistic Electronic Structure Modelling: The EXP-T Program Package. Commun. Comp. Inf. Sci. 1331, 375-386 (2020)  
[github.com/aoleynichenko/EXP-T](https://github.com/aoleynichenko/EXP-T)

# Geometry of FIO, CnO, and HgO



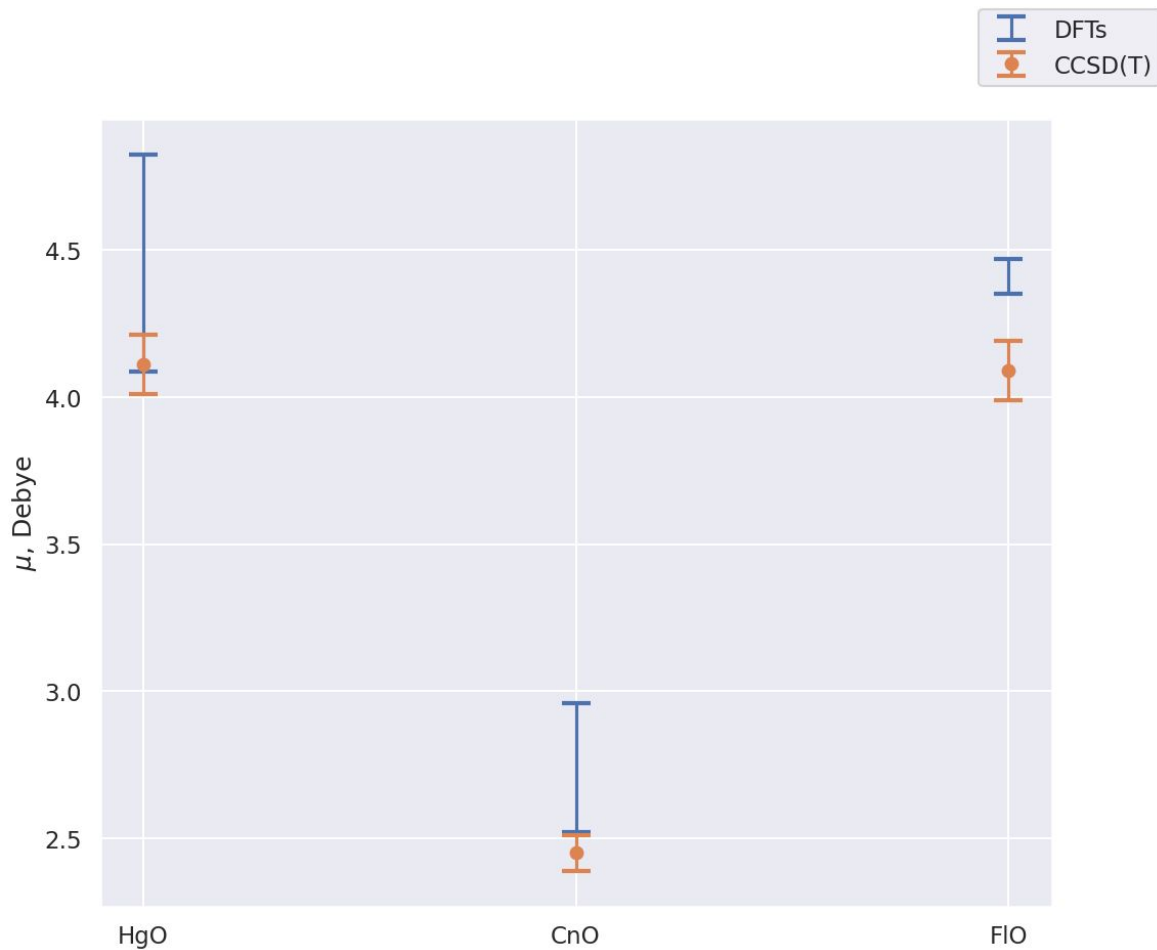
| Contrib.           | Value  |
|--------------------|--|
| X2C vs. DC         | -0.00028<br>(0.01%)                            |
| relativity         | -0.00023<br>(0.01%)                            |
| (3+)-excitations   | <b><math>\pm 0.013</math></b><br><b>(0.6%)</b> |
| <i>gh</i> orbitals | $\pm 0.0054$<br>(0.3%)                         |
| diffuse functions  | $\pm 0.0015$<br>(0.07%)                        |
| correlation space  | $\pm 0.00091$<br>(0.04%)                       |

# Ionization potential (IP)



| Contrib.          | Value                        |
|-------------------|------------------------------|
| X2C vs. DC        | +0.01<br>(0.1%)              |
| relativity        | -0.0084<br>(0.09%)           |
| 3-excitations     | <b>±0.098</b><br><b>(1%)</b> |
| geometry          | ±0.024<br>(0.3%)             |
| diffuse functions | ±0.0005<br>(0.005%)          |
| correlation space | ±0.0002<br>(0.002%)          |

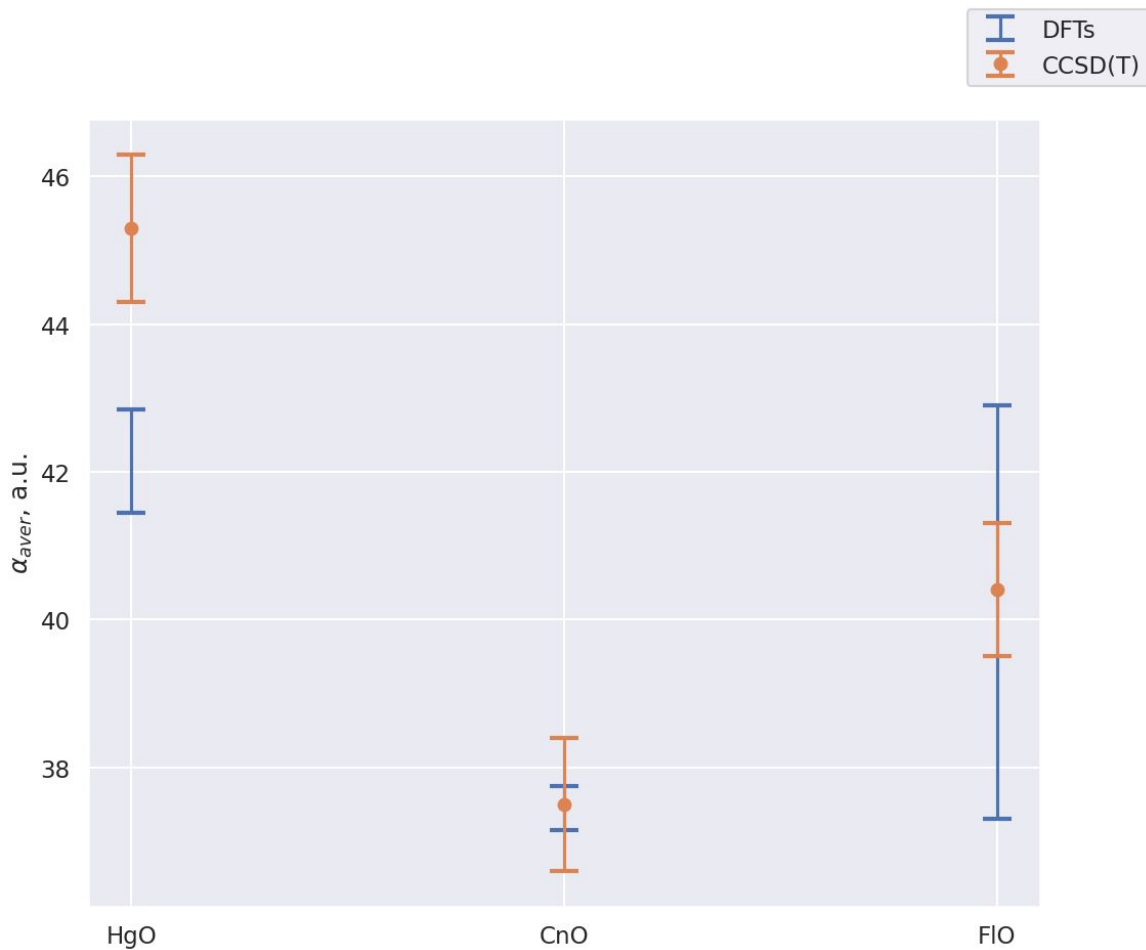
# Dipole moment $\mu$



| Contrib.           | Value  |
|--------------------|--|
| X2C vs. DC         | -0.016<br>(0.4%)                               |
| relativity         | -0.014<br>(0.3%)                               |
| (3+)-excitations   | <b><math>\pm 0.05</math></b><br><b>(1.2%)</b>  |
| geometry           | <b><math>\pm 0.036</math></b><br><b>(0.9%)</b> |
| <i>gh</i> orbitals | <b><math>\pm 0.088</math></b><br><b>(2.2%)</b> |
| diffuse functions  | $\pm 0.018$<br>(0.4%)                          |
| correlation space  | $\pm 0.009$<br>(0.2%)                          |

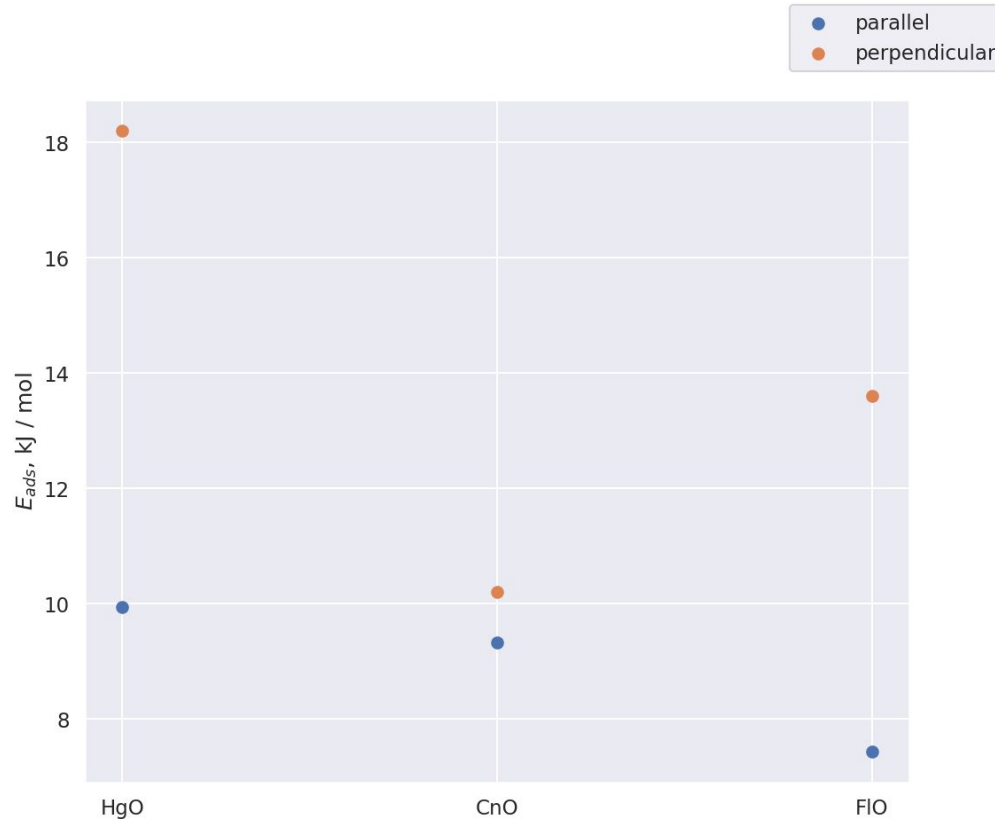


# Polarizability $\alpha_{\text{aver}}$ , a.e.



| Contrib.           | Value               |
|--------------------|---------------------|
| X2C vs. DC         | -0.11 (0.2%)        |
| relativity         | +0.12 (0.2%)        |
| (3+)-excitations   | <b>±0.52 (0.9%)</b> |
| geometry           | <b>±0.58 (1%)</b>   |
| <i>gh</i> orbitals | <b>±0.33 (0.6%)</b> |
| diffuse functions  | ±0.04 (0.07%)       |
| correlation space  | ±0.3 (0.5%)         |

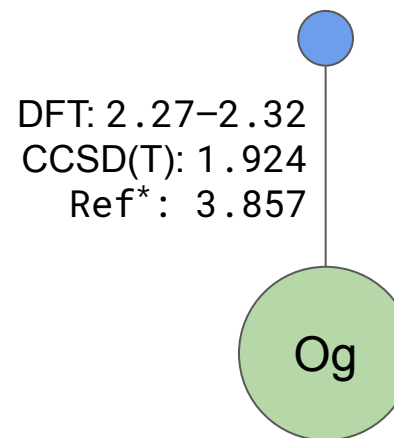
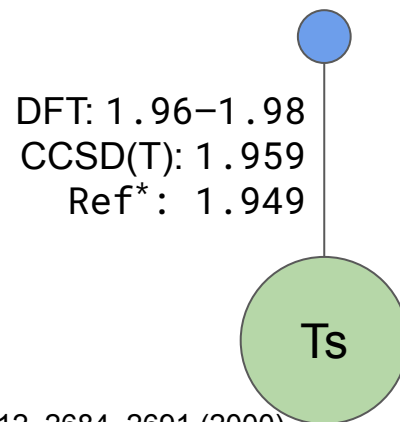
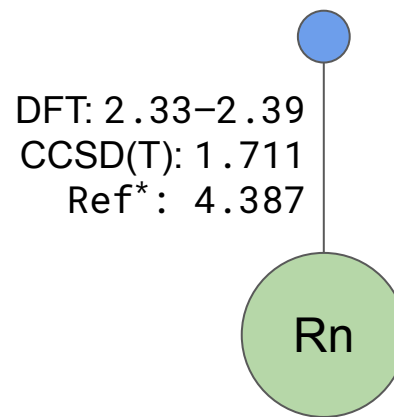
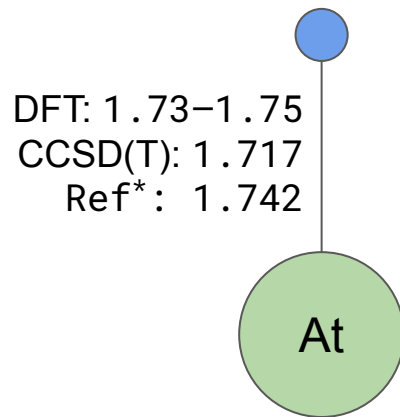
# Adsorption energy on Teflon



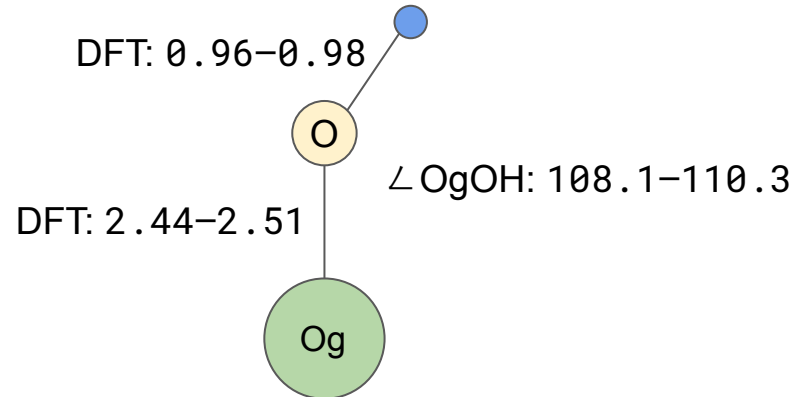
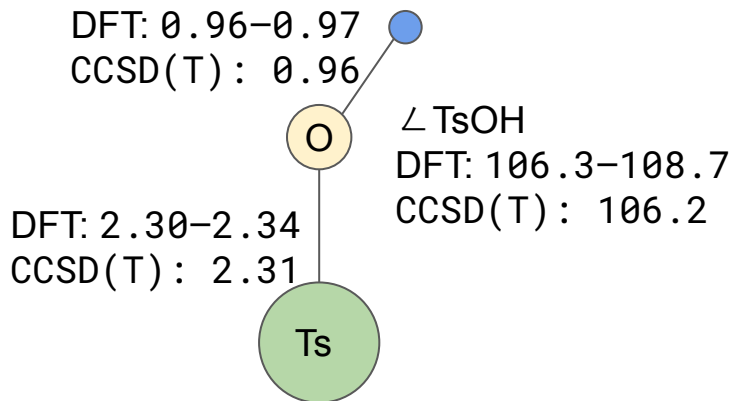
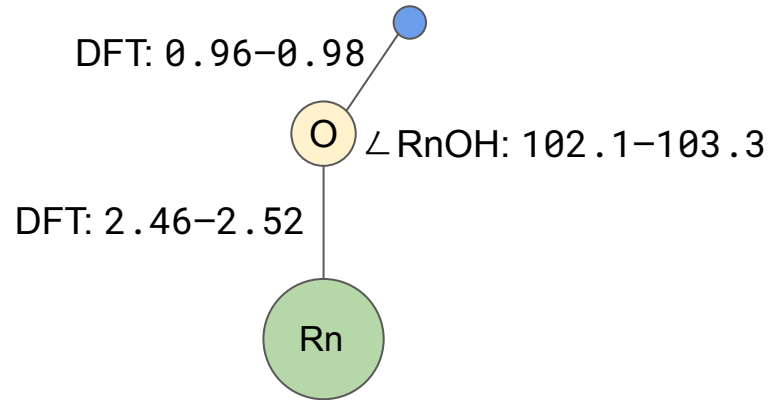
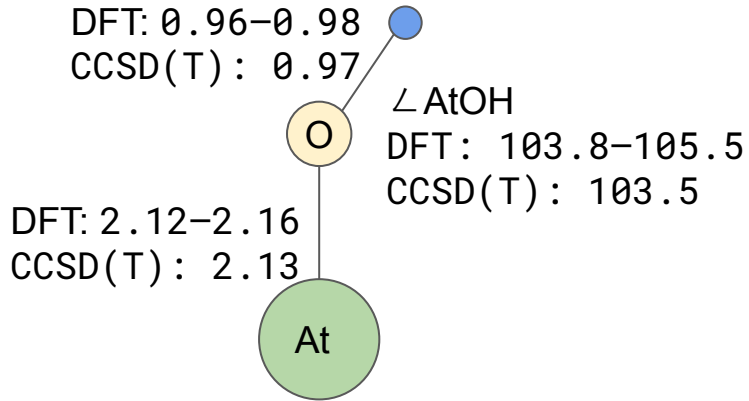
| Molecule | R, Å  | d <sub>par</sub> , Å | d <sub>per</sub> , Å |
|----------|-------|----------------------|----------------------|
| HgO      | 1.905 | 2.27                 | 3.103                |
| CnO      | 1.887 | 2.252                | 3.076                |
| FIO      | 2.064 | 2.429                | 3.341                |

The low  $E_{\text{ads}}$  (MO) values should guarantee delivery of the molecules from the recoil chamber to the chemistry setup.

# Geometry of hydrides from 17<sup>th</sup> and 18<sup>th</sup> groups



# Geometry of oxyhydrides from 17<sup>th</sup> and 18<sup>th</sup> groups



# Conclusion

- Ab-initio calculations of molecular properties of SHEs with oxygen and hydrogen within CCSD(T) approach:
  - The bond lengths of HgO and CnO are quite similar,
  - Dipole moment of FIO is more similar to HgO than CnO's is.
- Low value of  $E_{\text{ads}}$  with Teflon for oxydes should guarantee delivery of the molecules from the recoil chamber to the chemistry setup
- Evaluation of the reliability of the DFT application in comparison with the strong baseline calculation via CCSD(T).
  - For the geometry calculation DFT works well,
  - For properties (especially IP) DFT may yield erroneous values.
- Large deviation in the geometry of the hydrides of the 18<sup>th</sup> group between DFT and CCSD(T).

Many thanks to the LIT JINR for their comprehensive assistance in carrying out calculations on the GOVORUN supercomputer.

# Geometry R [ $\text{\AA}$ ] of FIO, CnO, and HgO

| Molecule | DFT       | CCSD(T)   |
|----------|-----------|-----------|
| HgO      | 1.88-1.91 | 1.905(14) |
| CnO      | 1.85-1.88 | 1.887(14) |
| FIO      | 2.04-2.07 | 2.064(14) |

| Contrib. | X2C vs. DC          | relativity          | (3+)-excitations                               | <i>gh</i> orbitals     | diffuse functions       | correlation space        |
|----------|---------------------|---------------------|--|------------------------|-------------------------|--------------------------|
| Value    | -0.00028<br>(0.01%) | -0.00023<br>(0.01%) | <b><math>\pm 0.013</math></b><br><b>(0.6%)</b> | $\pm 0.0054$<br>(0.3%) | $\pm 0.0015$<br>(0.07%) | $\pm 0.00091$<br>(0.04%) |

Contributions and uncertainties for FIO

# Ionization potential (IP), eV

| Molecule | DFT       | FS-CCSD   |
|----------|-----------|-----------|
| HgO      | 10.4-10.9 | 9.76(10)  |
| CnO      | 10.7-11.5 | 10.38(10) |
| FIO      | 9.9-10.6  | 9.76(10)  |

| Contrib. | X2C vs. DC      | relativity         | (3+)-excitations       | geometry         | diffuse functions   | correlation space   |
|----------|-----------------|--------------------|------------------------|------------------|---------------------|---------------------|
| Value    | +0.01<br>(0.1%) | -0.0084<br>(0.09%) | <b>±0.098<br/>(1%)</b> | ±0.024<br>(0.3%) | ±0.0005<br>(0.005%) | ±0.0002<br>(0.002%) |

# Dipole moment $\mu$ , Debye

| Molecule | DFT       | CCSD(T)  |
|----------|-----------|----------|
| HgO      | 4.27-4.64 | 4.11(10) |
| CnO      | 2.63-2.85 | 2.45(6)  |
| FIO      | 4.38-4.44 | 4.09(10) |

| Contrib. | X2C vs. DC       | relativity       | (3+)-excitations                              | geometry                                       | <i>gh</i> orbitals                             | diffuse functions     | correlation space     |
|----------|------------------|------------------|---|--|--|-----------------------|-----------------------|
| Value    | -0.016<br>(0.4%) | -0.014<br>(0.3%) | <b><math>\pm 0.05</math></b><br><b>(1.2%)</b> | <b><math>\pm 0.036</math></b><br><b>(0.9%)</b> | <b><math>\pm 0.088</math></b><br><b>(2.2%)</b> | $\pm 0.018$<br>(0.4%) | $\pm 0.009$<br>(0.2%) |



# Polarizability $\alpha_{\text{aver}}$ , a.e.

| Molecule | DFT       | CCSD(T)  |
|----------|-----------|----------|
| HgO      | 41.8-42.5 | 45.3(10) |
| CnO      | 37.3-37.6 | 37.5(9)  |
| FIO      | 38.7-41.5 | 40.4(9)  |

| Contrib. | X2C vs. DC      | relativity      | (3+)-excitations                              | geometry                                    | <i>gh</i> orbitals                            | diffuse functions     | correlation space   |
|----------|-----------------|-----------------|---|---|---|-----------------------|---------------------|
| Value    | -0.11<br>(0.2%) | +0.12<br>(0.2%) | <b><math>\pm 0.52</math></b><br><b>(0.9%)</b> | <b><math>\pm 0.58</math></b><br><b>(1%)</b> | <b><math>\pm 0.33</math></b><br><b>(0.6%)</b> | $\pm 0.04$<br>(0.07%) | $\pm 0.3$<br>(0.5%) |

# Adsorption energy on Teflon

| Molecule | R, Å  | d <sub>par</sub> , Å | d <sub>per</sub> , Å | μ <sub>z</sub> , D | IP, eV | <α>, a.e. | α <sub>xx</sub> , a.e. | α <sub>zz</sub> , a.e. | E <sub>ads</sub> <sup>(par)</sup> , kJ/mol | E <sub>ads</sub> <sup>(per)</sup> , kJ/mol |
|----------|-------|----------------------|----------------------|--------------------|--------|-----------|------------------------|------------------------|--|--|
| HgO      | 1.905 | 2.27                 | 3.103                | 4.109              | 9.76   | 45.31     | 33.9                   | 68.13                  | 9.94                                       | 18.2                                       |
| CnO      | 1.887 | 2.252                | 3.076                | 2.451              | 10.38  | 37.45     | 30.08                  | 52.19                  | 9.32                                       | 10.2                                       |
| FIO      | 2.064 | 2.429                | 3.341                | 4.086              | 9.76   | 40.36     | 31.09                  | 58.9                   | 7.44                                       | 13.6                                       |

The low E<sub>ads</sub><sup>(MO)</sup> values should guarantee delivery of the molecules from the recoil chamber to the chemistry setup.

# Polarizability $\alpha$ [a.e.] of FIO, CnO, and HgO

|          |                 | DFT         |             |             |                 |  |
|----------|-----------------|-------------|-------------|-------------|-----------------|--|
| Molecule | component       | B3LYP       | PBE0        | BP86        | CCSD(T)         |  |
| HgO      | $\alpha_{xx}$   | 33.6        | 33.5        | 34.2        | 33.9(10)        |  |
|          | $\alpha_{zz}$   | 59.2        | 60.4        | 57.1        | 68.1(10)        |  |
|          | $\alpha_{aver}$ | <b>42.1</b> | <b>42.5</b> | <b>41.8</b> | <b>45.3(10)</b> |  |
| CnO      | $\alpha_{xx}$   | 30.9        | 30.5        | 31.6        | 30.1(9)         |  |
|          | $\alpha_{zz}$   | 51.1        | 51.1        | 50.8        | 52.2(9)         |  |
|          | $\alpha_{aver}$ | <b>37.6</b> | <b>37.4</b> | <b>37.3</b> | <b>37.5(9)</b>  |  |
| FIO      | $\alpha_{xx}$   | 30.2        | 29.5        | 32.0        | 31.1(9)         |  |
|          | $\alpha_{zz}$   | 58.1        | 57.1        | 60.4        | 58.9(9)         |  |
|          | $\alpha_{aver}$ | <b>39.5</b> | <b>38.7</b> | <b>41.5</b> | <b>40.4(9)</b>  |  |

| Contrib.          | Value                               |
|-------------------|-------------------------------------|
| X2C vs. DC        | -0.11 (0.2%)                        |
| relativity        | +0.12 (0.2%)                        |
| (3+)-excitations  | <b><math>\pm 0.52</math> (0.9%)</b> |
| geometry          | <b><math>\pm 0.58</math> (1%)</b>   |
| gh orbitals       | <b><math>\pm 0.33</math> (0.6%)</b> |
| diffuse functions | $\pm 0.04$ (0.07%)                  |
| correlation space | $\pm 0.3$ (0.5%)                    |