Computational Molecular Physics at Work

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Talk overview

- Motivation
- Brief theory – Quantum Mechanics and Molecular Mechanics
- About available software
- About hands-on-excercises
- Conclusions

Motivation – why Comp.Mol.Phys. ?

- Scientific field of Computational Molecular Physics (CMP) – deals with atomic and molecular systems (called also as Computational and Theoretical Chemistry)

- CMP has big predictive power - can compute plenty of physico-chemical properties

- The main workhorse is the dedicated scientific software, with various implemented method

Basic theory of CMC – Quantum Mechanics

- Many body systems – atomic nuclei and electrons (atoms, molecules)
- Numerically solving Schrödinger equation for electrons and frozen nuclei (so called Born-Oppenheimer approximation)
- Many electron wave-function (wf) is Slater determinant (one or many), composed on one-electron wf's, called molecular orbitals or spinors

$$\hat{H}\Psi = E\Psi$$

$$\Psi(1,\ldots,\mathrm{N}) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N) \end{vmatrix}$$

Solving many-body electronic problem: Hartree-Fock approximation

closed-shell system: $$\psi_i = \begin{cases} \varphi_i \alpha, & \text{if } i \le N/2 \\ \varphi_{i-N/2} \beta, & \text{if } i > N/2 \end{cases}$$

Linear combination of atomic orbitals (LCAO) approximation:

$$\varphi_i = \sum_j \chi_j c_{ji}$$

atomic orbitals ← χ_j ; c_{ji} → parameters to be varied

energy: $$E = 2\sum_{i=1}^{N/2} \langle \varphi_i | h | \varphi_i \rangle + \sum_{i,j=1}^{N/2} \left[2\langle \varphi_i \varphi_j | g | \varphi_i \varphi_j \rangle - \langle \varphi_i \varphi_j | g | \varphi_j \varphi_i \rangle \right]$$

Roothaan- or secular equation: $\mathrm{FC} = \mathrm{SC}\varepsilon$ or $\mathrm{Fc} = \varepsilon \mathrm{Sc}$

$$\mathrm{F}_{ij} = \langle \chi_i | F | \chi_j \rangle$$

$$\mathrm{C}_{ij} = c_{ij}$$

$$\mathrm{S}_{ij} = \langle \chi_i | \chi_j \rangle$$

$$\varepsilon_{ij} = \varepsilon_i \delta_{ij}$$

Fock-equation: $$F\varphi_i = \varepsilon_i \varphi_i$$

F: Fock-operator; φ_i: molecular orbitals (MO); ε_i: MO-energy

Density Functional Theory (DFT)

- Works with the electron density n(**r**), what is a function of 3 coordinates, instead of N-electronic wave function
- We solve Kohn-Sham equations, giving KS orbitals
- V_{XC} is the exchange-correlation potential, approximated to various degree
- We know LDA, GGA, m-GGA etc functionals..
- Inputs for DFT: basis set (or pseudopotential), xc-functional

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}),$$

$$V_s(\mathbf{r}) = V(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}^3\mathbf{r}' + V_{XC}[n(\mathbf{r})],$$

Ab-initio methods

- Starting from Hartree-Fock SCF method, they compute so-called correlation energy, which HF-SCF can not give
- Examples MP2, CCSD(T), CI … more computer demanding methods
- Used when we need higher accuracy for our calculations

Other factors in QM based methods…

- Relativistic effects – via relativistic Hamiltonian (scalar or spin-orbit), the most rigorous is the Dirac-Coulomb
- Solvent effects – COSMO, make a cavity around molecule
- Plenty properties, like excitation energies, NMR, EPR, IR, Raman…
- Semiempirical – valence electrons only, minimal valence basis, approximations in HF-SCF formulas

Molecular mechanics (or Force-Field) methods

- interatomic potential function or force field in chemistry, calculates the molecular system's potential energy (E) in a given conformation as a sum of individual energy terms
- In Avogadro2, we have UFF, MMFF94, Ghemical …

$$E_{\text{total}} = E_{\text{bonded}} + E_{\text{nonbonded}}$$

$$E_{\text{bonded}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}}$$

$$E_{\text{bond}} = \frac{k_{ij}}{2}(l_{ij} - l_{0,ij})^2$$

$$E_{\text{nonbonded}} = E_{\text{electrostatic}} + E_{\text{van der Waals}}$$

Geometry optimization – the very first step

- E = Emin(atomic coordinates)
- Minimization of the total system’s energy
- We use first (gradient) end second (Hessian) derivatives of energy wrt to geometry coordinates
- Can be analytical or numerical (less effective)
- One can combine geometry optimizers of different methods/programs to achieve better performance (like start with MM, continue with seMM, than with DFT)

Overview of software for hand-on-exercises…

- Installed by me on Govorun, available to everybody
- Launching scripts, inputs and reference outputs are provided in https://github.com/miroi/HybriLIT-workshop-2025
- MOPAC
- ORCA
- GAMESS-US
- NWChem
- DIRAC

MOPAC – semiempirical quantum mechanics (seQM)

- Semiempirical models: AM1, PM3, PM6,PM7
- Geometry optimization
- Transition-state optimization
- Vibrational analysis
- COSMO solvation model
- Periodic boundary conditions (Gamma point only, no Brillouin zone sampling)
- MOZYME for closed-shell systems (linear-scaling electronic structure algorithm)
- Gas-phase thermodynamics
- Molecular polarizability
- Automatic hydrogenation for pre-processing of Protein Data Bank structures

ORCA software

- general-purpose quantum chemistry package, featuring a variety of methods:
- semi-empirical
- density functional theory
- many-body perturbation
- coupled cluster
- multireference methods.

NWChem software

- Molecular mechanics
- Molecular dynamics
- Hartree–Fock (self-consistent field method)
- Density functional theory
- Time-dependent density functional theory
- Post-Hartree–Fock methods, including MP2, multiconfigurational self-consistent-field (MCSCF) theory, selected configuration interaction (CI), Møller–Plesset perturbation theory (MP2, MP3, MP4), configuration interaction (CISD, CISDT, CISDTQ), and coupled cluster theory (CCSD, CCSDT, CCSDTQ, EOMCCSD, EOMCCSDT, EOMCCSDTQ
- QM/MM

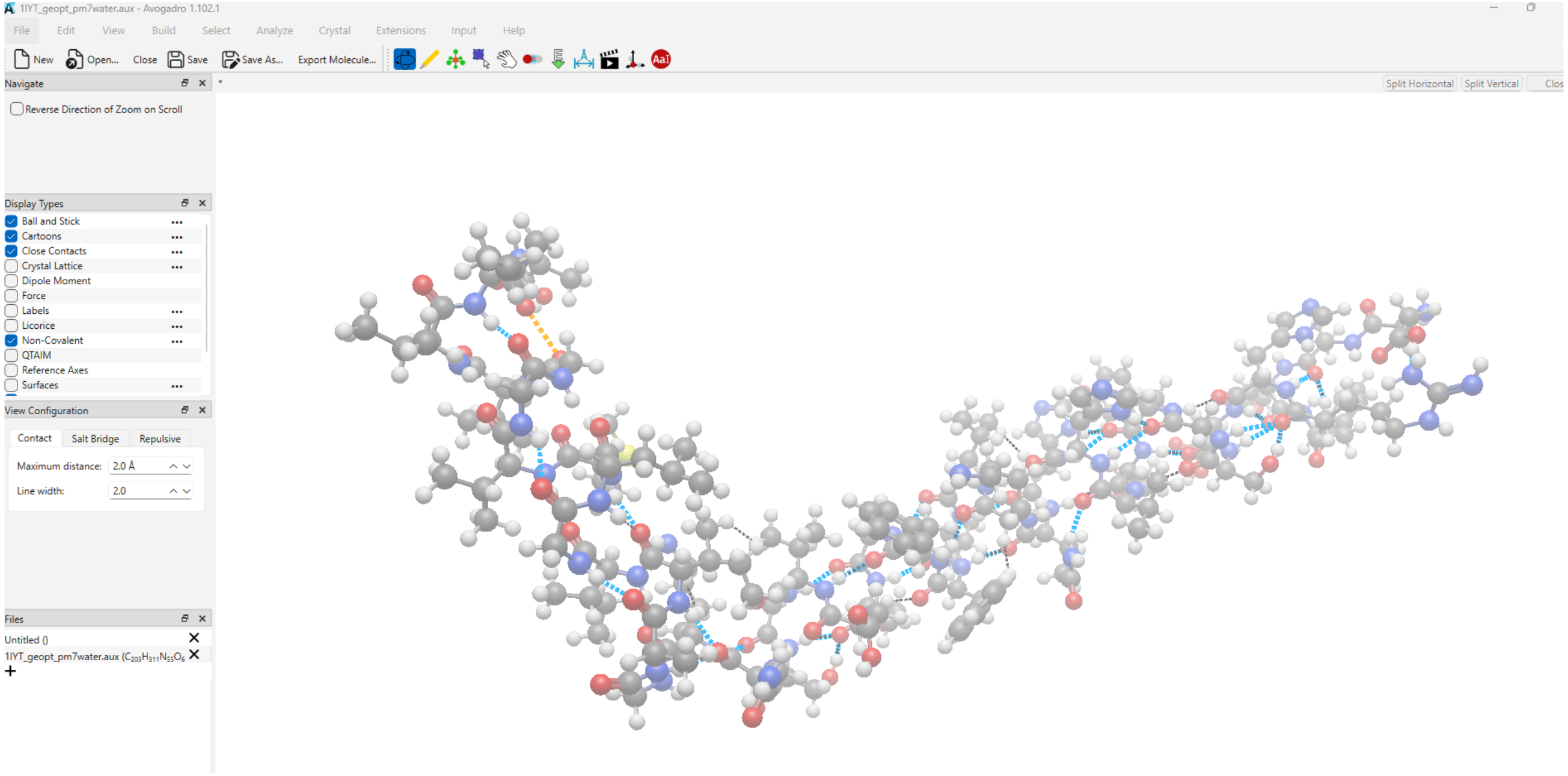
GAMESS-US software

- can perform several general computational chemistry calculations
- Hartree–Fock method
- density functional theory (DFT)
- generalized valence bond (GVB)
- multi-configurational self-consistent field (MCSCF)
- configuration interaction (CI)
- second order Møller–Plesset perturbation theory (MP2)
- coupled cluster (CC) theory.
- solvent effect through discrete effective fragment potentials or continuum models (such as PCM)
- relativistic corrections up to third order Douglas-Kroll scalar terms

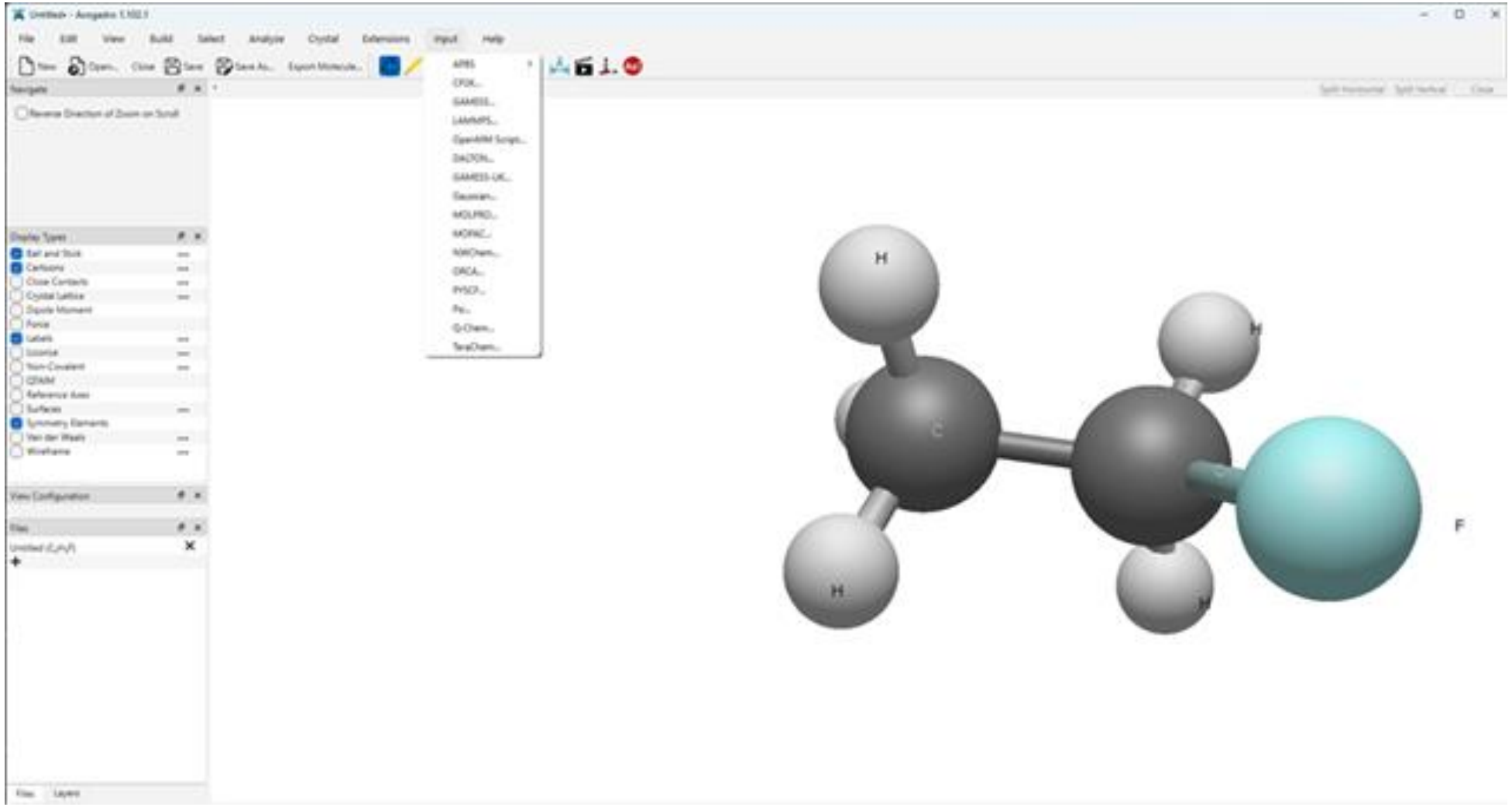
DIRAC software

- relativistic ab initio quantum chemistry program
- general-purpose quantum chemistry packages that provides accurate description of relativistic effects in molecules, using the Dirac equation as its starting point
- capable of calculating various molecular properties using the Hartree–Fock, MP2, density functional theory, configuration interaction and coupled cluster electronic structure theories
- Myself (M.I.) co-developed X2c infinite-order two-component Hamiltonian into DIRAC

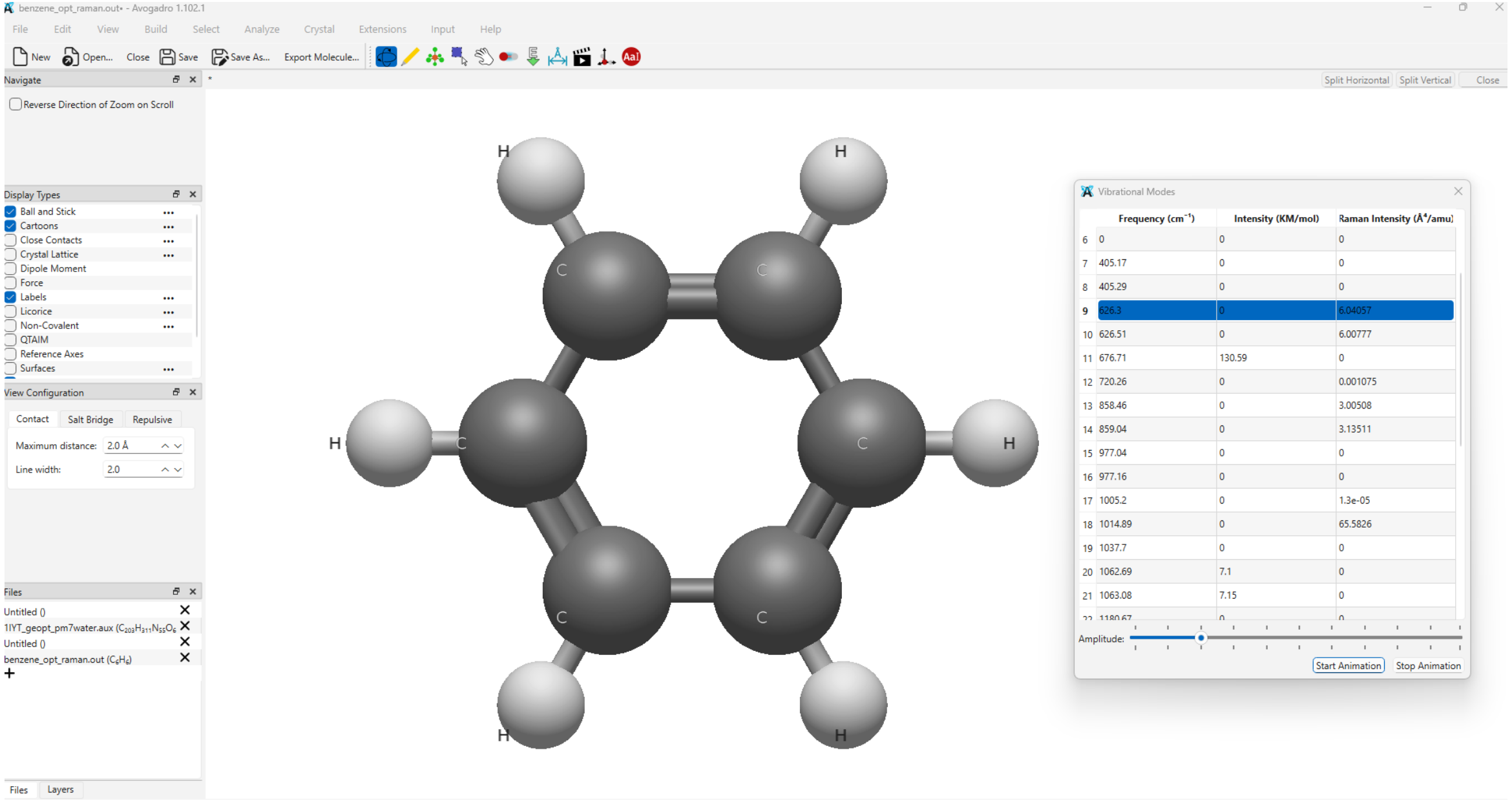
GUI at your personal PC: Avogadro2



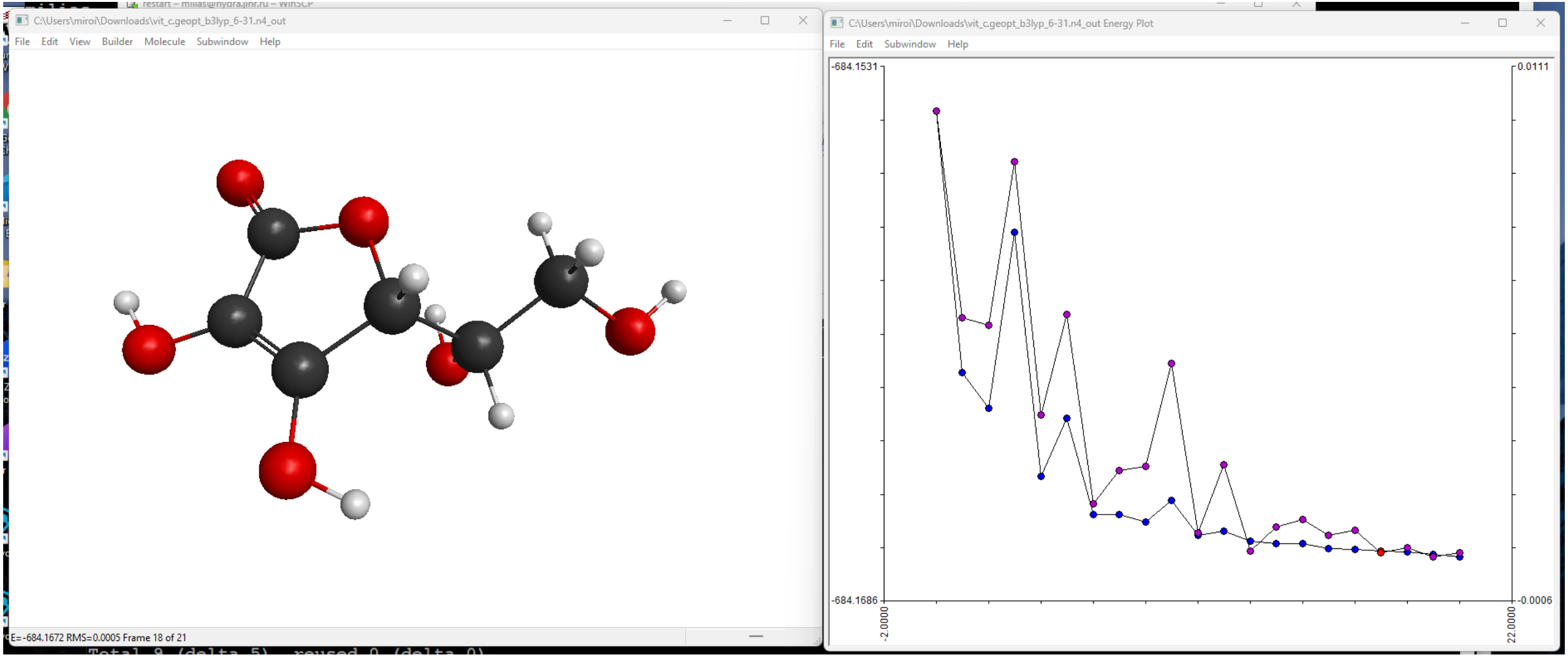
Avogadro2: prepare input for a software (1)



Avogadro2 visualizer for ORCA



MacMolPlt GUI (Windows) for GAMESS-US



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- To learn more about the topic - in February 2026, we plan our next (second) online school on Computational Molecular & Materials Physics - hands-on-exercises

Towards hands-on-exercises- common user of CMP methods …

- He is interested in running the scientific code (codes)
- He does not bother with code buildup, he just wants to get results from the installed, working code
- Prefers prepared, simple software running scripts
- His focus is on science with the code
- He does good job with getting and processing computed results