A QUANTUM LEAP INTO THE FUTURE OF CHEMISTRY

Interpreting the results of Hartree-Fock calculations: Ionized states and Koopmans theorem

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Description: Students learn how to interpret the results of Hartree-Fock calculations. The focus of this lab is on physical significance of the canonical molecular orbitals (MOs) and their energies.

Suggested level: Beginning graduate.

Learning objectives: Learn how to compute and visualize molecular orbitals and how to connect the computed orbital energies with experimental observables such as ionization energies (IEs). By analyzing the shapes of the MOs, make predictions about anticipated shapes of photoelectron spectra. Learn how to determine symmetry of the ionized states.

I. HARTREE-FOCK CALCULATIONS AND KOOPMANS THEOREM

Hartree-Fock wave function is given by a single Slater determinant:

$$\Phi_0(N) = |\phi_1 \phi_2 \dots \phi_N > \tag{1}$$

composed of N spin-orbitals that satisfy the following equations:

$$\hat{F}[\{\phi_i\}_{i=1}^{N}]\phi_i(x) = \epsilon_i \phi_i(x) \tag{2}$$

The Fock operator, $\hat{F}[\{\phi_i\}_{i=1}^{N}]$, is an effective one electron operator that consists of the one-electron Hamiltonian (kinetic energy and Coulomb potential due to nuclei) plus a mean-field Coulomb potential created by all other electrons. Eqns. (1) and (2) look like equations describing non-interacting electrons (except for the mean-field part in the Fock operator); that is why Hartree-Fock model is often referred to as a pseudo-independent electron model. The solutions of Eq. (2) can be interpreted as the states of such pseudo-independent electrons.

Unlike the case of truly non-interacting electrons, the total Hartree-Fock energy is not the sum of one-electron energies, ϵ_i:

$$E_{HF} =< \Phi_0|H|\Phi_0 >= \sum_{i \in \Phi_0} \epsilon_i - \frac{1}{2} \sum_{i,j \in \Phi_0} < ij||ij > \tag{3}$$

Interestingly, E_{HF} and Φ_0 are invariant with respect to any unitary transformation of the *occupied* orbitals, i.e., those solutions of Eq. (2) that were selected to construct Φ_0. One might therefore wonder whether the solutions of Eq. (2), that is orbitals ϕ_i and the respective energies, ϵ_i, have any physical significance. The answer is given by Koopmans' theorem that states that the canonical Hartree-Fock MOs (those that diagonalize the matrix of the Fock operator) can be interpreted as the states from which an electron is removed in an ionization process and the respective energies approximate the IEs:

$$IE(\cancel{\phi_i}) = -\epsilon_i \tag{4}$$

The key assumption of the Koopmans theorem is that the ionized state can be approximated by the Slater determinant composed of the orbitals computed for the neutral species:

$$\Phi(N-1) \approx |\phi_1\phi_2\ldots\cancel{\phi_i}\ldots\phi_N> \tag{5}$$

A. Determining IEs and electronic configurations of the ionized states of formaldehyde

1. MOs and Koopmans theorem

Use the ωB97X-D/6-31G* optimized structure of formaldehyde from the *"Introduction to IQmol: Exploring potential energy surfaces"* lab (refer to the *IQmol* tutorial how to build and optimize structures).

At this geometry, perform a single-point Hartree-Fock calculation using the 6-31G* basis set. Visualize the MOs and prepare a summary of all *occupied* orbitals. For each molecular orbital, write down its symmetry and energy.

Use these results and the Koopmans theorem to answer the following:

1. Write down the electronic configuration of the Hartree-Fock wave function of CH_2O using the symmetry labels of the MOs. What is the symmetry of this wave function?
2. What is the lowest IE of formaldehyde? Write down the electronic configuration of the ground state CH_2O^+. What is the symmetry of this wave function?
3. What is the lowest excited state of CH_2O^+? Determine the excitation energy and electronic configuration of this state, assign symmetry.
4. Analyze the shapes of the respective MOs and predict what kind of structural relaxation (relative to the neutral geometry) these ionized states are likely to undergo.

2. Koopmans theorem versus ΔSCF calculations

Calculate the lowest IE of formaldehyde as the Hartree-Fock energy difference between the neutral and the cation:

$$IE = E_{HF}(CH_2O) - E_{HF}(CH_2O^+) \tag{6}$$

Use the same geometry and the same basis set as above. To perform the calculation of CH_2O^+, specify 'Charge=1' and 'Multiplicity=2' (doublet state). Compare this so-called ΔE IE with Koopmans' IE. Answer the following:

1. Which effects are included in ΔE calculations that Koopmans' theorem neglects?
2. Explain the difference between the two IEs. Do you expect one to be always lower than the other or the difference is likely to be system dependent? **Hint:** think variational principle.