Electronically excited states: Calculations by configuration inetraction singles method

Description: Students learn how to describe electronically excited states in terms of their electronic configurations. They compare the prediction of the Koopmans theorem with the results of CIS calculations.

Suggested level: Beginning graduate.

Learning Objectives: Learn how to use Koopmans theorem to predict the character of low-lying excited states. Learn how to perform CIS calculations and analyze the results. Learn about diffuse orbitals and Rydberg states.

I. KOOPMANS THEOREM AND EXCITED STATES

The Koopmans theorem is often used to predict the character of low-lying excited states. For independent electrons, the excitation energy is simply the difference between the orbital energies, $\epsilon_a - \epsilon_i$. Thus, one can expect that the lowest excited states will involve transitions between HOMOs and LUMOs. That is why the lowest excited state often has HOMO→LUMO character. Quantitatively, such description is rather crude, as it neglects orbital relaxation and electron-electron interaction (which is often referred to as a hole-electron attraction). The consequences are: (i) Excitation energies are predicted to be the same for singlet and triplet states; (ii) excitation energies are too high (in finite systems such as molecules). Another caveat with the Koopmans theorem is that in diffuse bases, the valence HOMO-LUMO gap becomes filled with diffuse orbitals, while the lowest excited state is likely to retain its valence character. Thus, Koopmans theorem should only be used to predict the character of excited states in valence (non-augmented) bases.

II. EXCITED STATES BY CONFIGURATION INTERACTION SINGLES

The simplest model for excited-state calculations is given by CIS (configuration interaction singles) — in this method, one describes target (excited-state) wave functions as a linear combination of singly excited determinants:

$$\Psi = \sum_{ia} c_i^a \Phi_i^a \tag{1}$$

The coefficients c_i^a are found by diagonalizing the Hamiltonian in the basis of all singly excited determinants. CIS calculations produce excitation energies and one can analyze the character of excited states by analyzing the MOs corresponding to the leading configuration(s).

III. EXCITED STATE CALCULATIONS BY CIS

Perform CIS calculation for the formaldehyde molecule (at the ωB97X-D/6-31G* geometry) using the 6-31G(d,p) and 6-31(2+)G(d,p) bases. To set up a CIS calculation in IQmol, select 'Energy' as a type of calculation and 'CIS' as a method. Specify 'Charge'

and 'Multiplicity' of the ground state. In the bottom panel, specify how many roots (i.e., excited state solutions) of each multiplicity you would like to compute. Note that you can disable triplets (or singlet) calculations (when your ground state is a closed-shell state).

Answer the following questions.

- Analyze relevant molecular orbitals (HOMO, HOMO-1, and several LUMOs). Does the HOMO character change when you increase the basis set? How does the character of LUMO change? Explain the observation.

- In each basis, analyze the wave functions of the 4 lowest singlets and 4 lowest triplets. Look at the MOs and write down electronic configuration for each state. Determine the symmetry of each state. Mark which transitions are optically allowed and which ones are dark. Assign the character of each transition (e.g., $\pi\pi^*$ or $lp\pi^*$, valence versus Rydberg, etc).

- Explain the observed difference between the 6-31G(d,p) and 6-31(2+)G(d,p) results.

- Compare the CIS results with the Koopmans theorem predictions, explain.