Now back to the excited states....
Excited states

\[ \mathcal{H} \Psi_L = E_L \Psi_L \]

L=0: ground state, L>0: excited states.

For non-interacting electrons, excited states are just excited determinants and the excitation energies are orbital energy differences

\[ E_{ex} = \epsilon_\alpha - \epsilon_i \]
# | Symmetry | Energy, au |
--- | --- | --- |
D1 | 1a\(_1\) | -20.56 |
D2 | 2a\(_1\) | -1.35 |
D3 | 1b\(_1\) | -0.71 |
D4 | 3a\(_1\) | -0.57 |
D5 | 1b\(_2\) | -0.50 |
V1 | 4a\(_1\) | 0.21 |
V2 | 2b\(_1\) | 0.31 |

Electronic configuration:

\[ \Phi_0 = (1a_1)^2(2a_1)^2(1b_1)^2(3a_1)^2(1b_2)^2 \]

HOMO->LUMO excitation \((1a_1)^2(2a_1)^2(1b_1)^2(3a_1)^2(1b_2)^1(4a_1)^1\):

\[ E = 0.21 - (-0.50) = 0.71 \text{ hartree} = 19.3 \text{ eV} \]

Compare: \( IE = 0.5 \text{ hartree} = 13.61 \text{ eV} \)
What is missing in Koopmans description of excited states?

1. Energies of virtual orbitals are too high.
2. Other electrons do not “feel“ the changes due to one excited electron (independent electrons).
3. No spin-coupling (singlets are the same as triplets). The electrons are non-interacting, so they do not care…

What is the next level of theory then?
Configuration Interaction

CIS wave function: \( \Psi_{ex} = \sum_{ia} C_{i}^{a} \Phi_{i}^{a} \)

Symmetry of the state: \( \text{Irrep}(\Phi_{0}) \times \text{Irrep}(i) \times \text{Irrep}(a) \)

Multiplicity of the state: spin-coupling of \( i, a \)
(triplet ‘+’; singlet ‘-‘)

Character of the state: orbitals \( i, a \) for the leading amplitude \( C_{i}^{a} \)
Assigning excited-state character

1. Determine spin-coupling (singlet or triplet), either from the amplitudes or from $\langle S^2 \rangle$.
2. Determine symmetry of the state (note symmetry of the state may not be the same as symmetry of the transition).
3. Look at dominant amplitude. Which orbitals are involved? What is their character?
4. More sophisticated methods: Attachment-detachment densities, natural transition orbitals, etc.

See, for example:

Different types of excited states: Valence, Rydberg, and charge-transfer

**Figure 2.** Schematic sketch of a typical valence-excited state, in which the transition occurs on one of the individual molecules, that is, the orbitals $i$, $j$ and $a$, $b$ are located on the same molecule in contrast to a charge-transfer excited state in which an electron is transferred from orbital $i$ on molecule A to orbital $a$ on molecule B. When the molecules A and B are spatially separated from each other the orbitals $i$ and $j$ do not overlap with $a$ and $b$. 

Excited-state character

Diazomethane example

Relevant MOs:
I. Fedorov, L. Koziol, G. Li, J.A. Parr, A.I. Krylov, and H. Reisler *Theoretical and experimental investigations of the electronic Rydberg states of diazomethane: Assignments and state interactions*  
Excited state character

Consequences of different state character:

\( \pi^* \) state: large changes in geometry, vibrational progressions;

Rydberg states: similar to the cation (sharp REMPI).
Caveats with diffuse orbitals:

Use smaller isovalue to visualize them (Why?)

May need to adjust visualization box size in IQmol

If you have loaded a FChk file, then there should be a 'MO Surfaces' item in the Model View (this is what you normally double click to plot an orbital). If you right-click on this item, a context menu appears with the settings for the bounding box. If you edit these before plotting the orbital then it will be evaluated in the larger 'cube' and you should be able to avoid the clipping.
Exercise: CIS for water

Compute CIS/6-31G* excited states for water
Geometry: Use structure from ‘Molecules’
Select ‘CIS’ in ‘Method’ and ‘6-31G*’ in ‘Basis’
Specify number of roots, request both singlets and triplets
## CIS Excitation Energies

<table>
<thead>
<tr>
<th>Excited state</th>
<th>Excitation energy (eV)</th>
<th>Total energy for state</th>
<th>Multiplicity</th>
<th>Trans. Mom. (X, Y, Z)</th>
<th>Strength</th>
<th>D(5) --&gt; V(1) amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.6926</td>
<td>-75.691119421932</td>
<td>Triplet</td>
<td>0.0000 X 0.0000 Y 0.0000 Z</td>
<td>0.0000000000</td>
<td>0.9857</td>
</tr>
<tr>
<td>2</td>
<td>9.6604</td>
<td>-75.65554472911</td>
<td>Singlet</td>
<td>0.0000 X -0.0000 Y 0.2723 Z</td>
<td>0.0175427089</td>
<td>0.9919</td>
</tr>
<tr>
<td>3</td>
<td>10.6863</td>
<td>-75.617851691692</td>
<td>Triplet</td>
<td>0.0000 X 0.0000 Y 0.0000 Z</td>
<td>0.0000000000</td>
<td>0.9734</td>
</tr>
</tbody>
</table>

**Remarks:**
- ‘D’: doubly occupied
- ‘V’: virtual
- See orbital energies and symmetries at the end of the output

**Note:**
1. The character of the lowest state: dominated by HOMO-LUMO (but energy is different from Koopmans).
2. Singlet and triplet are split by 1 eV.
Water

Visual summary of excited states calculations: Click on ‘Excited States’
Expand orbital diagram (2 fingers)
Scroll orbital diagram:
(1 finger still on pad, one moving)

To view orbitals: go to ‘MO surfaces’
Excited states beyond CIS

Excited-state wave functions have many configurations, but the leading character can be described in simple terms, e.g., HOMO-LUMO excitation.

Methods for excited states:
- State-specific and multi-state methods;

My personal preference: single-reference multi-state methods complying with John Pople definition of “Theoretical Model Chemistry”
Methods for excited states in Q-Chem:

1. CIS: Hartree-Fock ground state; Single excitations from HF wfn.

2. TDDFT
   Kohn-Sham ground state; Excited states are single excitations from the KS determinant.
   Available in RPA and TDA implementations; analytic gradients are available.
   Strengths: inexpensive and often accurate.
   Weaknesses: Cannot describe doubly-excited states (but SF variant can);
               Problems with Rydberg/charge-transfer states (but LRC functionals help).

3. CIS(D) and SOS-CIS(D): CIS + perturbative account of double excitations.
   Rather robust and cheap ($N^4$-$N^5$); remarkably accurate ($\sim$0.2 eV or less), but need to be careful (quite bad failures are known, as with many low-order methods).

See Chapter 6 of the manual.
Advanced methods for excited states in Q-Chem:

4. EOM-CCSD: CCSD for the ground state and single and double excitations for the excited states. \( N^6 \) scaling, reliable (accuracy \( \sim 0.3 \) eV). EOM-MP2 methods: approximation to EOM-CCSD.

5. ADC methods:
   \[ \text{ADC}(2) \sim \text{CIS}(D) \]
   \[ \text{ADC}(3) \sim \text{EOM-CCSD} \]

6. Other methods: RASCI-SF, Delta-E, C-DFT, etc.

7. Properties and excited-state analysis (Chapter 10).

See Chapter 6 of the manual.
Excited-state methods

Hierarchy of approximations to the exact wave function: Single-reference models for the ground and excited states

SCF: $\Psi = \Phi_0 = |\varphi_1 \ldots \varphi_n>$

$\Psi_{\text{ex}} = R_1 \Psi_0$ (CIS)

MP2: SCF + $T_2$ by PT

CIS + $R_2$ by PT [CIS(D)]

CCSD: $\Psi = \exp(T_1 + T_2) \Phi_0$

$\Psi_{\text{ex}} = (R_1 + R_2) \Psi_0$ (EOM-CCSD)

CCSD(T): CCSD + $T_3$ by PT

CCSDT: $\Psi = \exp(T_1 + T_2 + T_3) \Phi_0$

$\Psi_{\text{ex}} = (R_1 + R_2 + R_3) \Psi_0$ (EOM-CCSDT)

FCI: $\Psi = (1 + T_1 + T_2 + \ldots + T_n) \Phi_0$ - exact!

$\Phi_0$

$T_1 \Phi_0$

$T_2 \Phi_0$

$T_1 = \sum_{ia} t_{ij}^{a} a^{+} j$

$T_2 = 0.25 \sum_{ijab} t_{ijab} a^{+} b^{+} j i$
Excited-states: Wfn vs DFT

1. Perform SCF calculations: find Hartree-Fock orbitals. 
   \( \Phi_0 \): zero-order w.f. for the ground state.
2. Include correlation (MP2, CCSD,...): improve zero-order wave function.
3. Excited states: diagonalize \( H/\text{effective } H \): 
   Hartree-Fock-> single excitations only (CIS)
   Correlated methods (CC): larger space.

1. Perform SCF calculations with \( V_{xc} \): find Kohn-Sham orbitals. 
   \( \Phi_0 \): correlated density for the ground state.
2. Excited states: diagonalize Kohn-Sham H in the space of singles.

Both schemes rely on \( \Phi_0 \) being good approximation for the ground-state w.f.
1. Take formaldehyde (use structure from ‘Molecules’).

2. Compute 4 lowest CIS singlet excited states using 6-31+G* basis.

3. Assign states symmetries and characters (need to look at the MOs).

For later (not now):
4. Compute SOS-CIS(D) excitation energies [CORRELATION=SOS CIS(D) and aux_basis=rimp2-aug-cc-pVDZ]. **Specify CIS_N_ROOTS = 4 manually. IQmol summary shows CIS energies: look in the output for SOS-CIS(D) values.**
Summary

Remarks:
‘D’: doubly occupied
‘V’: virtual
See orbital energies at the end of the output

Leading amplitudes:
State 1: 8->1 (HOMO->LUMO)
State 2: 8->2
State 3: 8->3
State 4: 7->1 (HOMO-1->LUMO)

Note transition dipole and oscillator strength
Excited states: Analysis

MO pictures:

#7 b2, \( \pi^{*}(\text{CO}) \)

#8 b1, \( \text{lp(O)/}\sigma_{\text{CH}} \) (HOMO)

#9 b2, \( \pi^{*}_{\text{CO}} \) (LUMO)

#10 a1 (Rydberg)

#11 a1 (Rydberg)
Formaldehyde

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.623</td>
<td>0.000</td>
</tr>
<tr>
<td>8.910</td>
<td>0.023</td>
</tr>
<tr>
<td>9.587</td>
<td>0.058</td>
</tr>
<tr>
<td>9.844</td>
<td>0.316</td>
</tr>
</tbody>
</table>

Energy/Hartree

Alpha

Beta

Strength

Energy/eV
<table>
<thead>
<tr>
<th>State</th>
<th>CIS $E_{ex}$(eV)/$f_1$</th>
<th>Character</th>
<th>SOS-CIS(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1A_2$</td>
<td>4.62/0.0</td>
<td>lp-&gt;pi*</td>
<td>3.99</td>
</tr>
<tr>
<td>8(b$_1$)-&gt;1(b$_2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1^1B_1$</td>
<td>8.91/0.03</td>
<td>lp-&gt;Ry</td>
<td>7.30</td>
</tr>
<tr>
<td>8(b$_1$)-&gt;2(a$_1$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2^1B_1$</td>
<td>9.59/0.06</td>
<td>lp-&gt;Ry</td>
<td>8.07</td>
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<tr>
<td>8(b$_1$)-&gt;3(a$_1$)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$1^1A_1$</td>
<td>9.84/0.32</td>
<td>pi-&gt;pi*</td>
<td>9.55</td>
</tr>
<tr>
<td>7(b$_2$)-&gt;1(b$_2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Diagrams:**
- 8b$_1$
- 7b$_2$
- 1b$_2$
- 2a$_1$
- 3a$_1$