

# Supplementary Information

A Simple Definition of the Number of Excited Electrons

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Two-dimensional representations of the additional molecular systems.

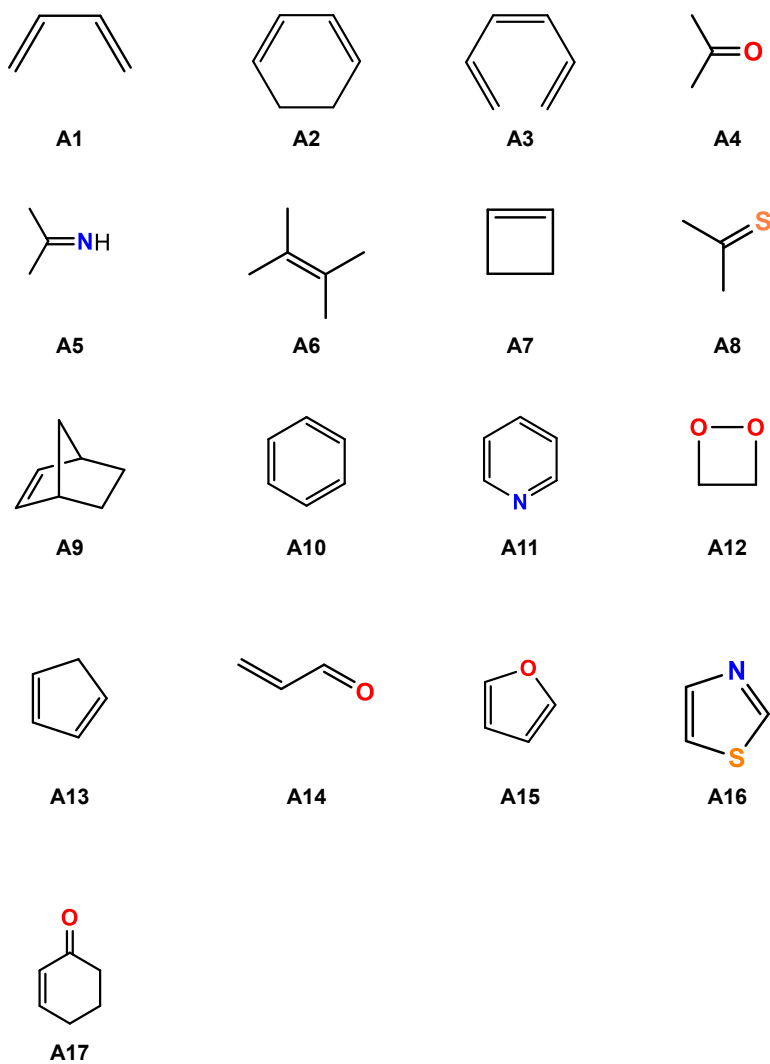


Figure S1: Two-dimensional representations of the additional molecular systems considered in this study.

## Number of excited electrons $\langle \hat{N}_{\text{ex}} \rangle$ at the Franck–Condon geometries for the additional systems.

Table S1: Number of excited electrons  $\langle \hat{N}_{\text{ex}} \rangle$  at the Franck–Condon geometries for the additional systems.

System	$S_1$	$S_2$	Active Space
A1	1.551	1.059	CAS(4,4)
A2	1.523	1.062	CAS(4,4)
A3	1.602	1.549	CAS(6,6)
A4	1.039	1.191	CAS(6,5)
A5	1.049	0.869	CAS(6,5)
A6	0.997	0.993	CAS(2,2)
A7	0.999	1.000	CAS(4,4)
A8	1.065	0.833	CAS(6,6)
A9	0.996	0.998	CAS(4,4)
A10	1.195	0.998	CAS(6,6)
A11	1.175	1.147	CAS(10,9)
A12	1.056	1.160	CAS(12,10)
A13	1.476	1.046	CAS(4,4)
A14	1.100	1.566	CAS(8,8)
A15	1.203	1.015	CAS(10,9)
A16	1.027	1.012	CAS(8,7)
A17	1.097	1.598	CAS(8,8)

## Number of excited electrons $\langle \hat{N}_{\text{ex}} \rangle$ at the minimum geometries for the additional systems.

Table S2: Number of excited electrons  $\langle \hat{N}_{\text{ex}} \rangle$  at the minimum geometries for the additional systems.

System	$S_1$	$S_2$	Active Space
A1	1.577	1.047	CAS(4,4)
A2	1.563	1.029	CAS(4,4)
A3	1.635	1.650	CAS(6,6)
A4	1.047	1.040	CAS(6,5)
A5	1.049	1.057	CAS(6,5)
A6	1.004	1.000	CAS(2,2)
A7	0.998	1.013	CAS(4,4)
A8	1.075	0.736	CAS(6,6)
A9	0.996	1.012	CAS(4,4)
A10	1.216	1.017	CAS(6,6)
A11	1.182	1.176	CAS(10,9)
A12	1.440	1.421	CAS(12,10)
A13	1.527	1.036	CAS(4,4)
A14	1.118	1.521	CAS(8,8)
A15	1.244	1.037	CAS(10,9)
A16	1.026	1.017	CAS(8,7)
A17	1.119	1.527	CAS(8,8)

# Evolution of $\langle \hat{N}_{\text{ex}} \rangle$ during the dissociation of CO, N<sub>2</sub>, and HF.

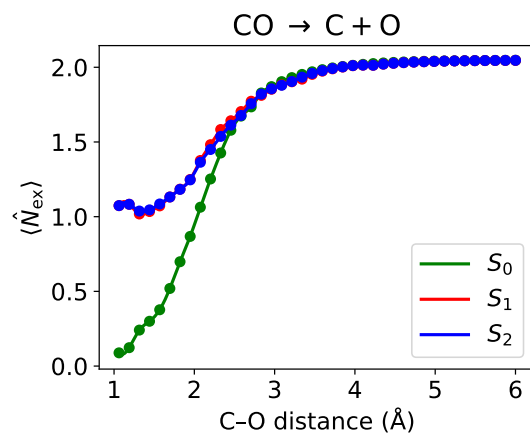


Figure S2: Evolution of  $\langle \hat{N}_{\text{ex}} \rangle$  during the dissociation of CO in states  $S_0$ ,  $S_1$ , and  $S_2$  calculated at CAS(8,8)/aug-cc-PVQZ level.

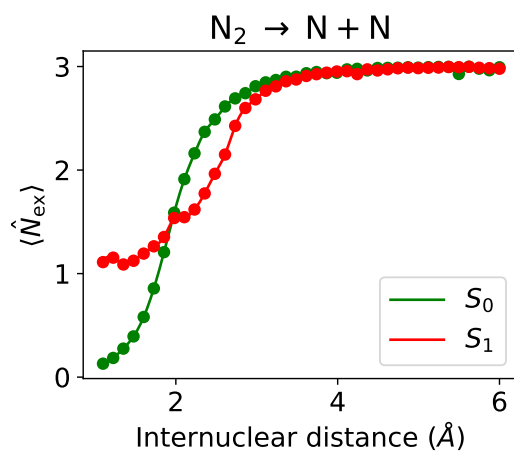


Figure S3: Evolution of  $\langle \hat{N}_{\text{ex}} \rangle$  during the dissociation of N<sub>2</sub> in states  $S_0$ ,  $S_1$ , and  $S_2$  calculated at CAS(10,8)/aug-cc-PVQZ level.

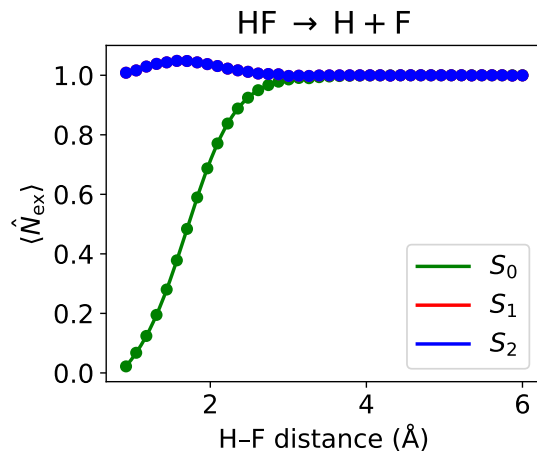


Figure S4: Evolution of  $\langle \hat{N}_{\text{ex}} \rangle$  during the dissociation of HF in states  $S_0$ ,  $S_1$ , and  $S_2$  calculated at CAS(6,4)/aug-cc-PVQZ level.

## Example of execution of the $\langle \hat{N}_{\text{ex}} \rangle$ analysis script

### Script execution

The Python script `Nex_normalized.py` was used to compute the number of excited electrons  $\langle \hat{N}_{\text{ex}} \rangle$  from configuration–interaction (CI) expansions. The script is executed from the command line by providing a CI configuration file as input:

```
python Nex_normalized.py input.conf
```

For the example discussed here, the following command was used:

```
python Nex_normalized.py A1_cas_s2.conf
```

### Description of the procedure

The script parses the CI expansions for each electronic root contained in the input file. The reference configuration is automatically selected as the configuration with the largest squared CI coefficient ( $c^2$ ) in ROOT 0. For each root, the printed CI coefficients are explicitly normalized, and the total number of excited electrons  $\langle \hat{N}_{\text{ex}} \rangle$  is computed. Additionally,  $\langle \hat{N}_{\text{ex}} \rangle$  is decomposed into fractional contributions  $f_{\text{ex}}^{(k)}$  associated with excitation order  $k$ .

### Example output

A representative output obtained from the execution above is reported below:

Reference configuration (ROOT 0, largest c2): 2200

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ROOT 0: N\_ex = 0.179612

Printed CI weight before normalization: 0.998040

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k = 0: f\_ex^(0) = 0.000000 (0.00%), count = 1  
k = 1: f\_ex^(1) = 0.112574 (11.26%), count = 1  
k = 2: f\_ex^(2) = 0.887426 (88.74%), count = 5  
Total sum of fractions: 1.000000000000  
The sum of fractions is correct ( 1.0)

ROOT 1: N\_ex = 1.593526

Printed CI weight before normalization: 0.999670

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k = 1: f\_ex^(1) = 0.259868 (25.99%), count = 2  
k = 2: f\_ex^(2) = 0.725763 (72.58%), count = 5  
k = 3: f\_ex^(3) = 0.014369 (1.44%), count = 2  
Total sum of fractions: 1.000000000000  
The sum of fractions is correct ( 1.0)

ROOT 2: N\_ex = 1.061621

Printed CI weight before normalization: 0.997870

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k = 1: f\_ex^(1) = 0.887489 (88.75%), count = 2  
k = 2: f\_ex^(2) = 0.101778 (10.18%), count = 2  
k = 3: f\_ex^(3) = 0.010733 (1.07%), count = 1  
Total sum of fractions: 1.000000000000  
The sum of fractions is correct ( 1.0)

ROOT 3: N\_ex = 1.205492

Printed CI weight before normalization: 0.999360

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k = 0: f\_ex^(0) = 0.000000 (0.00%), count = 1  
k = 1: f\_ex^(1) = 0.627299 (62.73%), count = 2  
k = 2: f\_ex^(2) = 0.270503 (27.05%), count = 5  
k = 3: f\_ex^(3) = 0.102198 (10.22%), count = 2  
Total sum of fractions: 1.000000000000  
The sum of fractions is correct ( 1.0)