Excited States of Large Open-Shell Molecules: An Efficient, General and Spin-Adapted Approach Based on a Restricted Open-Shell Ground State Wavefunction

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1) Calculated Transition Energies of Organic Closed Shell Compounds with DFT/ROCIS, DFT/MRCI and TD-DFT

Table 1 presents the calculated transition energies obtained from DFT/ROCIS, DFT/MRCI and TD-DFT calculations together with the 'best estimate' values from reference 1, which are here denoted as 'reference values'. Those transition energies have been obtained from *ab initio* calculations using highly correlated method such as MRCI, MRMP, coupled cluster, CC3 or CAS-PT2. Like the reference values, the calculated transition energies for the DFT/MRCI method are reproduced from reference 2. All DFT/ROCIS and TD-DFT calculations were conducted with the ORCA program package. The B3LYP functional[3,4] in conjunction with the def2-TZVP(-f) basis set[5] was used throughout these calculations. Moreover the resolution of identity (RI) approximation[6-8] was employed utilizing the def2-TZV/C auxiliary basis set.[9]

Table 1. Vertical singlet excitation energies ΔE in eV of all molecules in the test set

Molecule	State	Reference value	DFT/ROCIS	DFT/MRCI	TD-DFT
Ethene	$1^1B_{1u}(\pi\rightarrow\pi^*)$	7.80	6.13	7.96	7.70
Butadiene	$2^1A_g(\pi\rightarrow\pi^*)$	6.18	7.12	6.02	6.82
Butadiene	$1^1B_u(\pi\rightarrow\pi^*)$	6.55	7.38	6.18	5.74
Hexatriene	$2^1A_g(\pi\rightarrow\pi^*)$	5.09	5.76	4.92	5.69
Octatetraene	$2^1A_g(\pi\rightarrow\pi^*)$	4.47	4.69	4.01	4.84
Octatetraene	$1^1B_u(\pi\rightarrow\pi^*)$	4.66	3.05	4.25	4.02
Cyclopropene	$1^1B_2(\pi\rightarrow\pi^*)$	6.76	5.52	6.73	6.31
Cyclopropene	$1^1B_1(\sigma\rightarrow\pi^*)$	7.06	6.52	6.74	6.46
Cyclopentadiene	$1^1B_2(\pi\rightarrow\pi^*)$	5.55	4.26	5.42	5.02
Cyclopentadiene	$2^1A_1(\pi\rightarrow\pi^*)$	6.31	6.46	6.15	6.52
Norbornadiene	$1^1A_2(\pi\rightarrow\pi^*)$	5.34	4.41	5.30	4.79
Norbornadiene	$1^1B_2(\pi\rightarrow\pi^*)$	6.11	5.30	6.12	5.52
Benzene	$1^1B_2(\pi\rightarrow\pi^*)$	5.08	5.08	5.04	5.40
Benzene	$1^1B_{1u}(\pi\rightarrow\pi^*)$	6.54	5.21	6.31	6.10
Benzene	$1^1E_{1u}(\pi\rightarrow\pi^*)$	7.13	7.25	7.19	7.07
Benzene	$1^1E_{2g}(\pi\rightarrow\pi^*)$	8.41	8.92	7.51	8.91
Naphtalene	$1^1B_{3u}(\pi\rightarrow\pi^*)$	4.24	3.79	4.10	4.44
Naphtalene	$1^1B_{2u}(\pi\rightarrow\pi^*)$	4.77	4.13	4.60	4.35
Naphtalene	$2^1A_g(\pi\rightarrow\pi^*)$	5.90	5.09	5.65	6.18
Naphtalene	$1^1B_{1g}(\pi\rightarrow\pi^*)$	6.00	5.40	5.53	5.58

Naphtalene	$2^1B_{3u}(\pi\rightarrow\pi^*)$	6.07	5.43	5.89	5.93
Naphtalene	$2^1B_{1g}(\pi\rightarrow\pi^*)$	6.48	5.68	6.26	6.32
Furan	$1^1B_2(\pi\rightarrow\pi^*)$	6.32	5.24	6.33	6.16
Furan	$2^1A_1(\pi\rightarrow\pi^*)$	6.57	6.34	6.32	6.70
Furan	$3^1A_1(\pi\rightarrow\pi^*)$	8.13	8.18	8.21	8.25
Pyrrole	$2^1A_1(\pi\rightarrow\pi^*)$	6.37	5.64	6.13	6.53
Pyrrole	$1^1B_2(\pi\rightarrow\pi^*)$	6.57	6.45	6.46	6.40
Pyrrole	$3^1A_1(\pi\rightarrow\pi^*)$	7.91	8.04	7.88	7.96
Imidazole	$2^1A'(\pi\rightarrow\pi^*)$	6.19	5.65	6.29	6.45
Imidazole	$1^1A''(n\rightarrow\pi^*)$	6.81	6.01	6.35	6.46
Imidazole	$3^1A'(\pi\rightarrow\pi^*)$	6.93	6.36	6.82	7.04
Pyridine	$1^1B_1(n\rightarrow\pi^*)$	4.59	4.62	4.75	4.80
Pyridine	$1^1B_2(\pi\rightarrow\pi^*)$	4.85	5.07	5.09	5.49
Pyridine	$1^1A_2(n\rightarrow\pi^*)$	5.11	5.20	5.41	5.11
Pyridine	$2^1A_1(\pi\rightarrow\pi^*)$	6.26	5.37	6.47	6.31
Pyrazine	$1^1B_{3u}(n\rightarrow\pi^*)$	3.95	3.81	4.00	3.96
Pyrazine	$1^1B_{2u}(\pi\rightarrow\pi^*)$	4.64	4.79	4.94	5.37
Pyrazine	$1^1A_u(n\rightarrow\pi^*)$	4.81	4.80	5.02	4.69
Pyrazine	$1^1B_{2g}(n\rightarrow\pi^*)$	5.56	5.24	5.26	5.55
Pyrimidine	$1^1B_1(n\rightarrow\pi^*)$	4.55	4.19	4.36	4.27
Pyrimidine	$1^1A_2(n\rightarrow\pi^*)$	4.91	4.63	4.82	4.60
Pyrimidine	$1^1B_2(\pi\rightarrow\pi^*)$	5.44	5.50	5.35	5.74
Pyridazine	$1^1B_1(n\rightarrow\pi^*)$	3.78	3.40	3.63	3.58
Pyridazine	$1^1A_2(n\rightarrow\pi^*)$	4.32	4.16	4.25	4.18
Pyridazine	$2^1A_1(\pi\rightarrow\pi^*)$	5.18	5.10	5.16	5.61
Pyridazine	$2^1A_2(n\rightarrow\pi^*)$	5.77	5.37	5.29	5.44
Triazine	$1^1A1''(n\rightarrow\pi^*)$	4.60	4.42	4.69	4.45
Triazine	$1^1A2''(n\rightarrow\pi^*)$	4.66	4.48	4.56	4.54
Triazine	$1^1E''(n\rightarrow\pi^*)$	4.71	4.52	4.77	4.54
Tetrazine	$1^1B_{3u}(n\rightarrow\pi^*)$	2.24	2.12	2.35	2.24
Tetrazine	$1^1A_u(n\rightarrow\pi^*)$	3.48	3.55	3.70	3.51
Tetrazine	$1^1B_{1g}(n\rightarrow\pi^*)$	4.73	4.34	4.45	4.73
Tetrazine	$1^1B_{2u}(\pi\rightarrow\pi^*)$	4.91	4.92	5.07	5.58
Formaldehyde	$1^1A_2(n\rightarrow\pi^*)$	3.88	3.91	3.71	3.89
Formaldehyde	$1^1B_1(\sigma\rightarrow\pi^*)$	9.10	9.15	8.76	8.89
Acetone	$1^1A_2(n\rightarrow\pi^*)$	4.40	4.36	4.23	4.34
Acetone	$1^1B_1(\sigma\rightarrow\pi^*)$	9.10	8.40	8.56	8.60
Acetone	$2^1A_1(\pi\rightarrow\pi^*)$	9.40	9.17	8.53	9.04
Benzoquinone	$1^1B_{1g}(n\rightarrow\pi^*)$	2.78	2.22	2.29	2.43
Benzoquinone	$1^1A_u(n\rightarrow\pi^*)$	2.80	2.35	2.22	2.58
Benzoquinone	$1^1B_{3g}(\pi\rightarrow\pi^*)$	4.25	3.54	3.99	3.73
Benzoquinone	$1^1B_{1u}(\pi\rightarrow\pi^*)$	5.29	3.87	5.07	4.83
Formamide	$1^1A''(n\rightarrow\pi^*)$	5.63	5.61	5.47	5.55
Acetamide	$1^1A''(n\rightarrow\pi^*)$	5.80	5.58	5.48	5.56
Acetamide	$2^1A'(\pi\rightarrow\pi^*)$	7.27	6.70	7.51	7.46
Propanamide	$1^1A''(n\rightarrow\pi^*)$	5.72	5.61	5.47	5.59
Propanamide	$2^1A'(\pi\rightarrow\pi^*)$	7.20	7.44	7.46	7.76
Cytosine	$2^1A'(\pi\rightarrow\pi^*)$	4.66	4.19	4.62	4.64
Cytosine	$1^1A''(n\rightarrow\pi^*)$	4.87	4.46	4.86	4.76
Cytosine	$2^1A''(n\rightarrow\pi^*)$	5.26	5.30	5.32	5.11
Cytosine	$3^1A'(\pi\rightarrow\pi^*)$	5.62	5.51	5.43	5.42

Thymine	$1^1A''(n\rightarrow\pi^*)$	4.82	4.34	4.48	4.70
Thymine	$2^1A'(\pi\rightarrow\pi^*)$	5.20	4.35	5.18	5.00
Thymine	$2^1A''(n\rightarrow\pi^*)$	6.16	5.55	5.93	5.80
Thymine	$3^1A'(\pi\rightarrow\pi^*)$	6.27	5.64	5.98	5.97
Uracil	$1^1A''(n\rightarrow\pi^*)$	4.80	4.27	4.41	4.63
Uracil	$2^1A'(\pi\rightarrow\pi^*)$	5.35	4.52	5.33	5.19
Uracil	$2^1A''(n\rightarrow\pi^*)$	6.10	5.50	5.84	5.74
Uracil	$3^1A'(\pi\rightarrow\pi^*)$	6.26	5.52	5.92	5.87
Adenine	$1^1A''(n\rightarrow\pi^*)$	5.12	4.35	5.11	4.97
Adenine	$2^1A'(\pi\rightarrow\pi^*)$	5.25	4.83	4.99	5.00
Adenine	$3^1A'(\pi\rightarrow\pi^*)$	5.25	4.83	5.15	5.27
Adenine	$2^1A''(n\rightarrow\pi^*)$	5.75	5.51	5.72	5.61
Root Mean Square Deviation			0.61	0.32	0.34
Mean Abs Error			0.47	0.25	0.27
Mean Error			-0.36	0.00	-0.08
Max (+) Error			0.94	0.83	0.73
Max (-) Error			-1.49	-0.75	-0.81

As expected, DFT/MRCI gives the most accurate excitation energies for the presented set of organic closed shell molecules. Its features a large CI expansion space and its empirical parameters are optimized with respect to a similar test set of organic closed shell molecules. The combination of the TD-DFT methodology and the B3LYP functional gives results of only slightly worse accuracy than DFT/MRCI underlining its reliability for the prediction of excited states for such molecules. DFT/ROCIS gives the least accurate results reflected in a mean absolute error of 0.5 eV. However, in most cases it appears that DFT/ROCIS systematically underestimates the reference values. Accordingly, an increase of the calculated DFT/ROCIS excitation energies by 0.39 eV (which is the mean absolute error) leads to significantly improved results (see table **Table 2**). The mean absolute error reduces to a value of 0.38 eV.

Table 2. DFT/ROCIS and scaled DFT/ROCIS vertical singlet excitation energies ΔE in eV of all molecules in the test set.

Molecule	**State**	**Reference value**	**DFT/ROCIS**	**DFT/ROCIS (scaled)[a]**
Ethene	$1^1B_{1u}(\pi\rightarrow\pi^*)$	7.80	6.13	6.52
Butadiene	$2^1A_g(\pi\rightarrow\pi^*)$	6.18	7.12	7.51
Butadiene	$1^1B_u(\pi\rightarrow\pi^*)$	6.55	7.38	7.77

Hexatriene	$2^1A_g(\pi\rightarrow\pi^*)$	5.09	3.64	4.03
Octatetraene	$2^1A_g(\pi\rightarrow\pi^*)$	4.47	3.05	3.44
Octatetraene	$1^1B_u(\pi\rightarrow\pi^*)$	4.66	4.69	5.08
Cyclopropene	$1^1B_2(\pi\rightarrow\pi^*)$	6.76	5.52	5.91
Cyclopropene	$1^1B_1(\sigma\rightarrow\pi^*)$	7.06	6.52	6.91
Cyclopentadiene	$1^1B_2(\pi\rightarrow\pi^*)$	5.55	4.26	4.65
Cyclopentadiene	$2^1A_1(\pi\rightarrow\pi^*)$	6.31	6.46	6.85
Norbornadiene	$1^1A_2(\pi\rightarrow\pi^*)$	5.34	4.41	4.80
Norbornadiene	$1^1B_2(\pi\rightarrow\pi^*)$	6.11	5.30	5.69
Benzene	$1^1B_2(\pi\rightarrow\pi^*)$	5.08	5.08	5.47
Benzene	$1^1B_{1u}(\pi\rightarrow\pi^*)$	6.54	5.21	5.60
Benzene	$1^1E_{1u}(\pi\rightarrow\pi^*)$	7.13	7.25	7.64
Benzene	$1^1E_{2g}(\pi\rightarrow\pi^*)$	8.41	8.92	9.31
Naphtalene	$1^1B_{3u}(\pi\rightarrow\pi^*)$	4.24	3.79	4.18
Naphtalene	$1^1B_{2u}(\pi\rightarrow\pi^*)$	4.77	4.13	4.52
Naphtalene	$2^1A_g(\pi\rightarrow\pi^*)$	5.90	5.09	5.48
Naphtalene	$1^1B_{1g}(\pi\rightarrow\pi^*)$	6.00	5.40	5.79
Naphtalene	$2^1B_{3u}(\pi\rightarrow\pi^*)$	6.07	5.43	5.82
Naphtalene	$2^1B_{1g}(\pi\rightarrow\pi^*)$	6.48	5.68	6.07
Furan	$1^1B_2(\pi\rightarrow\pi^*)$	6.32	5.24	5.63
Furan	$2^1A_1(\pi\rightarrow\pi^*)$	6.57	6.34	6.73
Furan	$3^1A_1(\pi\rightarrow\pi^*)$	8.13	8.18	8.57
Pyrrole	$2^1A_1(\pi\rightarrow\pi^*)$	6.37	5.64	6.03
Pyrrole	$1^1B_2(\pi\rightarrow\pi^*)$	6.57	6.45	6.84
Pyrrole	$3^1A_1(\pi\rightarrow\pi^*)$	7.91	8.04	8.43
Imidazole	$2^1A'(\pi\rightarrow\pi^*)$	6.19	5.65	6.04
Imidazole	$1^1A''(n\rightarrow\pi^*)$	6.81	6.01	6.40
Imidazole	$3^1A'(\pi\rightarrow\pi^*)$	6.93	6.36	6.75
Pyridine	$1^1B_1(n\rightarrow\pi^*)$	4.59	4.62	5.01
Pyridine	$1^1B_2(\pi\rightarrow\pi^*)$	4.85	5.07	5.46
Pyridine	$1^1A_2(n\rightarrow\pi^*)$	5.11	5.20	5.59
Pyridine	$2^1A_1(\pi\rightarrow\pi^*)$	6.26	5.37	5.76
Pyrazine	$1^1B_{3u}(n\rightarrow\pi^*)$	3.95	3.81	4.20
Pyrazine	$1^1B_{2u}(\pi\rightarrow\pi^*)$	4.64	4.79	5.18
Pyrazine	$1^1A_u(n\rightarrow\pi^*)$	4.81	4.80	5.19
Pyrazine	$1^1B_{2g}(n\rightarrow\pi^*)$	5.56	5.24	5.63
Pyrimidine	$1^1B_1(n\rightarrow\pi^*)$	4.55	4.19	4.58
Pyrimidine	$1^1A_2(n\rightarrow\pi^*)$	4.91	4.63	5.02
Pyrimidine	$1^1B_2(\pi\rightarrow\pi^*)$	5.44	5.50	5.89
Pyridazine	$1^1B_1(n\rightarrow\pi^*)$	3.78	3.40	3.79
Pyridazine	$1^1A_2(n\rightarrow\pi^*)$	4.32	4.16	4.55
Pyridazine	$2^1A_1(\pi\rightarrow\pi^*)$	5.18	5.10	5.49
Pyridazine	$2^1A_2(n\rightarrow\pi^*)$	5.77	5.37	5.76
Triazine	$1^1A1''(n\rightarrow\pi^*)$	4.60	4.42	4.81
Triazine	$1^1A2''(n\rightarrow\pi^*)$	4.66	4.48	4.87
Triazine	$1^1E''(n\rightarrow\pi^*)$	4.71	4.52	4.91
Tetrazine	$1^1B_{3u}(n\rightarrow\pi^*)$	2.24	2.12	2.51
Tetrazine	$1^1A_u(n\rightarrow\pi^*)$	3.48	3.55	3.94
Tetrazine	$1^1B_{1g}(n\rightarrow\pi^*)$	4.73	4.34	4.73
Tetrazine	$1^1B_{2u}(\pi\rightarrow\pi^*)$	4.91	4.92	5.31
Formaldehyde	$1^1A_2(n\rightarrow\pi^*)$	3.88	3.91	4.30

Formaldehyde	$1^1B_1(\sigma\rightarrow\pi^*)$	9.10	9.15	9.54
Acetone	$1^1A_2(n\rightarrow\pi^*)$	4.40	4.36	4.75
Acetone	$1^1B_1(\sigma\rightarrow\pi^*)$	9.10	8.40	8.79
Acetone	$2^1A_1(\pi\rightarrow\pi^*)$	9.40	9.17	9.56
Benzoquinone	$1^1B_{1g}(n\rightarrow\pi^*)$	2.78	2.22	2.61
Benzoquinone	$1^1A_u(n\rightarrow\pi^*)$	2.80	2.35	2.74
Benzoquinone	$1^1B_{3g}(\pi\rightarrow\pi^*)$	4.25	3.54	3.93
Benzoquinone	$1^1B_{1u}(\pi\rightarrow\pi^*)$	5.29	3.87	4.26
Formamide	$1^1A''(n\rightarrow\pi^*)$	5.63	5.61	6.00
Acetamide	$1^1A''(n\rightarrow\pi^*)$	5.80	5.58	5.97
Acetamide	$2^1A'(\pi\rightarrow\pi^*)$	7.27	6.70	7.09
Propanamide	$1^1A''(n\rightarrow\pi^*)$	5.72	5.61	6.00
Propanamide	$2^1A'(\pi\rightarrow\pi^*)$	7.20	7.44	7.83
Cytosine	$2^1A'(\pi\rightarrow\pi^*)$	4.66	4.19	4.58
Cytosine	$1^1A''(n\rightarrow\pi^*)$	4.87	4.46	4.85
Cytosine	$2^1A''(n\rightarrow\pi^*)$	5.26	5.30	5.69
Cytosine	$3^1A'(\pi\rightarrow\pi^*)$	5.62	5.51	5.90
Thymine	$1^1A''(n\rightarrow\pi^*)$	4.82	4.34	4.73
Thymine	$2^1A'(\pi\rightarrow\pi^*)$	5.20	4.35	4.74
Thymine	$2^1A''(n\rightarrow\pi^*)$	6.16	5.55	5.94
Thymine	$3^1A'(\pi\rightarrow\pi^*)$	6.27	5.64	6.03
Uracil	$1^1A''(n\rightarrow\pi^*)$	4.80	4.27	4.66
Uracil	$2^1A'(\pi\rightarrow\pi^*)$	5.35	4.52	4.91
Uracil	$2^1A''(n\rightarrow\pi^*)$	6.10	5.50	5.89
Uracil	$3^1A'(\pi\rightarrow\pi^*)$	6.26	5.52	5.91
Adenine	$1^1A''(n\rightarrow\pi^*)$	5.12	4.35	4.74
Adenine	$2^1A'(\pi\rightarrow\pi^*)$	5.25	4.83	5.22
Adenine	$3^1A'(\pi\rightarrow\pi^*)$	5.25	4.83	5.22
Adenine	$2^1A''(n\rightarrow\pi^*)$	5.75	5.51	5.90
Root Mean Square Deviation			0.64	0.49
Mean Abs Error			0.50	0.38
Mean Error			-0.39	0.00
Max (+) Error			0.94	1.33
Max (-) Error			-1.49	-1.28

[a] Excitation energies are obtained from $E = E\left(DFT/ROCIS\right) - 0.39$

Although DFT/MRCI uses a selection scheme the number of excited CSF's in a DFT/MRCI calculation generally exceeds the number of excited CSF's included in the ROCIS expansion space. Calculations of the electronic spectrum of 1.3.5.7.9.11.13.15.17.19.21.23.25-hexacosatridecaene (Chart 1) with both methods demonstrate the differently sized expansion spaces. In the DFT/MRCI calculation performed by Marian and co-workers[10] on 1.3.5.7.9.11.13.15.17.19.21.23.25-hexacosatridecaene utilizing the SVP basis set[11] the CI expansion space included 1164939 CSF's while a DFT/ROCIS calculation with standard settings features only 27193 CSF's. The DFT/ROCIS standard settings exclude all CSF's in

the CI treatment that involve excitations from orbitals that have an orbitals energy lower than -5 E_h or excitations to orbitals with an orbital energy higher than +5E_h.

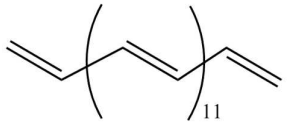

Chart 1. Lewis structure of 1.3.5.7.9.11.13.15.17.19.21.23.25-hexacosatridecaene.

2) Parameterized Diagonal Elements of the DFT/ROCIS Matrix

The parameterized diagonal elements of the CI matrix in the DFT/ROCIS method in the basis of CSF's with $S' = S$ are given by:

$$\left\langle \Phi_i^t \middle| \hat{H}^{DFT/ROCIS} \middle| \Phi_i^t \right\rangle = F_{tt}^{O(KS)} - F_{ii}^{C(KS)} - c_1\left(ii \mid tt\right) + c_2\left(it \mid it\right) + \sum_T^{SOMOs} c_{HF}\left\{\left(tT \mid tT\right) - \frac{1}{2}\left(iT \mid iT\right)\right\}$$

$$\left\langle \Phi_t^a \middle| \hat{H}^{DFT/ROCIS} \middle| \Phi_t^a \right\rangle = F_{aa}^{O(KS)} - F_{tt}^{C(KS)} - c_1\left(tt \mid aa\right) + c_2\left(ta \mid ta\right)$$

$$\left\langle \Phi_i^a \middle| \hat{H}^{DFT/ROCIS} \middle| \Phi_i^a \right\rangle = F_{aa}^{C(KS)} - F_{ii}^{C(KS)} - c_1\left(ii \mid aa\right) + 2c_2\left(ia \mid ia\right)$$

$$\begin{aligned}\left\langle \Phi_{iw}^{ta} \middle| \hat{H}^{DFT/ROCIS} \middle| \Phi_{wi}^{at} \right\rangle = {} & F_{aa}^{O(KS)} + F_{tt}^{O(KS)} - F_{ii}^{C(KS)} - F_{ww}^{O(KS)} + c_1\left(ii \mid ww\right) + c_1\left(tt \mid aa\right) \\ & - c_1\left(ii \mid tt\right) - c_1\left(ww \mid tt\right) - c_1\left(ii \mid aa\right) - c_1\left(ww \mid aa\right) \\ & + c_2\left(it \mid it\right) + c_2\left(wa \mid wa\right) + \sum_T^{SOMOs} c_{HF}\left\{\left(tT \mid tT\right) - \frac{1}{2}\left(iT \mid iT\right)\right\}\end{aligned}$$

$$\begin{aligned}\left\langle \Phi_{it}^{ta} \middle| \hat{H}^{DFT/ROCIS} \middle| \Phi_{ti}^{at} \right\rangle = {} & F_{aa}^{C(KS)} - F_{ii}^{C(KS)} - \frac{2}{3}c_1\left(tt \mid tt\right) - c_1\left(ii \mid aa\right) + 2c_2\left(it \mid it\right) + \frac{4}{3}c_2\left(ta \mid ta\right) \\ & + \sum_T^{SOMOs}\left\{\frac{2}{3}c_2\left(tT \mid tT\right) - \frac{1}{3}c_{HF}\left(iT \mid iT\right)\right\}\end{aligned}$$

Off-diagonal matrix elements of two "trip-doublet" basis functions $\left|\Phi_{ti}^{at}\right\rangle$ and $\left|\Phi_{ui}^{au}\right\rangle$, that share the same internal and external labels i and a but have different active labels t and u, are treated as diagonal elements with respect to the parameterization.

$$\begin{aligned}\left\langle \Phi_{it}^{ta} \middle| \hat{H}^{DFT/ROCIS} \middle| \Phi_{ui}^{au} \right\rangle = {} & \frac{1}{3}F_{aa}^{C(KS)} - \frac{1}{3}F_{ii}^{C(KS)} + \frac{1}{3}c_2\left(it \mid it\right) + \frac{1}{3}c_2\left(iu \mid iu\right) - \frac{2}{3}c_2\left(tu \mid tu\right) \\ & - \frac{1}{3}c_1\left(ii \mid aa\right) + \frac{1}{3}c_2\left(ta \mid ta\right) + \frac{1}{3}c_2\left(ua \mid ua\right)\end{aligned}$$

3) Equations for Density Matrices

$$\left\langle 0\middle| E_q^p \middle|0\right\rangle = \sum_k^{DOMOs} 2\delta_{pq}\delta_{pk} + \sum_v^{SOMOs} \delta_{pq}\delta_{pv}$$

$$\left\langle 0\middle| E_q^p \middle|\Phi_j^u\right\rangle = \delta_{pj}\delta_{qu}$$

$$\left\langle 0\middle| E_q^p \middle|\Phi_u^b\right\rangle = \delta_{pu}\delta_{qb}$$

$$\left\langle 0\middle| E_q^p \middle|\Phi_j^b\right\rangle = \delta_{pj}\delta_{qb}$$

$$\left\langle 0\middle| E_q^p \middle|\Phi_{vj}^{bu}\right\rangle = 0$$

$$\left\langle 0\middle| E_q^p \middle|\Phi_{uj}^{bu}\right\rangle = 0$$

$$\left\langle \Phi_i^t\middle| E_q^p \middle|\Phi_j^u\right\rangle = \sum_k^{DOMOs} 2\delta_{pq}\delta_{pk}\delta_{ij}\delta_{tu} + \sum_v^{SOMOs} \delta_{pq}\delta_{pv}\delta_{ij}\delta_{tu} + \delta_{ij}\delta_{pt}\delta_{qu} - \delta_{tu}\delta_{pj}\delta_{qi}$$

$$\left\langle \Phi_i^t\middle| E_q^p \middle|\Phi_u^b\right\rangle = 0$$

$$\left\langle \Phi_i^t\middle| E_q^p \middle|\Phi_j^b\right\rangle = \frac{1}{\sqrt{2}}\delta_{ij}\delta_{pt}\delta_{qb}$$

$$\left\langle \Phi_i^t\middle| E_q^p \middle|\Phi_{vj}^{bu}\right\rangle = \delta_{ij}\delta_{tu}\delta_{pv}\delta_{qb}$$

$$\left\langle \Phi_i^t\middle| E_q^p \middle|\Phi_{uj}^{bu}\right\rangle = -\frac{1}{\sqrt{6}}\left\{\delta_{ij}\delta_{pt}\delta_{qb} + 2\delta_{ij}\delta_{tu}\delta_{pt}\delta_{qb}\right\}$$

$$\left\langle \Phi_t^a\middle| E_q^p \middle|\Phi_u^b\right\rangle = \sum_k^{DOMOs} 2\delta_{pq}\delta_{pk}\delta_{tu}\delta_{ab} + \sum_v^{SOMOs} \delta_{pq}\delta_{pv}\delta_{tu}\delta_{ab} + \delta_{tu}\delta_{pa}\delta_{qb} - \delta_{ab}\delta_{pu}\delta_{qt}$$

$$\left\langle \Phi_t^a\middle| E_q^p \middle|\Phi_j^b\right\rangle = -\frac{1}{\sqrt{2}}\delta_{ab}\delta_{pj}\delta_{qt}$$

$$\left\langle \Phi_t^a\middle| E_q^p \middle|\Phi_{vj}^{bu}\right\rangle = \delta_{ab}\delta_{tv}\delta_{pj}\delta_{qu}$$

$$\left\langle \Phi_t^a\middle| E_q^p \middle|\Phi_{uj}^{bu}\right\rangle = -\frac{1}{\sqrt{6}}\left\{\delta_{ab}\delta_{pj}\delta_{qt} + 2\delta_{ab}\delta_{tu}\delta_{pj}\delta_{qu}\right\}$$

$$\left\langle \Phi_i^a\middle| E_q^p \middle|\Phi_j^b\right\rangle = \sum_k^{DOMOs} 2\delta_{pq}\delta_{pk}\delta_{ij}\delta_{ab} + \sum_v^{SOMOs} \delta_{pq}\delta_{pv}\delta_{ij}\delta_{ab} + \delta_{ij}\delta_{pa}\delta_{qb} - \delta_{ab}\delta_{pj}\delta_{qj}$$

$$\left\langle \Phi_i^a\middle| E_q^p \middle|\Phi_{vj}^{bu}\right\rangle = 0$$

$$\left\langle \Phi_i^a\middle| E_q^p \middle|\Phi_{uj}^{bu}\right\rangle = \frac{1}{\sqrt{3}}\left\{\delta_{ab}\delta_{pj}\delta_{qj} - \delta_{ij}\delta_{pa}\delta_{qb}\right\}$$

$$\left\langle \Phi_{iw}^{ta}\middle| E_q^p \middle|\Phi_{vj}^{bu}\right\rangle = \sum_k^{DOMOs} 2\delta_{pq}\delta_{pk}\delta_{ij}\delta_{tu}\delta_{vw}\delta_{ab} + \sum_v^{SOMOs} \delta_{pq}\delta_{pv}\delta_{ij}\delta_{tu}\delta_{vw}\delta_{ab}$$
$$+\delta_{ij}\delta_{vw}\delta_{ab}\delta_{pt}\delta_{qu} + \delta_{ij}\delta_{tu}\delta_{vw}\delta_{pa}\delta_{qb} - \delta_{ij}\delta_{tu}\delta_{ab}\delta_{pv}\delta_{qw} + \delta_{tu}\delta_{vw}\delta_{ab}\delta_{pj}\delta_{qi}$$

$$\left\langle \Phi_{iw}^{ta}\middle| E_q^p \middle|\Phi_{uj}^{bu}\right\rangle = \frac{1}{\sqrt{6}}\left\{2\delta_{ij}\delta_{tu}\delta_{ab}\delta_{pu}\delta_{qw} - 2\delta_{ij}\delta_{uw}\delta_{ab}\delta_{pt}\delta_{qu}\right\}$$

$$\left\langle \Phi_{it}^{ta} \middle| E_q^p \middle| \Phi_{uj}^{bu} \right\rangle = \sum_k^{DOMOs} 2\delta_{pq}\delta_{pk}\delta_{ij}\delta_{tu}\delta_{ab} + \sum_v^{SOMOs} \delta_{pq}\delta_{pv}\delta_{ij}\delta_{tu}\delta_{ab}$$
$$+\frac{2}{6}\left\{ \sum_k^{DOMOs} 2\delta_{pq}\delta_{pk}\delta_{ij}\left(1-\delta_{tu}\right)\delta_{ab} + \sum_v^{SOMOs} \delta_{pq}\delta_{pv}\delta_{ij}\left(1-\delta_{tu}\right)\delta_{ab} \right\}$$
$$+\frac{1}{6}\left\{ 2\delta_{ij}\delta_{pa}\delta_{qb} + 4\delta_{ij}\delta_{tu}\delta_{pa}\delta_{qb} - 2\delta_a\delta_{pj}\delta_{qi} - 4\delta_{ab}\delta_{tu}\delta_{pj}\delta_{qi} \right\}$$

All terms that are not listed here can easily be constructed using the symmetry relation:

$$\left\langle \Phi \middle| E_q^p \middle| \Phi' \right\rangle = \left\langle \Phi' \middle| E_p^q \middle| \Phi \right\rangle$$

4) Reference Contribution to the Electronic Ground State of Open-Shell Molecules

Table 3. Weight of Hartree-Fock reference in the electronic ground state of some ROCIS calculations

Compound	ROCIS	DFT/ROCIS
[Cr(acac)3]	0.99	0.99
1	0.93	0.99
2	0.93	0.99
3	0.92	0.99
4	0.95	0.99
5	0.93	0.99
6	0.95	0.99
7		0.99
8	0.96	0.99
9	0.96	0.99
10	0.93	0.99
11	0.91	0.99

All corresponding DFT/ROCIS calculations exhibit a weight of 0.99 of the DFT reference function in the electronic ground state.

5) DFT/ROCIS results with BhLYP

Organic radicals

Table 4. Comparison of calculated vertical transition energies (in eV) obtained with DFT/ROCIS and BhLYP to experimentally determined 0→0 transition energies.

Compound	Experiment	DFT/ROCIS (BhLYP)	Scaled DFT/ROCIS (BhLYP)
1	2.12	4.97	3,21
2	4.05	5.61	3,70
3	4.04	5.36	3,51
4	1.97	3.60	2,14
5	1.87	2.93	1,62
6	1.53	3.19	1,82
7	2.11	3.22	1,85
8	1.62	2.80	1,52
9	2.01	3.47	2,04
9	3.34	5.33	3,49
10	1.46	2.99	1,67
10	3.16	4.29	2,68
11	1.72	2.98	1,66
Root Mean Square Deviation		1.59	0.40
Mean Abs Error		1.52	0.31
Mean Error		1.52	0.01
Max (+) Error		2.85	1.06
Max (-) Error		-	-0.53

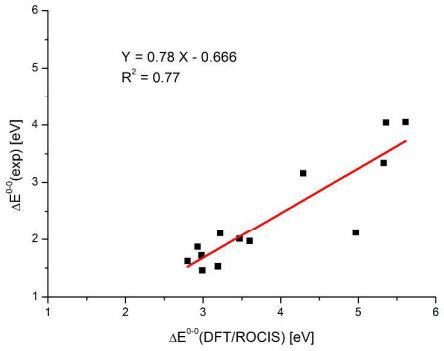

Figure 1. Correlation of calculated vertical transition energies ΔE^{vert} and experimentally determined 0→0 transition energies $\Delta E^{0-0}(\text{exp})$ for the the combination of DFT/ROCIS and BhLYP

[$Fe(CO)_5$]

Table 5. Calculated excitation energies to the low-lying states of [$Fe(CO)_5$] in wavenumbers (cm^{-1})

Transition	Dominant Electronic Excitation	MRCCI	DFT/ROCIS (BhLYP)
$^1A_1' \rightarrow a\,^1E'$	$3d_\sigma \rightarrow 3d_{z^2}$	27680	59150
$^1A_1' \rightarrow a\,^1E''$	$3d_\pi \rightarrow 3d_{z^2}$	36760	
$^1A_1' \rightarrow {}^1A_1''$	$3d_\sigma \rightarrow \pi^*_{CO}$	33280	49990
$^1A_1' \rightarrow b\,^1E''$	$3d_\sigma \rightarrow \pi^*_{CO}$	35540	51080
$^1A_1' \rightarrow {}^1A_2''$	$3d_\sigma \rightarrow \pi^*_{CO}$	37030	52180
$^1A_1' \rightarrow {}^1A_2'$	$3d_\sigma \rightarrow \pi^*_{CO}$	38050	52430
$^1A_1' \rightarrow b\,^1E'$	$3d_\sigma \rightarrow \pi^*_{CO}$	39330	53180
$^1A_1' \rightarrow {}^1A_1'$	$3d_\sigma \rightarrow \pi^*_{CO}$	45030	57430

[$Cr(CO)_6$]

Table 6. Calculated excitation energies to the low-lying states of [$Cr(CO)_6$] in wavenumbers (cm^{-1})

Transition	Dominant electronic excitation	CASPT2	DFT/ROCIS (BhLYP)
$^1A_{1g} \rightarrow a\,^1E_u$	$t_{2g} \rightarrow t_{1u}$	27500-28960	53150
$^1A_{1g} \rightarrow a\,^1A_{2u}$	$t_{2g} \rightarrow t_{1u}$	28870	52640
$^1A_{1g} \rightarrow a\,^1T_{2u}$	$t_{2g} \rightarrow t_{1u}$	28710-29840	52610
$^1A_{1g} \rightarrow b\,^1E_u$	$t_{2g} \rightarrow t_{2u}$	32020-32670	58060
$^1A_{1g} \rightarrow a\,^1A_{1u}$	$t_{2g} \rightarrow t_{2u}$	33070-33470	57870
$^1A_{1g} \rightarrow b\,^1T_{2u}$	$t_{2g} \rightarrow t_{2u}$	34840-35730	59300
$^1A_{1g} \rightarrow a\,^1T_{1u}$	$t_{2g} \rightarrow t_{1u}$	33150-36620	64360
	$t_{2g} \rightarrow t_{2u}$		
$^1A_{1g} \rightarrow a\,^1E_g$	$t_{2g} \rightarrow t_{2g}$	36940	59020
$^1A_{1g} \rightarrow a\,^1T_{1g}$	$t_{2g} \rightarrow t_{2g}$	38880	57340
$^1A_{1g} \rightarrow b\,^1T_{1g}$	$t_{2g} \rightarrow e_g$	39120	67630
$^1A_{1g} \rightarrow a\,^1T_{2g}$	$t_{2g} \rightarrow e_g$	40970	70270

6) References

(1) Schreiber, M.; Silva-Junior, M. R.; Sauer, S. P. A.; Thiel, W. *J. Chem. Phys.* **2008**, *128*, 134110.
(2) Silva-Junior, M. R.; Schreiber, M.; Sauer, S. P. A.; Thiel, W. *J. Chem. Phys.* **2008**, *129*, 104103.
(3) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(4) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(5) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys* **2005**, *7*, 3297.
(6) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.
(7) Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71*, 3396.
(8) Vahtras, O.; Almlöf, J.; Feyereisen, M. W. *Chem. Phys. Lett.* **1993**, *213*, 514.
(9) Hellweg, A.; Hättig, C.; Höfener, S.; Klopper, W. *Theor. Chem. Acc.* **2007**, *117*, 587.
(10) Marian, C. M.; Gilka, N. *Journal of Chemical Theory and Computation* **2008**, *4*, 1501.
(11) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.