

# Macroscopic Quantum Electrodynamics and Density Functional Theory Approaches to Dispersion Interactions between Fullerenes – Supplemental Information

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## 1 Method of Transition Tracking

The TDDFT derived absorption spectra of  $C_{61}(CN)_2$ -dimers comprise of thousands of transitions populated by several molecular orbitals. To explain changes in the excitation energies, we identified how change in intermolecular angles affect the nature and shape of these orbitals. Therefore, major transitions with similar contributing orbitals at different spectral regions were identified as discussed below:

- The absorption spectra of the dimer with 0 degree angle is most identical, and the one with 170 degree rotation angle is most dissimilar to the monomer spectra.
- Thus, the 4 most intense transitions of the 0 degree dimer are first selected and the most dominant orbitals describing these transitions are noted. It is found that several orbitals contribute to these transitions. An example, for the transition with highest oscillator strength is provided below: 78 orbitals (39 occupied and 39 unoccupied) are needed to describe this intense transition. New contributing orbitals appear for other rotation angles, but the excitation energy is virtually constant. Thus we do not track these transitions. Instead, we track those transitions which can be completely described by changes in orbital energies as described below.

Excitation energy / eV: 4.560859854720713  
Excitation energy / nm: 271.8440117780391  
Oscillator strength:  
mixed representation: 0.1431629574598253

Table 1: Excitation energy for the fullerene-dimers.

Dominant contributions:

occ. orbital	energy / eV	virt. orbital	energy / eV	coeff.  <sup>2</sup> × 100
110 b1	-6.54	120 b1	-2.01	18.1
103 b1	-9.05	113 b1	-4.48	15.2
101 a1	-9.26	112 a1	-4.70	14.0
110 b1	-6.54	119 b1	-2.21	6.9
110 a1	-6.64	120 a1	-2.02	6.4
109 a1	-7.47	116 a1	-2.63	4.6
108 b1	-7.42	116 b1	-2.46	3.1
83 a2	-6.37	90 a2	-2.37	1.9
106 a1	-7.71	115 a1	-3.26	1.7
110 b1	-6.54	117 b1	-2.42	1.4
84 b2	-6.36	90 b2	-2.41	1.3
110 a1	-6.64	119 a1	-2.41	1.3
108 a1	-7.53	115 a1	-3.26	1.2
110 a1	-6.64	118 a1	-2.42	1.1
105 b1	-8.00	114 b1	-3.43	1.1
110 a1	-6.64	117 a1	-2.55	1.0
102 b1	-9.08	113 b1	-4.48	1.0

106 b1	-7.53	115 b1	-3.20	0.9
110 a1	-6.64	116 a1	-2.63	0.6
107 a1	-7.66	116 a1	-2.63	0.6
83 b2	-6.40	90 b2	-2.41	0.5
109 a1	-7.47	118 a1	-2.42	0.5
85 a2	-6.22	91 a2	-2.28	0.5
109 b1	-7.30	117 b1	-2.42	0.5
111 b1	-6.14	118 b1	-2.25	0.4
85 b2	-6.23	91 b2	-2.31	0.4
80 a2	-7.45	89 a2	-2.43	0.4
78 a2	-8.40	86 a2	-4.32	0.4
111 a1	-6.43	119 a1	-2.41	0.4
80 b2	-7.54	89 b2	-2.50	0.4
85 b2	-6.23	92 b2	-1.48	0.4
107 a1	-7.66	113 a1	-4.56	0.4
85 a2	-6.22	92 a2	-1.47	0.4
109 b1	-7.30	115 b1	-3.20	0.4
106 a1	-7.71	112 a1	-4.70	0.4
108 a1	-7.53	117 a1	-2.55	0.3
78 b2	-8.40	86 b2	-4.39	0.3

Table 2: Orbital energies for the fullerene-dimer.

Below we select few transitions which change upon rotation, given by changes in absorption spectra.

- c) The tracking procedure considers those transitions which can be described by shift in orbital energies contributing to shifts in absorption spectra, prominent in naked human-eye. The transitions tracked fall in the following zones:
1. Isosbestic point at 4.5 eV,
  2. Peak-splitting at 3.6 eV, and
  3. Shift in peak-maxima from 3 eV to 2.6 upon increased rotation angle, giving the impression of a second isosbestic point at, 2.8 eV.
- d) We select 3 intense transitions, at the vicinity of the energy regions in above-mentioned: a, b or c and describe them in the light of both TD-DFT and MQED.

(I) Isosbestic Point at 4.5 eV

Angle (°)	Excitation Energy (eV) @TDDFT	Unoccupied Orbital (UO) [eV] @DFT	Occupied Orbital (OO) [eV] @DFT	$\Delta$ Orbital Energy (UO-OO) [eV]	Mixing Coefficient (%)	Oscillator Strength
0	4.52612	-2.01	-6.54	4.53	65.2	5.82E-02
10	4.51728	-2.03	-6.55	4.52	53.2	1.92E-01
20	4.49976	-2.05	-6.55	4.5	39.4	2.80E-02
30	4.49134	-2.06	-6.55	4.49	78.8	2.58E-02
40	4.48221	-2.07	-6.55	4.48	76.8	1.15E-02
50	4.47688	-2.07	-6.55	4.48	64.9	1.84E-03
60	4.46216	-2.08	-6.54	4.46	81.4	2.93E-02
70	4.44641	-2.09	-6.53	4.44	82.3	1.40E-02
80	4.42726	-2.09	-6.52	4.43	92.9	0.9E-02
90	4.41096	-2.1	-6.51	4.41	90.1	6.53E-03
100	4.40398	-2.1	-6.5	4.4	83	0.5E-02
110	4.40184	-2.1	-6.49	4.39	84	0.43E-02
120	4.40045	-2.09	-6.49	4.4	83.7	3.34E-03
130	4.38893	-2.09	-6.48	4.39	57.4	1.38E-03

140	4.36878	-2.1	-6.46	4.36	73.1	2.45E-03
150	4.31782	-2.1	-6.43	4.33	44.1	1.84E-03
160	4.29355	-2.1	-6.39	4.29	72.5	8.87E-05
170	4.27282	-2.1	-6.37	4.27	40.3	4.46E-04

Table 3: Angle dependence of the excitation energies and occupied and unoccupied orbitals for the isosbestic point at 4.5 eV.

(II) Peak splitting region

Angle ( $^{\circ}$ )	Excitation Energy (eV) @TDDFT	Unoccupied Orbital (UO) [eV] @DFT	Occupied Orbital (OO) [eV] @DFT	$\Delta$ Orbital Energy (UO-OO) [eV]	Mixing Coefficient (%)	Oscillator Strength
0	3.53554	-4.48	-8	3.52	88	0.02116
10	3.53959	-4.49	-8.01	3.52	80.3	0.02303
20	3.54321	-4.5	-8.02	3.52	79.9	0.0237
30	3.54441	-4.5	-8.03	3.53	79.5	0.02286
40	3.54074	-4.51	-8.03	3.52	79.2	0.01972
50	3.53279	-4.52	-8.03	3.51	75.1	0.01605
60	3.52431	-4.52	-8.03	3.51	48.7	0.01475
70	3.52124	-4.52	-8.03	3.51	53.2	0.017
80	3.52473	-4.51	-8.03	3.52	60.3	0.019
90	3.52747	-4.5	-8.03	3.53	60.1	0.01708
100	3.52658	-4.5	-8.03	3.53	58	0.01819
110	3.52239	-4.51	-8.03	3.52	47.3	0.01107
120	3.48626	-4.52	-8.02	3.5	60.3	0.01186
130	3.46751	-4.53	-8	3.47	68.6	7.98062E-4
140	3.43397	-4.54	-7.97	3.43	81	0.01315
150	3.40127	-4.55	-7.94	3.39	82.7	0.00588
160	3.37353	-4.55	-7.91	3.36	68.1	0.00158
170	3.32948	-4.56	-7.89	3.33	48.6	1.16965E-4

Table 4: Angle dependence of the excitation energies and occupied and unoccupied orbitals for the peak-splitting at 3.6 eV.

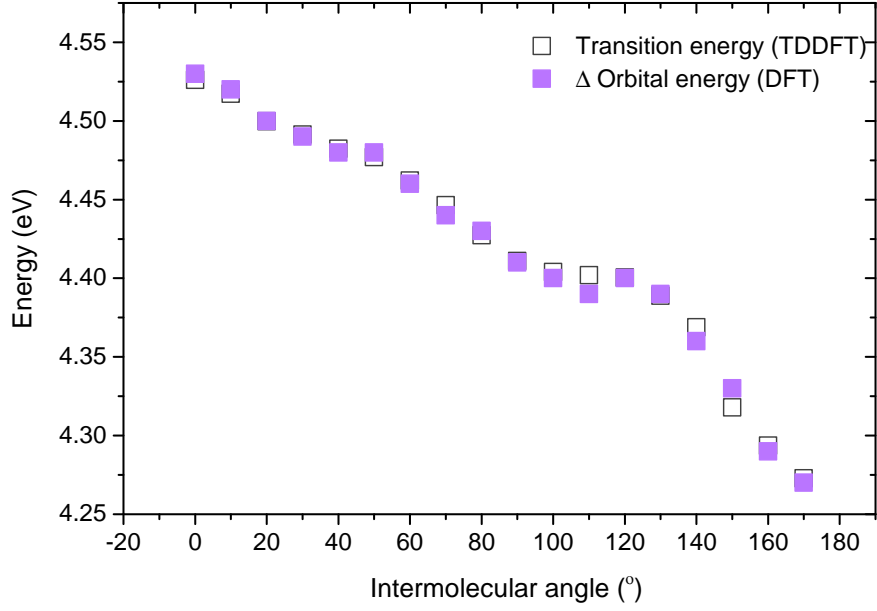


Figure 1: Excitation energy (TD-DFT) and Kohn Sham orbital energy difference at different intermolecular angles (first isosbestic region).

(III) Second Isosbestic point

Angle (°)	Excitation Energy (eV) @TDDFT	Unoccupied Orbital (UO) [eV] @DFT	Occupied Orbital (OO) [eV] @DFT	$\Delta$ Orbital Energy (UO-OO) [eV]	Mixing Coefficient (%)	Oscillator Strength
0	3.00897	-3.36	-6.36	3	57	1.21823E-4
10	3.01192	-3.38	-6.37	2.99	62	4.40075E-5
20	3.01608	-3.38	-6.38	3	65	9.08277E-6
30	3.02192	-3.4	-6.39	2.99	53.4	5.82045E-4
40	3.0249	-3.39	-6.41	3.02	51.2	6.39854E-5
50	3.03204	-3.39	-6.43	3.04	55.2	3.04819E-6
60	3.043	-3.4	-6.44	3.04	29.4	1.3827E-4
70	3.05324	-3.4	-6.44	3.04	41	2.1428E-5
80	3.04	-3.4	-6.44	-3.04	33	2.01372E-4
90	3.03851	-3.4	-6.43	3.03	39.3	9.23179E-4
100	3.03386	-3.41	-6.42	3.01	37	0.00188
110	3.02784	-3.42	-6.41	2.99	25	0.00219
120	2.98179	-3.42	-6.4	2.98	58	3.68902E-5
130	2.97257	-3.43	-6.39	2.96	76	3.6898E-6
140	2.9603	-3.45	-6.39	2.94	79.2	7.58989E-5
150	2.94546	-3.46	-6.39	2.93	63	2.23839E-4
160	2.93369	-3.47	-6.38	2.91	70	2.78303E-4
170	2.92649	-3.47	-6.38	2.91	74.4	9.55178E-6

Table 5: Angle dependence of the excitation energies and occupied and unoccupied orbitals for the second isosbestic point.

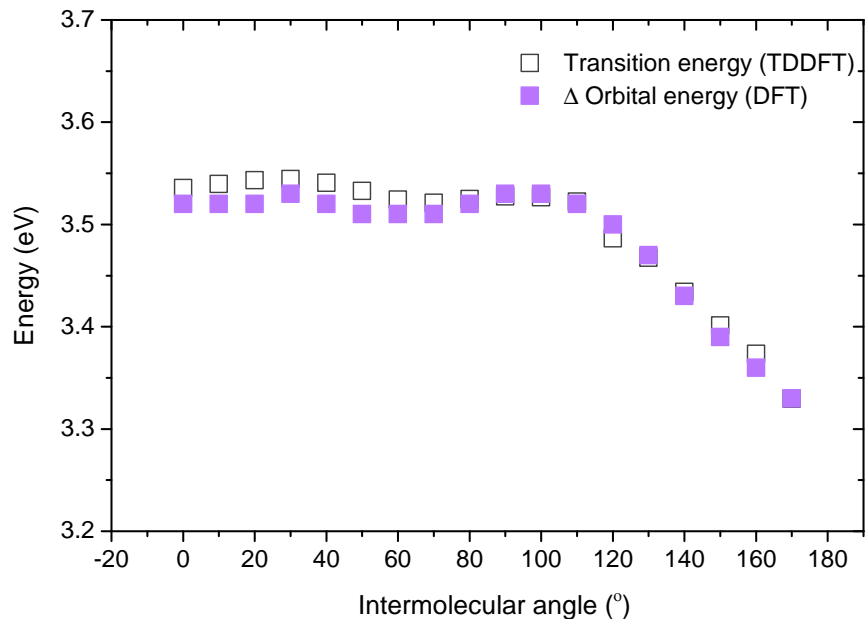


Figure 2: Excitation energy (TDDFT) and Kohn Sham orbital energy difference at different intermolecular angles (peak split region).

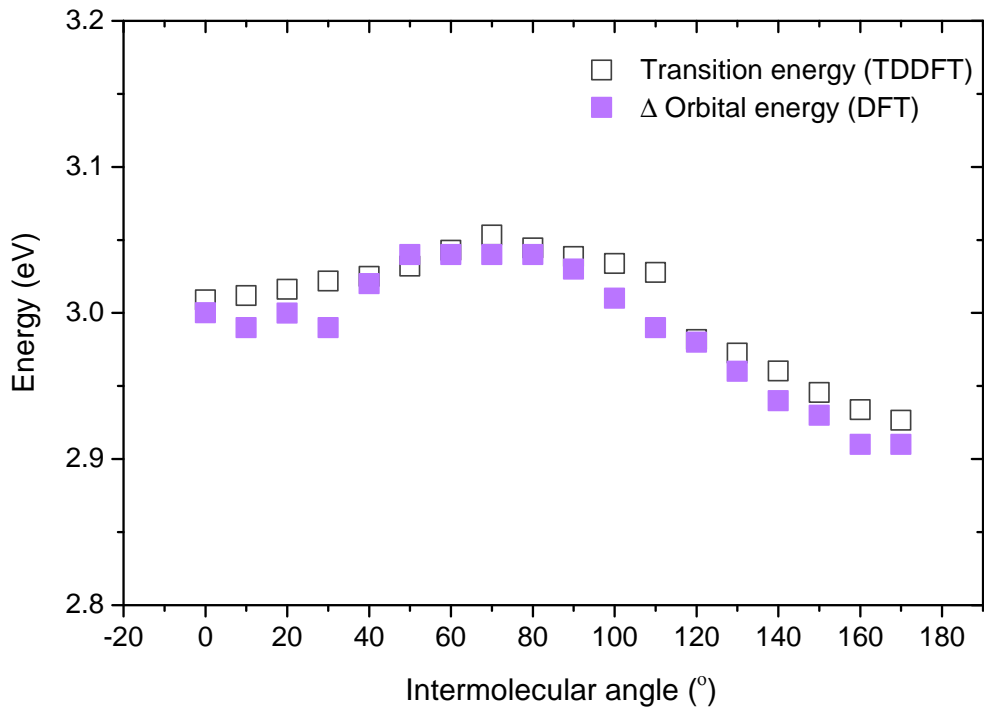


Figure 3: Excitation energy (TDDFT) and Kohn Sham orbital energy difference at different intermolecular angles (second isosbestic region).

## 2 Correlation between TD-DFT energies and orbital energies

Figure 4 describes the correlation between the transition energies for the dimer structures at different intermolecular angles and the difference between the energies of the main contributing orbitals. The plot graphed by linear fitting shows a correlation (Pearson's R) atleast 97% in each case.

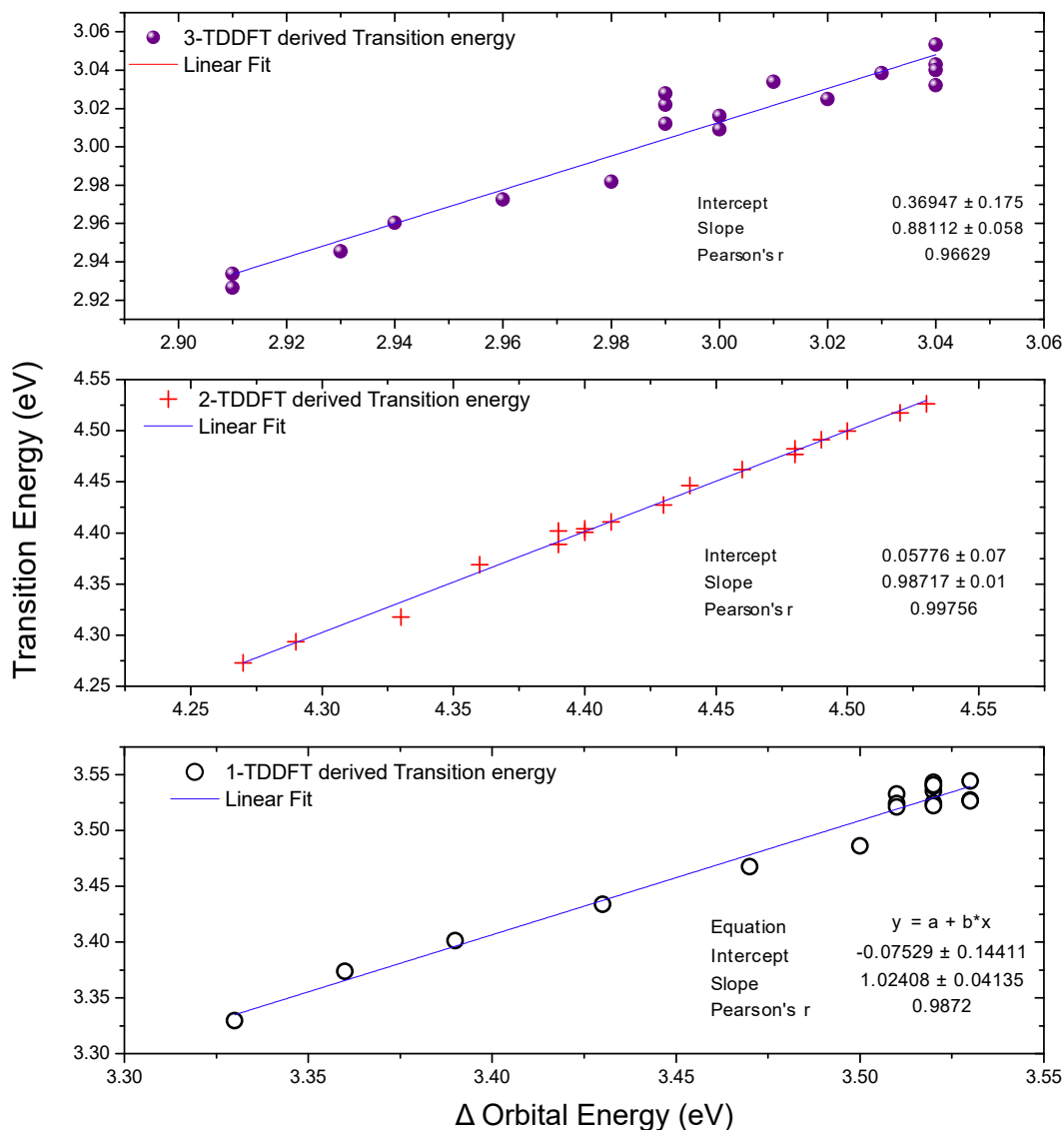


Figure 4: Correlation between transition energy (TDDFT) and Kohn Sham orbital energy difference for the three different transitions

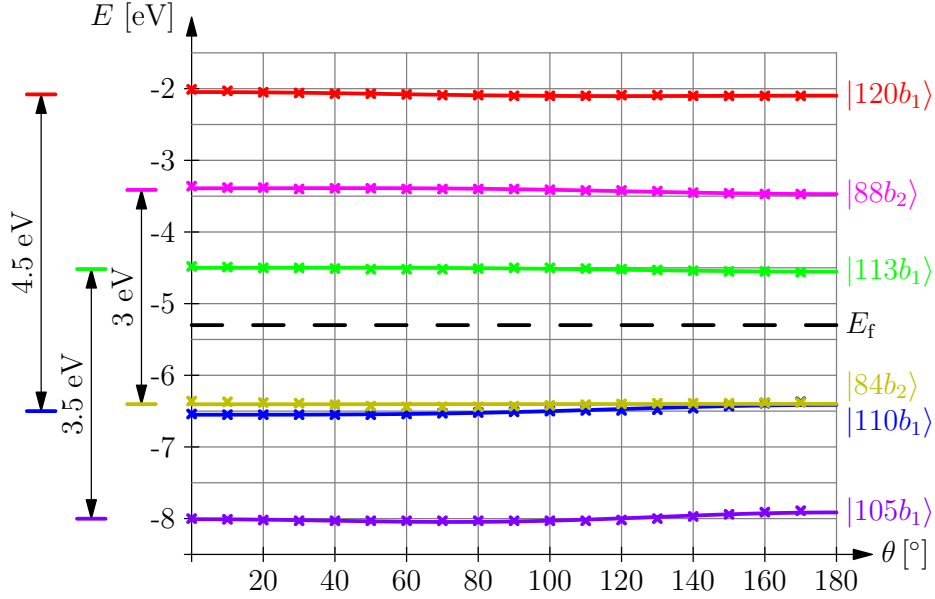


Figure 5: Variation of selected Kohn-Sham energies (see text) with dihedral angle. The DFT values are given by the dots in the highlighted  $\theta$  range. Solid lines are fits according to Eq. (1). Dashed line represents the position of the Fermi energy  $E_f$ .

### 3 Comparison with the Tracked Orbitals Estimated via DFT

We first study the impact of rotation on the energies of the Kohn-Sham orbitals governing the TD-DFT-derived intense transitions as listed in Table 1 in SI. The evolution of the orbital's energies are plotted in Fig. 5. The orbital energies have been fitted in good agreement to the orientational dependence via

$$\varepsilon_i(\theta) = \varepsilon_i + \Delta\varepsilon_i f(e_i, \theta), \quad (1)$$

with the fitting parameters  $\Delta\varepsilon_i$  determining the strength of the interaction and the eccentricity of the considered Kohn-Sham orbital  $e_i$ , the energy of the monomer's orbital  $\varepsilon_i$  and relation (16). The results are given in Table 6.

orbital	eccentricity	fitting agreement	colour
120b <sub>1</sub> >	1.419	98%	red
88b <sub>2</sub> >	0.610	91%	magenta
113b <sub>1</sub> >	0.613	72%	green
84b <sub>2</sub> >	0.969	79%	yellow
110b <sub>1</sub> >	0.472	95%	blue
105b <sub>1</sub> >	0.818	90%	purple

Table 6: Results of the fitting routine for the six tracked orbitals estimated via DFT simulations ( $|\varphi_n\rangle$ ), the corresponding eccentricities of the orbitals, the fitting agreement, which is the coefficient of determination  $R^2$ , and colour for fig. 5.

It can be observed that the single MOs fit quite well to the model (1). The deviation can be explain via the mismatch of the particle's inner-structure.