

# Supporting Information: Plane-Wave Implementation and Performance of *à-la-carte* Coulomb-Attenuated Exchange-Correlation Functionals for Predicting Optical Excitation Energies in Some Notorious Cases

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## 1 Convergence of Eigenvalues

### 1.1 HOMO-LUMO Gaps in a Plane Wave/Pseudopotential Basis

Gaps obtained from a soft pseudopotential show convergence at 120 Ry for all systems. For a small simulation supercell ( $l = 10 \text{ Å}$ ), choosing a lower cutoff value of 70 Ry introduces a substantial error of 0.3 eV. A notable error is still present at 70 Ry even for the two larger simulation cells, but it becomes less relevant for practical purposes, since the maximal error of 0.1 eV lies below the typical accuracy of the functional itself. Values at 100 Ry are essentially converged in all supercells, with errors being lower than 0.05 eV, and full convergence is reached at 120 Ry.

Table 1: HOMO-LUMO gap of a water molecule calculated using CAM-B3LYP and MT pseudopotentials at increasing energy cutoffs and varying simulation cell lengths  $l$  representing an isolated and periodic system, respectively.

$E_{\text{cut}}$ [Ry]	$\Delta\epsilon_i$ [eV], isolated system			$\Delta\epsilon_i$ [eV], periodic system		
	10 Å	20 Å	30 Å	10 Å	20 Å	30 Å
70	10.082	10.457	10.479	10.111	10.458	10.479
80	10.234	10.510	10.527	10.259	10.511	10.527
100	10.360	10.546	10.562	10.381	10.547	10.562
120	10.375	10.549	10.565	10.396	10.550	10.565
150	10.377	10.550	10.566	10.397	10.551	10.566
180	10.379	10.551	10.567	10.399	10.552	10.567

The convergence behaviour is analogous to the one observed for GGA or standard hybrid functionals once the simulation cell is of sufficient size: Changes in the gap are still substantial when increasing the side  $l$  of the cubic simulation cell from 10 Å to 20 Å, with changes in the converged gap of 0.2 eV. The change in gap is within the usual numerical tolerance ( $< 0.5$  eV) for a further extension to 30 Å, emphasising again the importance of an appropriately large cell for the correct description of the system’s LUMO.

The results for the truly periodic system (where the Poisson equations are not decoupled) show the same trend, with the only relevant difference with respect to the isolated system occurring in the 10 Å box. Given the trends observed for the isolated system, this is most likely attributed to spurious interactions between periodic images at this intermolecular distance. The considerable influence of these interactions on the gap supports the view that the requests on the Tuckerman-Martyna Poisson solver are not met yet either, since the simulation cell must span at least twice the spatial extent of the charge density.<sup>1</sup> The strong changes in gaps when increasing the cutoff within the small simulation cell is hence most probably due to an insufficient cell size for both the isolated and periodic system, resulting in an incomplete description of the electron density.

Table 2: Size  $l$  of the orthorhombic periodic supercell for all systems considered in this study. For structures and abbreviations, see ref. 2.

System	$l_x$ [a.u.]	$l_y/l_x$	$l_z/l_x$
7-azaindole	34.9555	1.00	1.00
AT nucleobase pair	71.8096	0.40	0.40
4-(N,N-dimethylamino)benzonitrile (DMABN)	34.9599	1.00	1.00
<i>p</i> -nitroaniline	34.9599	1.00	1.00
Acene (n=1 / naphthalene)	34.9556	1.00	1.00
Acene (n=2)	45.0000	1.00	0.50
Acene (n=3)	45.0000	1.00	0.50
Acene (n=4)	45.0000	0.75	0.50
Acene (n=5)	60.0000	0.50	0.33
Polyacetylene (PA) oligomer (n=2)	45.0000	0.66	0.50
Polyacetylene (PA) oligomer (n=3)	30.0000	1.00	0.50
Polyacetylene (PA) oligomer (n=4)	30.0000	1.00	0.50
Polyacetylene (PA) oligomer (n=5)	45.0000	0.50	0.50
N-phenylpyrrole (PP)	45.0000	0.66	0.50
Dipeptide	34.9599	1.00	1.00
Tripeptide	60.0000	0.50	0.25
$\beta$ -dipeptide	69.9199	0.50	0.50
Retinal protonated Schiff base	71.8096	0.40	0.40
CO	18.9036	1.00	1.00
H <sub>2</sub> CO	18.9036	1.00	1.00
HCl	20.0000	1.00	1.00
N <sub>2</sub>	10.0000	1.00	1.00

## 2 Supercell Size for Plane Wave Calculations

Plane wave calculations were carried out using the supercell sizes tabulated in table 2.

## 3 Excitation Energies for the Test Set by Peach *et al.*

Table 3: Excitation energies for the molecules contained in the test set by Peach *et al.*<sup>2</sup> that have not been tabulated in the main text. Calculations used a cutoff value for the KS orbitals of 75 Ry. For structures and abbreviations, see ref. 2.

State	CAM-B3LYP	CAM-O3LYP	Ref.	State	CAM-B3LYP	CAM-O3LYP	Ref.
Acene (n=2)				Acene (n=3)			
S1	3.71	3.83	4.46	S1	2.98	3.10	2.90
S2	4.05	4.08	4.88	S2	3.68	3.72	3.52
Acene (n=4)				Acene (n=5)			
S1	2.47	2.60	2.35	S1	2.16	2.30	1.95
S2	3.43	3.48	3.27	S2	3.20	3.33	3.09
CO				H <sub>2</sub> CO			
S1	8.89	8.86	8.51	S1	3.93	3.85	3.94
S2	8.89	8.86	9.88	S2	6.27	6.18	7.09
S3	9.77	9.80	10.23	S3	7.44	7.34	7.97
S4	9.86	9.81	10.87	S4	7.66	7.55	8.12
HCl				N <sub>2</sub>			
S1	7.43	7.43	8.23	S1	9.33	9.48	9.31
				S2	9.54	9.53	9.92
				S3	9.54	9.53	10.27
				S4	9.60	11.01	12.20
Polyacetylene (PA) oligomer (n=2)				Polyacetylene (PA) oligomer (n=3)			
S1	4.10	4.20	5.92	S1	5.55	5.77	4.95
Polyacetylene (PA) oligomer (n=4)				Polyacetylene (PA) oligomer (n=5)			
S1	3.21	3.21	4.49	S1	4.54	4.63	4.49
N-phenylpyrrole (PP)				Tripeptide			
S1	5.03	5.08	4.85	S1	3.82	5.74	5.74
S2	5.06	5.16	5.13	S2	4.16	5.95	5.61
S3	5.22	5.37	5.47	S3	4.68	5.98	5.91
S4	5.25	5.40	5.94	S4	5.02	6.00	7.01

Table 3 summarises the excitation energies for the molecules contained in the test set by Peach *et al.*<sup>2</sup> that have not been included in the main text. All excitation energies were calculated with both CAM-B3LYP and CAM-O3LYP in a plane-wave/pseudopotential

framework as described in the Computational Setup.

## References

- (1) Martyna, G. J.; Tuckerman, M. E. A reciprocal space based method for treating long range interactions in ab initio and force-field-based calculations in clusters. *The Journal of Chemical Physics* **1999**, *110*, 2810–2821.
- (2) Peach, M. J. G.; Benfield, P.; Helgaker, T.; Tozer, D. J. Excitation energies in density functional theory: An evaluation and a diagnostic test. *The Journal of Chemical Physics* **2008**, *128*, 044118.