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published in
Journal of Chemical Theory and Computation
2017

DOI (link to publisher)
10.1021/acs.jctc.7b00564

document version
Publisher's PDF, also known as Version of record

JCTC Journal of Chemical Theory and Computation

Erratum

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Correction to Efficient Calculation of Electronic Absorption Spectra by Means of Intensity-Selected Time-Dependent Density Functional Tight Binding

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J. Chem. Theory Comput. **2015**, *11* (1), 157−167. DOI: 10.1021/ct500838h

We have found a technical mistake in our implementation of TD-DFTB that led to wrong results for molecules with more than 64 atoms. A discrepancy between the mapping of rows/columns of overlap and the coefficient matrix to the basis functions led to erroneously calculated atomic transition charges, $q_{\mathrm{ia},\mathcal{A}}$. This mistake affects both the selection of the included single orbital transitions and the solution of Casida's equation, as one is essentially diagonalizing a wrong matrix. The problem has been fixed in ADF2014.06 and later versions. While the original article's results[1] for the C_{60} fullerene and the $Ir(ppy)_3$ complex are unaffected, we published wrong results for the ubiquitin example.

The Figures 4, 5, and 6 from the original article are affected and should be replaced with Figures 1, 2, and 3 from this erratum. The conclusion of the article is not affected. With the correct implementation, the computational savings of intensity selection are actually greater than we originally thought, as there are more single orbital transitions with small oscillator strengths. In the original article we reported that a selection threshold of $f_{ia} > 0.001$ removes 29% of the single orbital transitions in ubiquitin. With the corrected implementation we find that the same threshold actually removes 86% of the basis. The selection thresholds in Figure 2 have therefore been adjusted to show calculations of a quality equivalent to the calculations of the original article. Overall we find that for a constant quality of the absorption spectrum the computational savings are roughly an order of magnitude greater than originally reported. The precise timings can be found in Table 1, which should be compared with Table 3 from the original article.

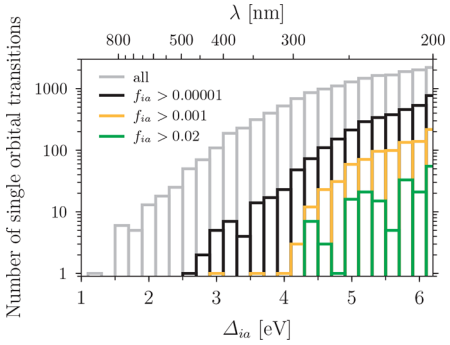

Figure 1. Number of single orbital transitions per energy interval for ubiquitin for different intensity selection thresholds. Note the large number of low intensity transitions below 3.5 eV that are removed by even a small threshold.

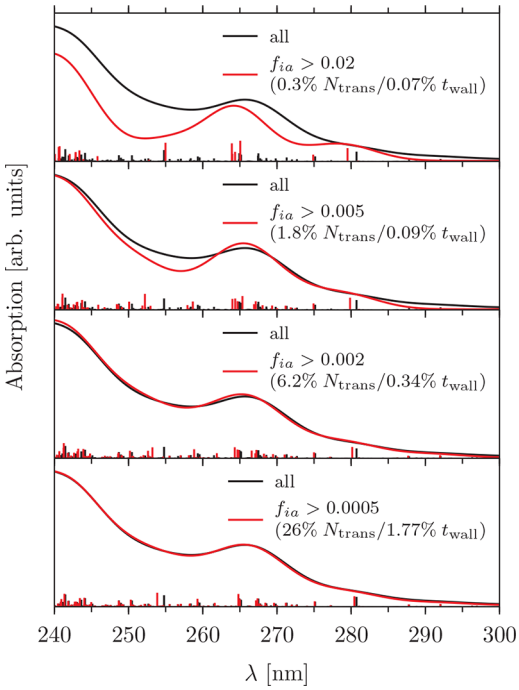

Figure 2. TD-DFTB calculated absorption spectra of ubiquitin with different intensity selection thresholds. The percentage in parentheses is the size of the remaining basis and the required computational time relative to the full calculation. Note that the intensity-selected calculations were run on fewer cluster nodes than the full calculation so that the shown wall times underestimate the speedup. Detailed timings can be found in Table 1.

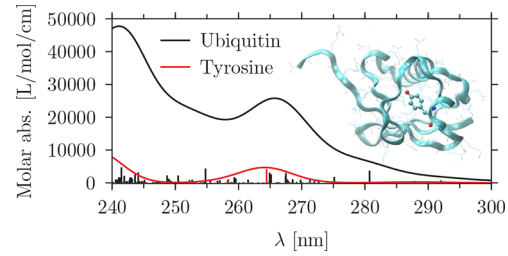

Figure 3. Comparison of the absorption spectra of tyrosine and ubiquitin.

A major difference between the corrected results and the originally published data is revealed if the absorption spectrum of ubiquitin is compared with the absorption of the isolated

Published: June 8, 2017

DOI: 10.1021/acs.jctc.7b00564
J. Chem. Theory Comput. 2017, 13, 3424−3425

Table 1. Measured Runtimes of the Example TD-DFTB Calculations on Ubiquitin Using Intensity Selection (Corrected Version of Table 3 from the Original Article)

$f_{ia}^{\min}$	N_{trans}	N_{excit}	no. CPU	t_{wall}	t_{CPU}
–	2284880	15820	128	12.7 h	68 days
0.0005	598085	939	32	811 s	7.2 h
0.002	141999	513	16	159 s	2544 s
0.005	42055	292	16	42 s	672 s
0.02	6541	127	16	31 s	496 s

tyrosine amino acid in vacuum; see Figure 3. Originally we reported that the low energy end of the absorption spectrum was dominated by one of the tyrosine absorption lines that was slightly red-shifted in the protein environment. This was in agreement with both the experimental and theoretical spectra published in ref 2 and supported a picture in which tyrosine is acting as the chromophore of ubiquitin. However, with the correct implementation we find that while the shape of the spectrum is surprisingly similar to our original spectrum, the absolute absorptivity is overall much larger and many more individual excitations (sticks at the bottom of Figure 3) contribute to the absorption in this frequency range. This is inconsistent with the idea of tyrosine being the chromophore, and visualization of the involved orbitals indeed shows contributions from other parts of the protein.

Unfortunately, the spectra in both our original publication and ref 2 are shown with "arbitrary units" on the *y*-axis, making it impossible to compare absolute absorptivity. While the use of arbitrary units is still commonly seen in the literature, this practice should really be abolished as it is actually straightforward to calculate[3] the molar absorptivity

$$\epsilon(E) = \frac{\pi}{2\ln(10)} \frac{N_A e^2 \hbar}{m_e c \varepsilon_0} \sum_I f_I \Gamma(E - E_I) \tag{1}$$

from the oscillator strengths, f_I, and excitation energies E_I. Here $\Gamma(E)$ is a normalized, typically a peaked function that models the experimental line broadening, e.g., a Gaussian or Lorentzian. In order to facilitate comparison with future results, we now show the molar absorptivity in liters per mole per centimeters in Figure 3.

However, even though we cannot compare our absorption spectrum directly to experimental data, we think that TD-DFTB results are unlikely to be accurate for this system. It is quite well established that from all the standard amino acids only tryptophan, tyrosine, and cysteine contribute significantly to the absorption around 280 nm.[4] As ubiquitin contains neither tryptophan nor cysteine and only one tyrosine unit, its absorptivity is expected to be close to that of a single tyrosine, which is not what our calculation predicts. What appears to be happening is that excitations with charge-transfer character are predicted with too low energies and overlay the part of the spectrum that should be dominated by tyrosine. This is supported by our observation that single orbitals transitions involved in many of the excitations in this range tend to connect orbitals with small but still nonzero overlap. (Transitions between orbitals without any overlap are completely dark and would be removed by the intensity selection.) The problem of energetically too low charge-transfer excitations is well-known in local density functional approaches and usually circumvented with range-separated hybrid functionals, also called long-range corrected functionals. This has only very recently been developed for the DFTB framework[5,6] and is not yet implemented in the DFTB implementation in the ADF Modeling Suite. Ubiquitin would make an interesting test case for these new methods though, and we will investigate this in more detail when the long-range correction becomes available in our implementation.

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DOI: 10.1021/acs.jctc.7b00564
J. Chem. Theory Comput. 2017, 13, 3424−3425