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# Assessing accuracy of exchange–correlation functionals for singlet–triplet excitations

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ABSTRACT

The performance of exchange–correlation functionals for the description of the lowest-energy singlet–triplet excitations is investigated. The benchmark set of molecular triplet states is constructed and experimental data is compared to Density Functional Theory calculations. The accuracy of functionals is evaluated both in terms of adiabatic excitation energies and, where possible, reproduction of structural data and harmonic frequencies. The benchmark results show that for the selected group of functionals very good accuracy may be achieved and the quality of predictions provided is competitive to computationally more demanding coupled-cluster approaches.

## 1. Introduction

Electronically excited states properties play a significant role in many fields of contemporary chemistry and biochemistry. To get a reliable description of those properties one needs theoretical models and methods that are both accurate and practically applicable. The approaches based on multi-determinantal expansion of the wave function form a nice hierarchy of approximations and promise in principle unlimited accuracy in the limit of infinite expansion. However in practice, the convergence of the series of models is quite slow while the cost of calculations for even the most crude approximations scales very unfavourably with the system size. As a result such calculations are viable for small molecules, but they become unmanageable for many systems of biological or technological importance. Due to these factors, nowadays probably the most common theoretical tools employed in routine investigations of electronically excited states are the methods based on Density Functional Theory (DFT). They typically provide relatively good accuracy coupled with relatively moderate computational demands. Nonetheless, the accuracy of DFT-based approaches strongly depends on so-called exchange–correlation (xc) functional. While it is proved that the universal xc functional exists, the expectation that we will ever know its exact structure is unrealistic and in practice we are left with plethora of various approximate models. Although there have been many benchmarks of xc functionals published, only few of them have focused on the reproduction of excited state properties. As a result, the choice of functional for this kind of applications may be still regarded more art than science at the moment.

Typically, for the purpose of exchange–correlation functional benchmarking for the excited states, vertical excitation energies (VEEs) are discussed, with benchmark values taken either from high level of theory (CASPT2 or coupled-cluster type methods) or estimated from experimentally measured absorption spectra. A comprehensive set of VEE-based benchmarks have been published by Jacquemin and coworkers [1] and Leang and coworkers [2]. For atomic systems, where VEEs are perfectly defined experimentally, Yang et al. [3] provided the thorough evaluation of plethora of approximations for the exchange–correlation functional. Also a few recent articles addressing specifically triplet excitations [4–6] are worth to mention.

While obtainable quite easily in computations, VEEs are rather poorly comparable with experimental data in molecular case as many additional assumptions have to be made to deduce the counterpart value from the measured spectra. On the other hand, such theory versus experiment comparison can be done in truly exhaustive manner by the simulation of full vibronic spectra. However, full spectra reproduction path is severely narrowed by both computational complexity and demand for high expertise required to build an appropriate vibronic model. Using the adiabatic excitation energy (AEE) allows to reach a fruitful compromise. From experimental point of view the AEE quantity manifests nicely in well resolved spectra through the band origin location, from the computational one it requires only the knowledge of the optimized geometries of the ground and relevant excited electronic states.

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Furthermore, the accuracy of calculated AEEs can be improved by implementing a number of adjustments that may include zero-point vibrational energy corrections or introduction of relativistic effects. Although AEE-benchmark approach is attractive and well motivated, there exists only limited literature on the subject with Send's [7] and Jacquemin's [8] studies being probably the most comprehensive made so far.

In this paper, we present the benchmark of exchange–correlation functionals in the context of reproduction of singlet to triplet adiabatic excitation energies. We consider the triplet states which are energetically the lowest for this spin manifold, which allows us to use the standard DFT methodology instead of its time-dependent counterpart. The case researched, while technically relatively straightforward, presents an interesting object of study both due to its challenging nature from the perspective of computational models accuracy and physical importance of low-lying triplet states.

## 2. Benchmark set

The benchmark set consists of 20 molecular triplet states. The structure of chemical species studied is presented in Fig. 1.

We considered only the gas-phase experiments that provide vibrationally well resolved spectra, which allows for the firm assignment of 0 → 0 vibronic transition. The dominant source of experimental data were Herzberg's Molecular Spectra and Molecular Structures volumes [9,10]. Complementary data was extracted from individual papers [11–18]. The experimental excitation energies are presented in Table 1, while experimental bondlengths and vibrational constants collected for a few diatomic molecules are shown in Table 2.

**Table 1**
Experimental 0 → 0 excitation energies.

| Molecule | Triplet state | Excitation energy (eV) | Reference |
|---|---|---|---|
| Acetophenone | A | 3.20 | [11] |
| Acrolein | $A''$ | 3.01 | [12] |
| BCl | $\Pi$ | 2.50 | [10] |
| Benzaldehyde | $A''$ | 3.12 | [11] |
| Benzophenone | A | 3.00 | [11] |
| BF | $\Pi$ | 3.61 | [10] |
| $Cl_2$ | $\Pi_u$ | 2.21 | [10] |
| CO | $\Pi$ | 6.04 | [10] |
| 2-Cyclopentenone | A | 3.22 | [13] |
| Formaldehyde | A | 3.12 | [14] |
| GaF | $\Pi$ | 4.10 | [10] |
| $N_2$ | $\Pi_g$ | 7.39 | [10] |
| p-Benzoquinone | $B_1$ | 2.32 | [15] |
| Quinoline | $A'$ | 2.79 | [16] |
| Quinoxaline | $B_2$ | 2.68 | [17] |
| SiO | $\Pi$ | 4.20 | [10] |
| $SO_2$ | $B_1$ | 3.19 | [9] |
| Thioacetaldehyde | A | 2.02 | [18] |
| Thioacetone | A | 2.14 | [18] |
| Thioformaldehyde | $A''$ | 1.80 | [14] |

**Table 2**
Experimental bondlengths and $\omega_e$ vibrational constants.

| Molecule | $S_0$ state | | T state | | Reference |
|---|---|---|---|---|---|
| | Bondlength (Å) | $\omega_e$ ($cm^{-1}$) | Bondlength (Å) | $\omega_e$ ($cm^{-1}$) | |
| BCl | 1.716 | 839 | 1.698 | 911 | [10] |
| BF | 1.263 | 1402 | 1.308 | 1324 | [10] |
| $Cl_2$ | 1.988 | 560 | 2.435 | 260 | [10] |
| CO | 1.128 | 2170 | 1.206 | 1743 | [10] |
| GaF | 1.774 | 622 | 1.747 | 663 | [10] |
| $N_2$ | 1.098 | 2359 | 1.213 | 1733 | [10] |
| SiO | 1.510 | 1242 | 1.562 | 1014 | [10] |

## 3. Computational details

We selected thirteen exchange–correlation functionals of all main types. The local density approximation category, involved only one, the most popular SVWN functional. We have chosen two popular gradient-corrected models, namely OLYP and PBEPBE (PBE) plus one meta-GGA functional – tHCTH. The global hybrid functional set included the most popular B3LYP and PBE1PBE (PBE0) models; B97-2, which is the B97 Becke's functional reparameterized by Wilson, Bradley and Tozer; BMK which includes meta-GGA part and M06-HF that incorporates full Hartree–Fock type exchange. Screened hybrids were represented by long-range corrected CAM-B3LYP and short-range corrected HSEH1PBE and MN12-SX functionals. Double hybrids, which incorporate perturbative correction in correlation part and are known for typically very good accuracy, were represented by the most popular B2PLYP model. While the cost of the calculations employing double-hybrid functionals is significantly higher due to the necessity of performing extra MP2-type calculations, it should be mentioned that the computational burden may be limited either by the use of density fitting and local approximations for the MP2 part [19] or through the usage of methods that employ smaller basis sets for MP2-type correction [20]. To evaluate the performance of DFT models against wavefunction-based methods we also included the simplest Hartree–Fock method and more accurate and far more expensive CCSD approximation. The computational models used are summarized in Table 3.

All the calculations were performed using Gaussian09 [28] computational package. To avoid significant basis set incompleteness errors, high-quality aug-cc-pVTZ [39–44] basis set was employed. For the molecules including Si, S or Cl elements, additional tight d-functions has been added for those atoms [45]. The pruned grids of 99 radial shells and 550 angular points for each radial shell were used for numerical quadratures. This choice of grids corresponded to UltraFineGrid in Gaussian09 nomenclature.

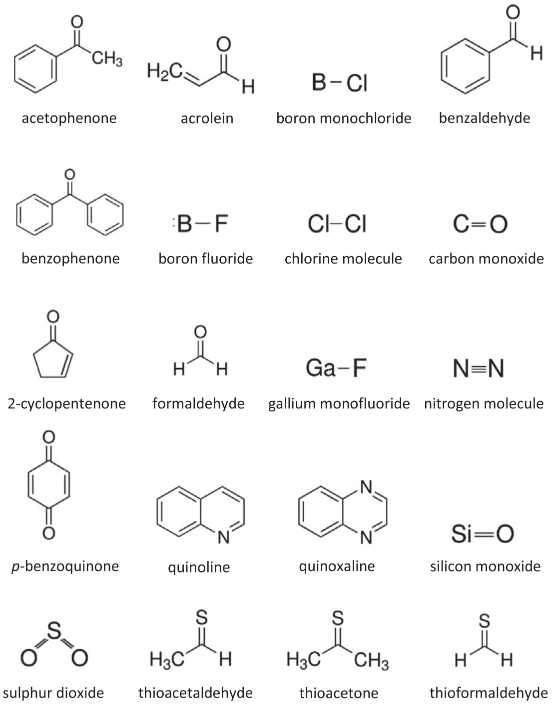

**Fig. 1.** Molecules included in the benchmark set.