

QUESTDB

A database of highly accurate vertical excitation energies

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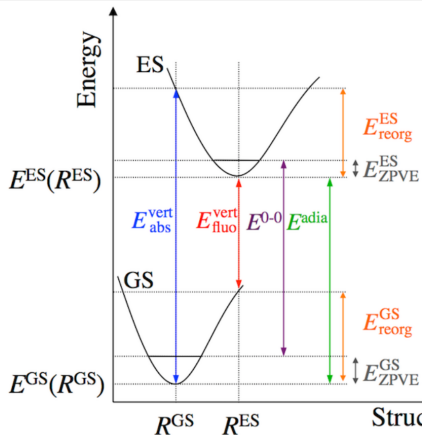
September 2, 2021



Electronic transitions

First photochemistry law

Photoexcitation is the first step in a photochemical process where the reactant is elevated to a state of higher energy, an excited state.



The QUEST Project

A Mountaineering Strategy to Excited States: Highly Accurate Reference Energies and Benchmarks

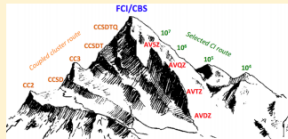
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S Supporting Information

ABSTRACT: Striving to define very accurate vertical transition energies, we perform both high-level coupled cluster (CC) calculations (up to CCSDTQP) and selected configuration interaction (sCI) calculations (up to several millions of determinants) for 18 small compounds (water, hydrogen sulfide, ammonia, hydrogen chloride, dinitrogen, carbon monoxide, acetylene, ethylene, formaldehyde, methanimine, thioformaldehyde, acetaldehyde, cyclopropene, diazomethane, formamide, ketene, nitrosomethane, and the smallest streptocyanine). By systematically increasing the order of the CC expansion, the number of determinants in the CI expansion as well as the size of the one-electron basis set, we have been able to reach near full CI (FCI) quality transition energies. These calculations are carried out on CC3/aug-cc-pVTZ geometries, using a series of increasingly large atomic basis sets systematically including diffuse functions. In this way, we define a list of 110 transition energies for states of various characters (valence, Rydberg, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, singlet, triplet, etc.) to be used as references for further calculations. Benchmark transition energies are provided at the aug-cc-pVTZ level as well as with additional basis set corrections, in order to obtain results close to the complete basis set limit. These reference data are used to benchmark a series of 12 excited-state wave function methods accounting for double and triple contributions, namely ADC(2), ADC(3), CIS(D), CIS(D₂), CC2, STEOM-CCSD, CCSD, CCSDR(3), CCSDT-3, CC3, CCSDT, and CCSDT_Q. It turns out that CCSDT_Q yields a negligible difference with the extrapolated CI values with a mean absolute error as small as 0.01 eV, whereas the coupled cluster approaches including iterative triples are also very accurate (mean absolute error of 0.03 eV). Consequently, CCSDT-3 and CC3 can be used to define reliable benchmarks. This observation does not hold for ADC(3) that delivers quite large errors for this set of small compounds, with a clear tendency to overcorrect its second-order version, ADC(2). Finally, we discuss the possibility to use basis set extrapolation approaches so as to tackle more easily larger compounds.



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Theoretical Best Estimate

Theoretical Best Estimate TBE

The most accurate values we can obtain at the ab initio level.

TBE calculation methods

- Selected Configuration Interaction (SCI)
 - Configuration Interaction using a Perturbative Selection made Iteratively (CIPSI)



Quantum Package

- Equation-of-motion coupled-cluster Highest possible level depending on the system size up to EOM-CCSDTQ

Quantum Package demo



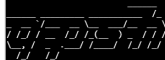
TUTORIALS

QP terminal

You can try *Quantum Package* in the terminal below. To configure the terminal for your favorite text editor, set the `EDITOR` environment variable:

```
export EDITOR=vim
```

```
Your ID is : 212ec67e0130ec195a8c53467b677e786131136194a2eef8f0b0ba1296b4a261  
Session allocated.  
There are 3 sessions left available
```



```
-- Quantum Package Shell --
```

```
user@qp-demo:~$ s  
examples qp2  
user@qp-demo:~$
```

<https://quantumpackage.github.io/qp2/page/try>

https://github.com/mveril/qp_demo




https://hub.docker.com/r/mveril/qp_demo

The two usage of the QUEST project

Two type of users

- Create new methods and want to benchmark it
- Use methods to compute photochemical properties and want to choose the most suitable method

Live demo

 https://lcpq.github.io/QUESTDB_website
 https://github.com/LCPQ/QUESTDB_website
 [10.1002/wcms.1517](https://doi.org/10.1002/wcms.1517)

Reference Energies for Intramolecular Charge-Transfer Excitations

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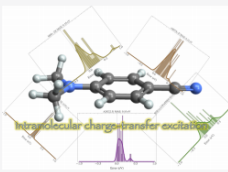
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Supporting Information

ABSTRACT: With the aim of completing our previous efforts devoted to local and Rydberg transitions in organic compounds, we provide a series of highly accurate vertical transition energies for intramolecular charge-transfer transitions occurring in (π -conjugated) molecular compounds. To this end, we apply a composite protocol consisting of linear-response CCSDT excitation energies determined with Dunning's double- ζ basis set corrected by CC3/CCSDT-3 energies obtained with the corresponding triple- ζ basis. Further basis set corrections (up to aug-cc-pVQZ) are obtained at the CCSD and CC2 levels. We report 30 transitions obtained in 17 compounds (aminobenzonitrile, aniline, azulene, benzonitrile, benzothiadiazole, dimethylaminobenzonitrile, dimethylamine, dipeptide, β -dipeptide, hydrogen chloride, nitroaniline, nitrobenzene, nitrodimethylaniline, nitropyridine *N*-oxide, *N*-phenylpyrrole, phthalazine, and quinoxaline). These reference values are then used to benchmark a series of

wave functions [CIS(D), SOPPA, RPA(D), EOM-MP2, CC2, CCSD, CCSD(T)(a)*, CCSDR(3), CCSDT-3, CC3, ADC(2), ADC(3), and ADC(2.5)], the Green's function-based Bethe–Salpeter equation (BSE) formalism performed on top of the partially self-consistent evGW scheme considering two different starting points (BSE/evGW@HF and BSE/evGW@PBE0), and time-dependent density-functional theory (TD-DFT) combined with several exchange–correlation functionals (B3LYP, PBE0, M06-2X, CAM-B3LYP, LC- ω HPBE, ω B97X, ω B97X-D, and M11). It turns out that the CC methods including triples, namely, CCSD(T)(a)*, CCSDR(3), CCSDT-3, and CC3, provide rather small average deviations (≤ 0.10 eV), with CC3 emerging as the only chemically accurate approach. ADC(2.5) also performs nicely with a mean absolute error of 0.11 eV for a $O(N^6)$ formal scaling, whereas CC2 and BSE/evGW@PBE0 also deliver very satisfying results given their respective $O(N^5)$ and $O(N^4)$ computational scalings. In the TD-DFT context, the best performing functional is ω B97X-D, closely followed by CAM-B3LYP and M06-2X, all providing mean absolute errors around 0.15 eV relative to the theoretical best estimates.



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Accurate full configuration interaction correlation energy estimates for five- and six-membered rings

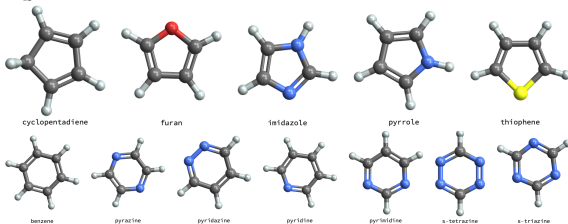
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Following our recent work on the benzene molecule [J. Chem. Phys. **153**, 176101 (2020)], itself motivated by the blind challenge of Eriksen *et al.* [J. Phys. Chem. Lett. **11**, 8922 (2020)] on the same system, we report accurate full configuration interaction (FCI) frozen-core correlation energy estimates for twelve five- and six-membered ring molecules (cyclopentadiene, furan, imidazole, pyrrole, thiophene, benzene, pyrazine, pyridazine, pyridine, s-tetrazine, and s-triazine) in the standard correlation-consistent double- ζ Dunning basis set (cc-pVDZ). Our FCI correlation energy estimates, with estimated error smaller than 1 millihartree, are based on energetically optimized-orbital selection configuration interaction (SCI) calculations performed with the *Configuration Interaction using a Perturbative Selection made Iteratively* (CIPS) algorithm. Having at our disposal these accurate reference energies, the respective performance and convergence properties of several popular and widely-used families of single-reference quantum chemistry methods are investigated. In particular, we study the convergence properties of i) the Møller-Plesset perturbation series up to fifth-order (MP2, MP3, MP4, and MP5), ii) the iterative approximate coupled-cluster series CC2, CC3, and CC4, and iii) the coupled-cluster series CCSD, CCSDT, and CCSDTQ. The performance of the ground-state gold standard CCSD(T) as well as the completely renormalized CC model, CR-CC(2,3), are also investigated. We show that MP4 provides an interesting accuracy/cost ratio, while MP5 systematically worsens the correlation energy estimates. In addition, CC3 outperforms CCSD(T) and CR-CC(2,3), as well as its more expensive parent CCSDT. A similar trend is observed for the methods including quadruple excitations, where the CC4 model is shown to be slightly more accurate than CCSDTQ, both methods providing correlation energies within 2 millihartree of the FCI limit.

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Talk

