

# Electronic transitions, statistics and digital tools for quantum chemistry

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# Outline

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## Unphysical discontinuities in GW methods

Chapter 3

Arjan Berger, Pina Romaniello, Pierre-François Loos

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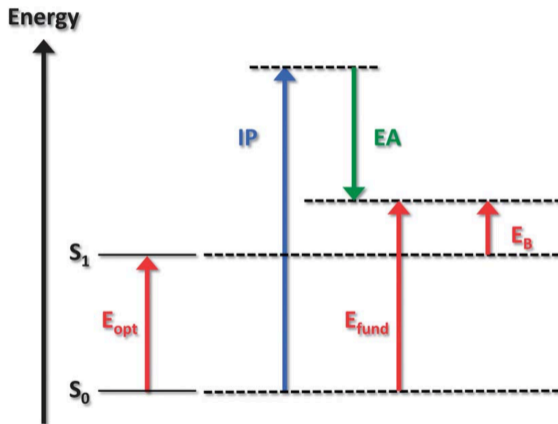
## Accurate full configuration interaction correlation energy estimates for five- and six-membered rings

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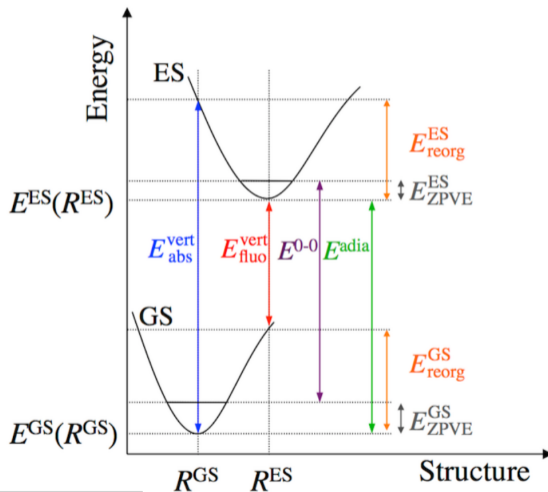
## General conclusion and perspectives

# Excited states and methods



J.-L. Bredas, Mater. Horiz. 1, 17–19 (2014)

# Excited states and methods



P. F. Loos et al., J. Phys. Chem. Lett. 11, 2374–2383 (2020)

# Excited states methodes.

Method	Formal scaling	Oscillator strength	Analytical gradients
TD-DFT	$\mathcal{O}(N^4)$	✓	✓
BSE@GW	$\mathcal{O}(N^4)$	✓	✗
CIS	$\mathcal{O}(N^5)$	✓	✓
CIS(D)	$\mathcal{O}(N^5)$	✗	✓
ADC(2)	$\mathcal{O}(N^5)$	✓	✓
CC2	$\mathcal{O}(N^5)$	✓	✓
ADC(3)	$\mathcal{O}(N^6)$	✓	✗
EOM-CCSD	$\mathcal{O}(N^6)$	✓	✓
CC3	$\mathcal{O}(N^7)$	✓	✗
EOM-CCSDT	$\mathcal{O}(N^8)$	✗	✗
EOM-CCSDTQ	$\mathcal{O}(N^{10})$	✗	✗
CASPT2/NEVPT2	$\mathcal{O}(N!)$	✓	✓
SCI	$\mathcal{O}(N!)$	✗	✗
FCI	$\mathcal{O}(N!)$	✓	✓

P. F. Loos et al., J. Phys. Chem. Lett. 11, 2374–2383 (2020)

# QUANTUM PACKAGE

## A programming environment for wave function methods

### Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs

Yann Garniron,<sup>1</sup> Thomas Appellencourt,<sup>1</sup> Kevin Gasperich,<sup>1,4</sup> Anouar Benali,<sup>4</sup> Anthony Ferté,<sup>1</sup> Julien Paquier,<sup>1</sup> Barthélémy Pradines,<sup>1,2</sup> Roland Assaraf,<sup>1</sup> Peter Reinhardt,<sup>1</sup> Julien Toulouse,<sup>1</sup> Pierrette Barbaresco,<sup>5</sup> Nicolas Renon,<sup>3</sup> Grégoire David,<sup>3</sup> Jean-Paul Malrieu,<sup>6</sup> Mickaël Vériel,<sup>1</sup> Michel Caffarel,<sup>1</sup> Pierre-François Loos,<sup>7,8</sup> Emmanuel Giner,<sup>9,10</sup> and Anthony Scemama<sup>9,11</sup>

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<sup>2</sup>Computational Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

<sup>3</sup>Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

<sup>4</sup>Laboratoire de Chimie Théorique, Sorbonne Université, CNRS, Paris, France

<sup>5</sup>Institut des Sciences du Calcul et des Données, Sorbonne Université, F-75005 Paris, France

<sup>6</sup>CALMIP, Université de Toulouse, CNRS, INPT, INSA, UPS, UMS 3667, Toulouse, France

<sup>7</sup>Aix-Marseille Univ. CNRS, ICR, Marseille, France

**ABSTRACT:** Quantum chemistry is a discipline which relies heavily on very expensive numerical computations. The scaling of correlated wave function methods lies, in their standard implementation, between  $\mathcal{O}(N^3)$  and  $\mathcal{O}(e^N)$ , where  $N$  is proportional to the system size. Therefore, performing accurate calculations on chemically meaningful systems requires (i) approximations that can lower the computational scaling and (ii) efficient implementations that take advantage of modern massively parallel architectures. QUANTUM PACKAGE is an open-source programming environment for quantum chemistry specially designed for wave function methods. Its main goal is the development of determinant-driven selected configuration interaction (sCI) methods and multireference second-order perturbation theory (PT2). The determinant-driven framework allows the programmer to include any arbitrary set of determinants in the reference space, hence providing greater methodological freedom. The sCI method implemented in QUANTUM PACKAGE is based on the CIPSI (Configuration Interaction using a Perturbative Selection made Iteratively) algorithm which complements the variational sCI energy with a PT2 correction. Additional external plugins have been recently added to perform calculations with multireference coupled cluster theory and range-separated density-functional theory. All the programs are developed with the IRPF90 code generator, which simplifies collaborative work and the development of new features. QUANTUM PACKAGE strives to allow easy implementation and experimentation of new methods, while making parallel computation as simple and efficient as possible on modern supercomputer architectures. Currently, the code enables, routinely, to realize runs on roughly 2 000 CPU cores, with tens of millions of determinants in the reference space. Moreover, we have been able to push up to 12 288 cores in order to test its parallel efficiency. In the present manuscript, we also introduce some key new developments: (i) a renormalized second-order perturbative correction for efficient extrapolation to the full CI limit and (ii) a stochastic version of the CIPSI selection performed simultaneously to the PT2 calculation at no extra cost.



## CIPSI algorithm (SCI)

1. Variational wave function and energy

$$|\Psi_{\text{var}}\rangle = \sum_I c_I |I\rangle$$

$$E_{\text{var}} = \frac{\langle \Psi_{\text{var}} | \hat{H} | \Psi_{\text{var}} \rangle}{\langle \Psi_{\text{var}} | \Psi_{\text{var}} \rangle} \geq E_{\text{FCI}}$$

2. Second-order perturbative contribution

$$e_{\alpha} = \frac{\langle \Psi_{\text{var}} | \hat{H} | \alpha \rangle^2}{E_{\text{var}} - \langle \alpha | \hat{H} | \alpha \rangle}$$

3. Missing correlation energy estimation

$$E^{(2)} = \sum_{\alpha} e_{\alpha}$$

$$E_{\text{FCI}} \approx E_{\text{var}} + E^{(2)}$$

4. We select  $|\alpha\rangle^{(n)}$  the subset of external determinants with the largest contribution

$$\{I\} \leftarrow \{I\} \cup \{|\alpha\rangle^{*}\}$$

5. If convergence has not been reached, go back to 1

Y. Garniron et al., J. Chem. Theory Comput. 15, 3591 (2019)



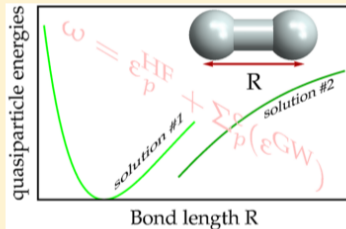


# Unphysical Discontinuities in GW Methods

Mickaël Véril,<sup>†</sup> Pina Romaniello,<sup>‡,¶</sup> J. A. Berger,<sup>†,¶</sup> and Pierre-François Loos<sup>\*,†,¶</sup>

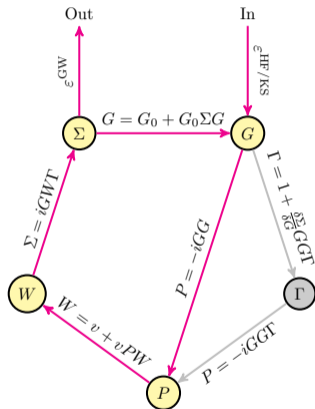
<sup>†</sup>Laboratoire de Chimie et Physique Quantiques, <sup>‡</sup>Laboratoire de Physique Théorique, and <sup>¶</sup>European Theoretical Spectroscopy Facility (ETSF), Université de Toulouse, CNRS, UPS, Toulouse, France

**ABSTRACT:** We report unphysical irregularities and discontinuities in some key experimentally measurable quantities computed within the GW approximation of many-body perturbation theory applied to molecular systems. In particular, we show that the solution obtained with partially self-consistent GW schemes depends on the algorithm one uses to self-consistently solve the quasiparticle (QP) equation. The main observation of the present study is that each branch of the self-energy is associated with a distinct QP solution and that each switch between solutions implies a significant discontinuity in the quasiparticle energy as a function of the internuclear distance. Moreover, we clearly observe “ripple” effects, i.e., when a discontinuity in one of the QP energies induces (smaller) discontinuities in the other QP energies. Going from one branch to another implies a transfer of weight between two solutions of the QP equation. The cases of occupied, virtual, and frontier orbitals are separately discussed on distinct diatomics. In particular, we show that multisolution behavior in frontier orbitals is more likely if the HOMO–LUMO gap is small.



M. Véril et al., *J. Chem. Theory. Comput.* **14**, 5220–5228 (2018)

# GW



Hedin's pentagon<sup>1</sup>

## Lists of the main GW methods (Green's function and screened Coulomb interaction $W$ )

- ▶  $G_0 W_0$   
Perturbative GW ou one-shot GW
- ▶ **evGW**  
Eigenvalues **GW**  
Self-consistent on the energies of the orbitals
- ▶ **qsGW**  
Quasiparticle **self-consistent GW**  
Self-consistent on the orbitals and their energies

<sup>1</sup> L. Hedin, Phys. Rev. **139**, A796 (1965)

# Theory

## Quasiparticle equation

$$\omega = \epsilon_p^{\text{HF}} + \Sigma_p^c(\omega)$$

## In practice

perturbative ( $G_0W_0$ )

$$\epsilon_p^{\text{QP}} = \epsilon_p^{\text{HF}} + Z_p(\epsilon_p^{\text{HF}})\Sigma_p^c(\epsilon_p^{\text{HF}})$$

self-consistent (evGW/qsGW)

$$\epsilon_p^{\text{QP}} = \epsilon_p^{\text{HF}} + \Sigma_p^c(\epsilon_p^{\text{QP}-1})$$

# Theory

## Self-energy

### Self-energy and renormalization factor

$$\Sigma_p^c(\omega) = \sum_m \left[ \sum_i^{\text{occ}} \frac{|(ip|\rho_m)|^2}{\omega - \epsilon_i + \Omega_m} + \sum_a^{\text{virt}} \frac{|(ap|\rho_m)|^2}{\omega - \epsilon_a - \Omega_m} \right]$$

$$Z_p(\omega) = \left[ 1 - \frac{\partial}{\partial \omega} \Sigma_p^c(\omega) \right]^{-1}$$

$$0 \leq Z_p(\omega) \leq 1$$

# Theory

## Self-energy

### Self-energy and renormalization factor

$$\Sigma_p^c(\omega) = \sum_m \left[ \sum_i^{\text{occ}} \frac{|(ip|\rho_m)|^2}{\omega - \epsilon_i + \Omega_m} + \sum_a^{\text{virt}} \frac{|(ap|\rho_m)|^2}{\omega - \epsilon_a - \Omega_m} \right]$$

$$Z_p(\omega) = \left[ 1 - \frac{\partial}{\partial \omega} \Sigma_p^c(\omega) \right]^{-1}$$

$$0 \leq Z_p(\omega) \leq 1$$

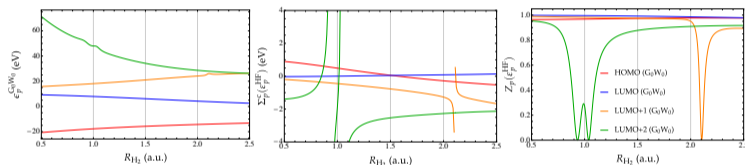
### Poles of $\Sigma_p^c(\omega)$

$$\omega = \epsilon_i - \Omega_m \quad \text{or} \quad \omega = \epsilon_a + \Omega_m$$

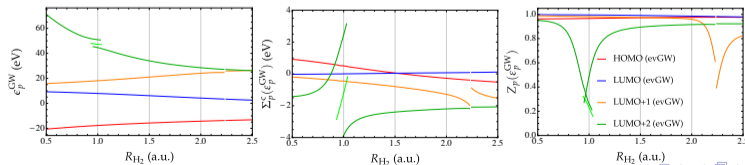
# Results

## Virtual orbitals: $H_2$

### $G_0W_0@HF/6-31G$



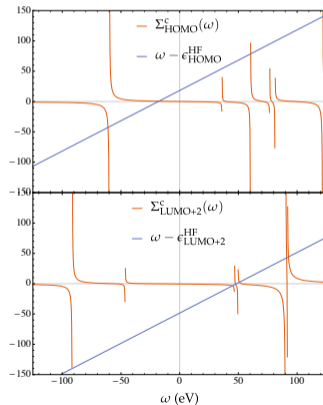
### evGW@HF/6-31G



# Results

## Graphical view

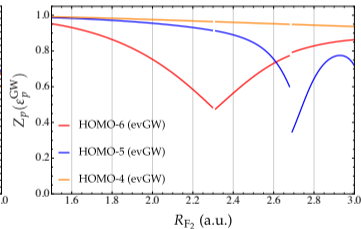
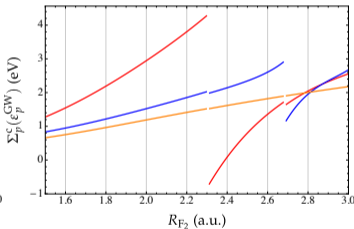
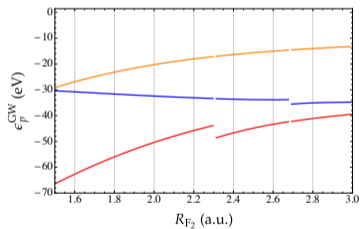
$\text{H}_2$  evGW@HF/6-31G  $R_{\text{H}_2} = 1.0 a_0$



# Results

## Occupied orbitals

### F<sub>2</sub> evGW@HF/STO-3G





# Results

## KS/HF

### Frontier orbitals stable GW interval

$$\omega = \epsilon_i - \Omega_m \quad \text{or} \quad \omega = \epsilon_a + \Omega_m$$

$$\epsilon_{\text{HOMO}}^{\text{HF/KS}} - \Omega_1 < \omega < \epsilon_{\text{LUMO}}^{\text{HF/KS}} + \Omega_1$$

$$\Omega_1 \simeq E_{\text{gap}}$$

$$E_F - \frac{3}{2}E_{\text{gap}} < \omega < E_F + \frac{3}{2}E_{\text{gap}}$$

### HF vs KS gap

$$E_{\text{KS}} \ll E_{\text{HF}}$$

# The QUEST database of vertical excitation energies

## Introduction

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

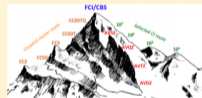
Pierre-François Loos,<sup>\*,†</sup> Anthony Scemama,<sup>†</sup> Aymeric Blondel,<sup>‡</sup> Yann Garniron,<sup>†</sup> Michel Caffarel,<sup>†</sup> and Denis Jacquemin<sup>\*,†</sup>

<sup>\*</sup>Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, 31013 Toulouse Cedex 6, France

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#### 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(D<sub>ext</sub>), CC2, STEOM-CCSD, CCSD, CCSDR(3), CCSDT-3, CC3, CCSDT<sub>n</sub>, and CCSDTQ. It turns out that CCSDTQ 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.



# 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

# The two usage of the QUEST project

## Two type of usage

- ▶ 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://lcpq.github.io/QUESTDB_website)  
[https://github.com/LCPQ/QUESTDB\\_website](https://github.com/LCPQ/QUESTDB_website)

M. Vériel et al., WIREs Comput. Mol. Sci. 11, e1517 (2021)

# Before testing a quantum chemistry software

## Problematic

### The normal way

- ▶ Install dependency
- ▶ Configuring
- ▶ Compile

### The ideal way

Open a webpage

# 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=vin
```

```
Your ID is : 212ec67e0130ec195a8c53467b677e786151136394a2eef8f0b0ba1296b4a261
Session allocated.
There are 3 sessions left available

  QP
  QP
  QP

-- Quantum Package Shell --

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

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

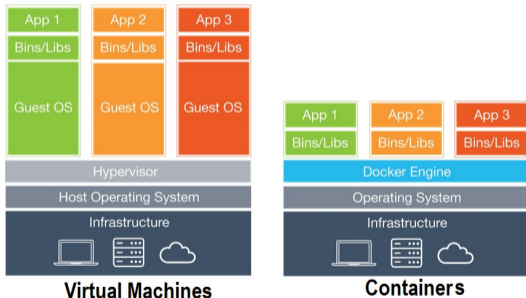
[https://github.com/mveril/qp\\_demo](https://github.com/mveril/qp_demo)

[https://hub.docker.com/r/mveril/qp\\_demo](https://hub.docker.com/r/mveril/qp_demo)

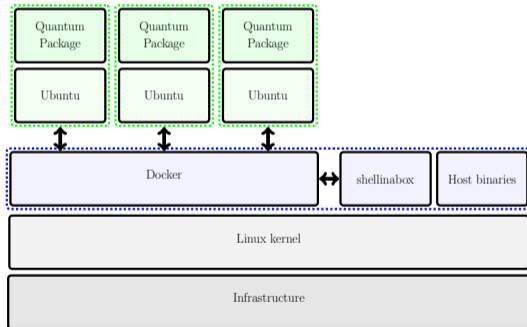
# QUANTUM PACKAGE demo

## Architecture

### DOCKER vs Virtual Machine <sup>1</sup>



### QUANTUM PACKAGE demo architecture



<sup>1</sup> <https://www.lebigdata.fr/docker-definition>



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

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Export Citation



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Yann Damour,<sup>1</sup> Mickaël Véril,<sup>1</sup> Fábris Kossoski,<sup>1</sup> Michel Caffarel,<sup>1</sup> Denis Jacquemin,<sup>2,4)</sup> Anthony Scemama,<sup>1,4)</sup> and Pierre-François Loos<sup>1,4)</sup>

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<sup>2</sup>Université de Nantes, CNRS, CEISAM UMR 6230, F-44000 Nantes, France

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<sup>4)</sup>Electronic mail: [scemama@irsamc.ups-tlse.fr](mailto:scemama@irsamc.ups-tlse.fr)

<sup>5)</sup>Author to whom correspondence should be addressed: [loos@irsamc.ups-tlse.fr](mailto:loos@irsamc.ups-tlse.fr)

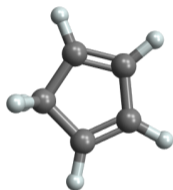
## ABSTRACT

Following our recent work on the benzene molecule [P.-F. Loos, Y. Damour, and A. Scemama, *J. Chem. Phys.* **153**, 176101 (2020)], 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 12 five- and six-membered ring molecules (cyclopentadiene, furan, imidazole, pyrrole, thiophene, benzene, pyrazine, pyridazine, pyridine, pyrimidine, *s*-tetrazine, and *s*-triazine) in the standard correlation-consistent double- $\zeta$  Dunning basis set (cc-pVDZ). Our FCI correlation energy estimates, with an estimated error smaller than 1 millihartree, are based on energetically optimized-orbital selected configuration interaction calculations performed with the *configuration interaction using a perturbative selection made iteratively* 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), is 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.

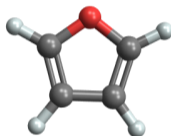
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# Molecules

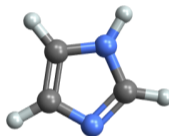
## 5-membered rings



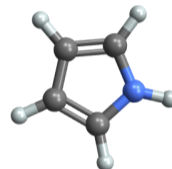
cyclopentadiene



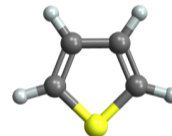
furan



imidazole

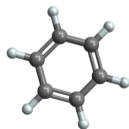


pyrrole

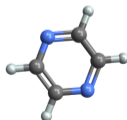


thiophene

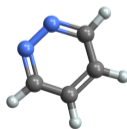
## 6-membered rings



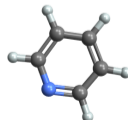
benzene



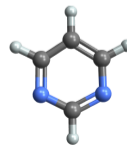
pyrazine



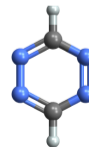
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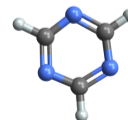
pyridine



pyrimidine

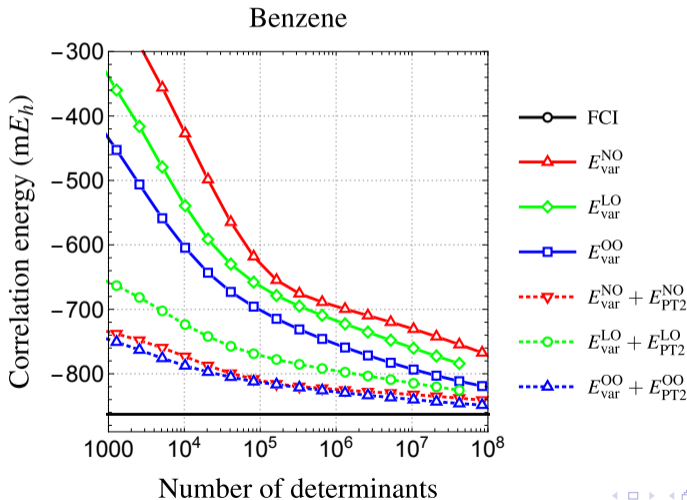


s-tetrazine

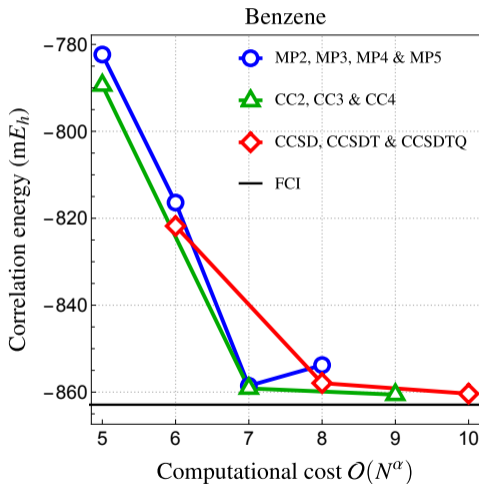


s-triazine

# Performance of optimized orbitals (cc-pVDZ)



# Benchmark (cc-pVDZ)



## Conclusion


- ▶ Multiple solution issues
- ▶ Irregularities in  $G_0W_0$
- ▶ Discontinuities in  $evGW$

## GW

## Perspectives

## Potential Energy Surfaces without Unphysical Discontinuities: The Coulomb Hole Plus Screened Exchange Approach


J. Arjan Berger,\* Pierre-François Loos, and Pina Romaniello

 Cite This: *J. Chem. Theory Comput.* 2021, 17, 191–200

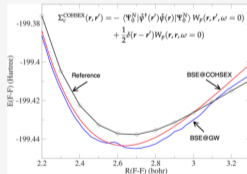
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**ABSTRACT:** In this work, we show the advantages of using the Coulomb hole plus screened exchange (COHSEX) approach in the calculation of potential energy surfaces (PES). In particular, we demonstrate that, unlike perturbative GW and partial self-consistent GW approaches, such as eigenvalue self-consistent GW and quasi-particle (QP) self-consistent GW, the COHSEX approach yields smooth PES without irregularities and discontinuities. Moreover, we show that the ground-state PES obtained from the Bethe–Salpeter equation (BSE), within the adiabatic connection fluctuation dissipation theorem, built with QP energies obtained from perturbative COHSEX on top of Hartree–Fock (BSE@COHSEX@HF) yield very accurate results for diatomic molecules close to their equilibrium distance. When self-consistent COHSEX QP energies and orbitals are used to build the BSE equation, the results become independent of the starting point. We show that self-consistency worsens the total energies but improves the equilibrium distances with respect to BSE@COHSEX@HF. This is mainly due to the changes in the screening inside the BSE.



J. A. Berger et al., *J. Chem. Theory. Comput.* 17, 191–200 (2021)

## Scrutinizing GW-Based Methods Using the Hubbard Dimer

S. Di Sabatino<sup>1,2\*</sup>, P.-F. Loos<sup>1</sup> and P. Romaniello<sup>2</sup>

<sup>1</sup>Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, Toulouse, France, <sup>2</sup>Laboratoire de Physique Théorique, Université de Toulouse, CNRS, UPS and ETSF, Toulouse, France

Using the simple (symmetric) Hubbard dimer, we analyze some important features of the GW approximation. We show that the problem of the existence of multiple quasiparticle solutions in the (perturbative) one-shot GW method and its partially self-consistent version is solved by full self-consistency. We also analyze the neutral excitation spectrum using the Bethe-Salpeter equation (BSE) formalism within the standard GW approximation and find, in particular, that 1) some neutral excitation energies become complex when the electron-electron interaction  $U$  increases, which can be traced back to the approximate nature of the GW quasiparticle energies; 2) the BSE formalism yields accurate correlation energies over a wide range of  $U$  when the trace (or plasmon) formula is employed; 3) the trace formula is sensitive to the occurrence of complex excitation energies (especially singlet), while the expression obtained from the adiabatic-connection fluctuation-dissipation theorem (ACFDT) is more stable (yet less accurate); 4) the trace formula has the correct behavior for weak (*i.e.*, small  $U$ ) interaction, unlike the ACFDT expression.

**Keywords:** hubbard dimer, multiple quasiparticle solutions, GW, bethe-salpter equation, trace formula, adiabatic-connection fluctuation-dissipation theorem

S. Di Sabatino et al., *Front. Chem.* **9**, 865 (2021)

# QUEST

## Conclusion

- ▶ Large database of vertical excitation energies (more than 600)
- ▶ Combine data from currently 6 main publications
- ▶ Easy to use using the [https://lcpq.github.io/QUESTDB\\_website](https://lcpq.github.io/QUESTDB_website)

## Perspectives

- ▶ Add new data from other publications
- ▶ Improve referece data using optimized orbitals
- ▶ Improve quality of the website code



## QUEST

## Perspectives

## Reference Energies for Intramolecular Charge-Transfer Excitations

Pierre-François Loos,\* Massimiliano Comin, Xavier Blase,\* and Denis Jacquemin\*

Cite This: *J. Chem. Theory Comput.* 2021, 17, 3666–3686

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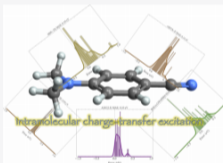


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Supporting Information

**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 ( $\pi$ -conjugated) molecular compounds. To this end, we apply a composite protocol consisting of linear-response CCSDT excitation energies determined with Dunning's double- $\zeta$  basis set corrected by CC3/CCSDT-3 energies obtained with the corresponding triple- $\zeta$  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,  $\beta$ -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- $\omega$ HPBE,  $\omega$ B97X,  $\omega$ 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 ( $\leq 0.10$  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  $\omega$ 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.

P.-F. Loos et al., *J. Chem. Theory Comput.* 17, 3666–3686 (2021)

## QUEST

## Perspectives

## A Mountaineering Strategy to Excited States: Highly Accurate Energies and Benchmarks for Bicyclic Systems

Published as part of *The Journal of Physical Chemistry virtual special issue "Vincenzo Barone Festschrift"*.

Pierre-François Loos\* and Denis Jacquemin\*



Cite This: *J. Phys. Chem. A* 2021, 125, 10174–10188



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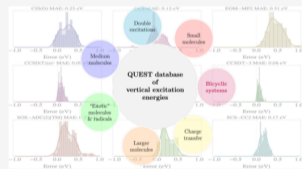
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Supporting Information

**ABSTRACT:** Pursuing our efforts to define highly accurate estimates of the relative energies of excited states in organic molecules, we investigate, with coupled-cluster methods including iterative triples (CC3 and CCSDT), the vertical excitation energies of 10 bicyclic molecules (azulene, benzoxadiazole, benzothiadiazole, diketopyrrolopyrrole, furofuran, phthalazine, pyrrolopyrrole, quinoxaline, tetrathiafulvalene, and thienothiophene). In total, we provide *aug-cc-pVTZ* reference vertical excitation energies for 91 excited states of these relatively large systems. We use these reference values to benchmark various wave function methods, i.e., CIS(D), EOM-MP2, CC2, CCSD, STEOM-CCSD, CCSD(T)-(a)\*, CCSDR(3), CCSDT-3, ADC(2), ADC(2.5), and ADC(3), as well as some spin-scaled variants of both CC2 and ADC(2).

These results are compared to those obtained previously on smaller molecules. It turns out that while the accuracy of some methods is almost unaffected by system size, e.g., CIS(D) and CC3, the performance of others can significantly deteriorate as the systems grow, e.g., EOM-MP2 and CCSD, whereas others, e.g., ADC(2) and CC2, become more accurate for larger derivatives.



P.-F. Loos and D. Jacquemin, *J. Phys. Chem. A* 125, 10174–10188 (2021)



# Quantum Package demo in a web browser

## Conclusion

- ▶ An ability for new users to test `QUANTUM PACKAGE` without any effort
- ▶ Allow to increase `QUANTUM PACKAGE` popularity
- ▶ Availability to download the container allow to use `QUANTUM PACKAGE` in more desktop scenario

## Perspectives

- ▶ `QUANTUM PACKAGE` container in HPC scenario (`SINGULARITY`)
- ▶ Dev container

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

## Conclusion

- ▶ A huge performance improvement for CIPSI calculation using optimized orbitals method (same results with  $100\times$  less determinants)
- ▶ Provide references data for ground state correlation energies

## Perspectives

- ▶ Apply the same methods for other challenging molecules like transition metal compounds
- ▶ Use the optimized orbitals for excited states



Anthony Scemama



Arjan Berger



Denis Jacquemin



Michel Caffarel



Pierre-François Loos

# THANKS !



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Martial  
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