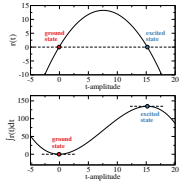
Higher roots of the Schrödinger equation

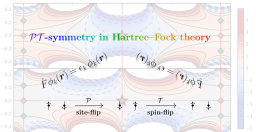
Pierre-François (Titou) LOOS & Friends

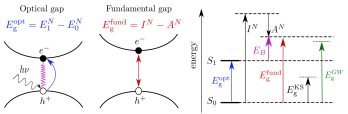
Laboratoire de Chimie et Physique Quantiques (UMR 5626),
Université de Toulouse, CNRS, UPS, Toulouse, France.

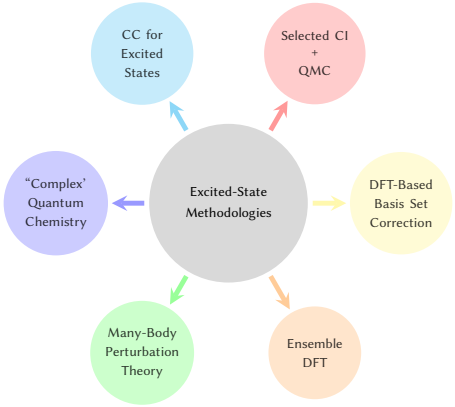
NanoX-FeRMI days (March 10th 2022)

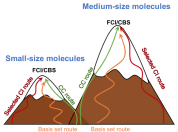
General overview of our research group

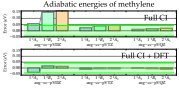


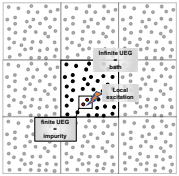






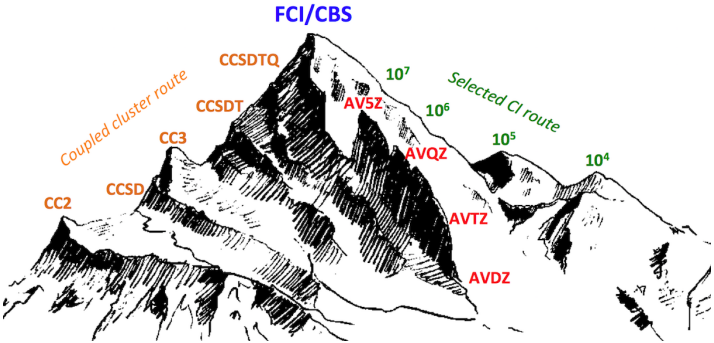






Section 1

Selected CI



Selected CI or how to create new methods with new acronyms

"SCI+PT2 methods provide near full CI (FCI) quality energies with only a small fraction of the determinants of the FCI space"

- CIPSI (Malrieu, Evangelisti, Angeli, Spiegelman, Giner, Caffarel, Scemama, etc)
- Semistochastic Heat-bath CI (Sharma & Umrigar)
- Adaptive sampling CI (Evangelista & Tubman)
- Incremental CI (Zimmerman)
- Iterative CI (Liu & Hoffmann)
- FCIQMC (Alavi & Booth)
- ...

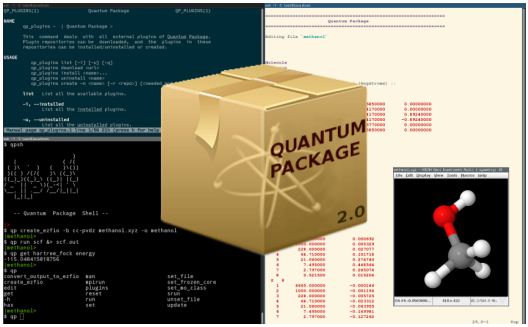
One selected CI (SCI) algorithm to rule them all

CIPSI = CI using a Perturbative Selection made Iteratively

- Developed in Toulouse many (many) years ago
  Huron, Malrieu & Rancurel, JCP 58 (1973) 5745
- Based on old idea by Bender and Davidson, and Whitten and Hackmeyer
  Bender & Davidson, Phys. Rev. 183 (1969) 23
  Whitten & Hackmeyer, JCP 51 (1969) 5584
- CIPSI (and SCI methods in general) has been recently resurrected!
  Giner, Scemama & Caffarel, CJC 91 (2013) 879
  Giner, Scemama & Caffarel, JCP 142 (2015) 044115
- CIPSI $\approx$ deterministic version of FCIQMC
  Caffarel et al., Recent Progress in Quantum Monte Carlo (2016) Chap. 2, 15-46.

Selected CI methods

"SCI+PT2 methods provide near full CI (FCI) quality energies with only a small fraction of the determinants of the FCI space"

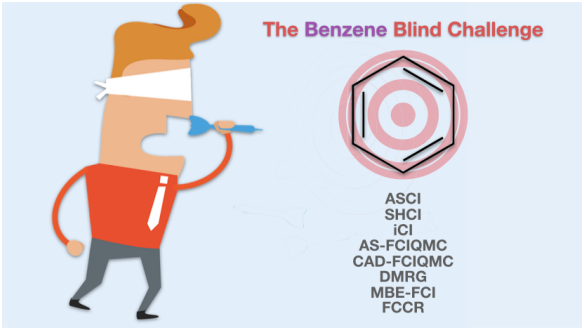


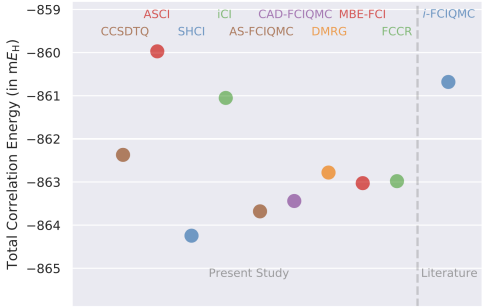
"Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs", Garniron et al., JCTC 15 (2019) 3591

Anthony Scemama

Michel Caffarel

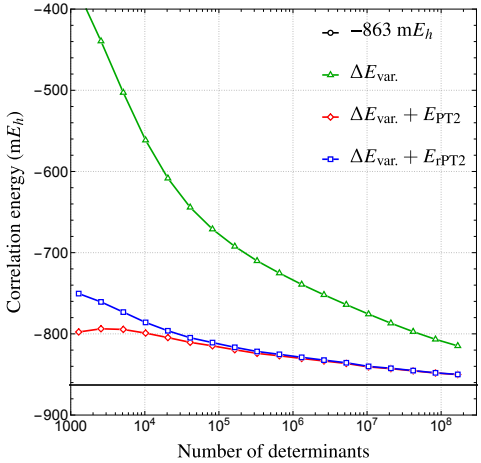
The Benzene Blind Challenge: Frozen-core correlation energy (cc-pVDZ)

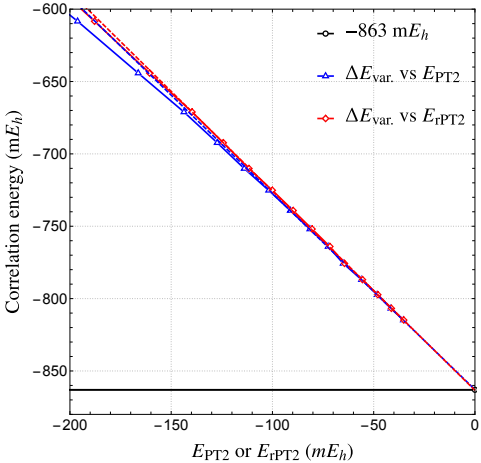




Eriksen et al. JPCL 11 (2020) 8922

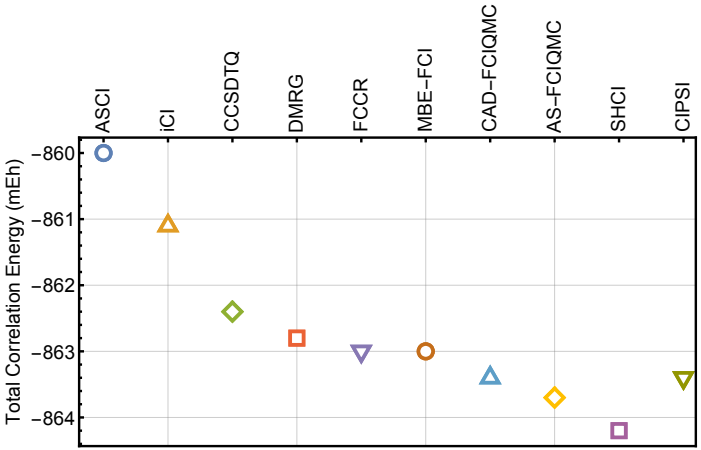
Performance of CIPSI for C_6H_6/cc-pVDZ (1)





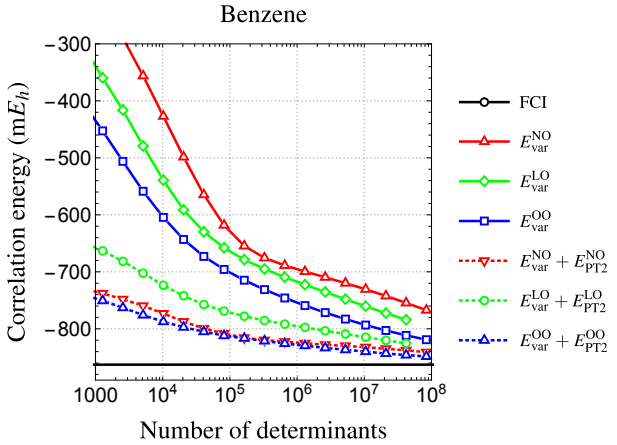
Loos, Damour & Scemama JCP 153 (2020) 176101

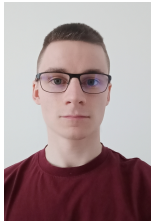
Performance of CIPSI for C_6H_6/cc-pVDZ (2)



Loos, Damour & Scemama JCP 153 (2020) 176101

Orbital-optimized CIPSI for C_6H_6/cc-pVDZ (and many others)





Yann Damour (PhD) ⇒ **POSTER**

Damour, Veril, Kossoski, Caffarel, Jacquemin, Scemama & Loos JCP 155 (2020) 176101

CIPSI trial wave functions for periodic solids

Toward a systematic improvement of the fixed-node approximation in diffusion Monte Carlo for solids—A case study in diamond

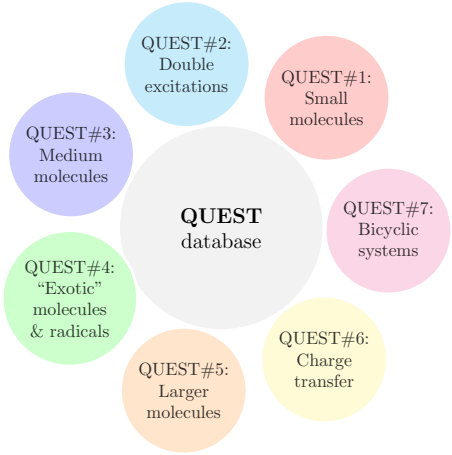
Cite as: J. Chem. Phys. **153**, 184111 (2020); https://doi.org/10.1063/5.0021036
Submitted: 06 July 2020 . Accepted: 12 October 2020 . Published Online: 11 November 2020

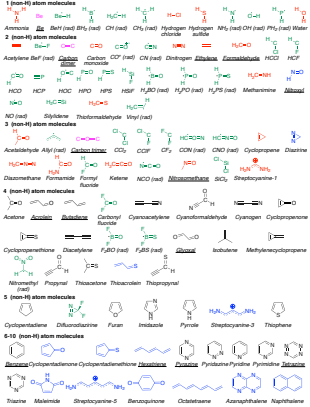
Anouar Benali, Kevin Gasperich, Kenneth D. Jordan, Thomas Applencourt, Ye Luo, M. Chandler Bennett, Jaron T. Krogel, Luke Shulenburger, Paul R. C. Kent, Pierre-François Loos, Anthony Scemama, and Michel Caffarel

See also Scemama, Giner, Benali & Loos JCP 153 (2021) 174107 for a range-separated approach in molecules

Highly-accurate excitation energies: The QUEST project (1)

"The aim of the QUEST project is to provide to the community a large set of highly-accurate excitation energies for various types of excited states"





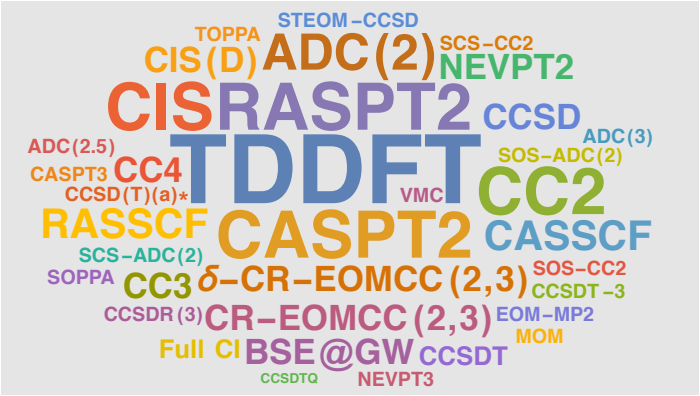
Mika Veril (PhD)

Martial Boggio-Pasqua

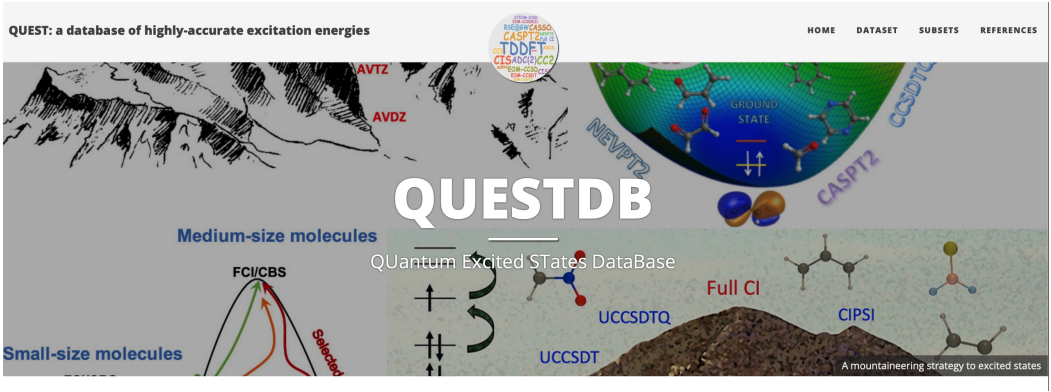
Denis Jacquemin

Electronic structure nightmare...

And this is just for excited states...



Highly-accurate excitation energies: The QUEST project (2)

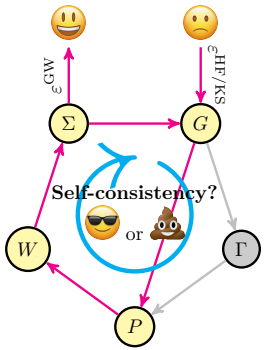


Véril et al. WIREs Comput. Mol. Sci. 11 (2021) e1517

https://lcpq.github.io/QUESTDB_website/

Section 2

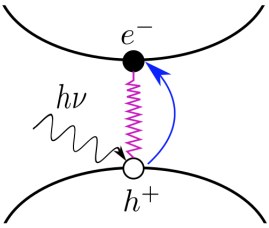
Many-body perturbation theory



Fundamental gap vs Optical gap

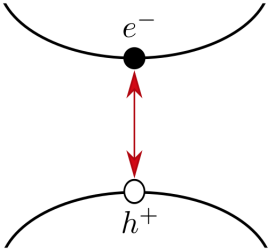
Optical gap

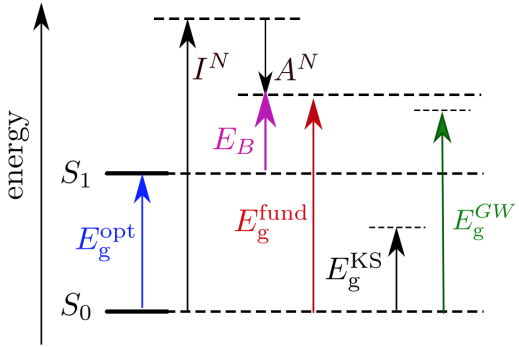
$$E_{\rm g}^{\rm opt} = E_1^N - E_0^N$$



Fundamental gap

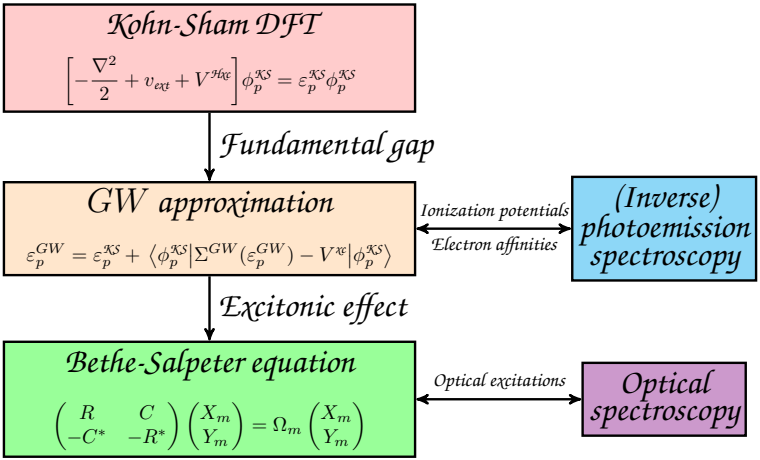
$$E_{\rm g}^{\rm fund} = I^N - A^N$$





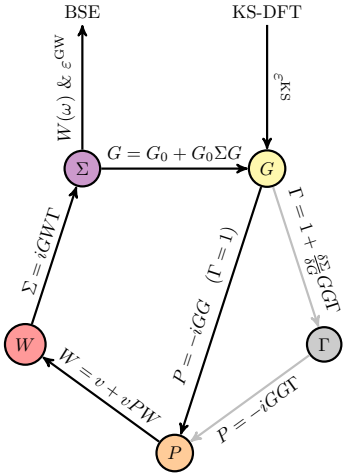
Blase, Duchemin, Jacquemin & Loos JPCL 11 (2020) 7371

The MBPT chain of actions



Blase, Duchemin, Jacquemin & Loos JPCL 11 (2020) 7371

The *GW* approximation: Hedin's pentagon



Hedin, Phys. Rev. 139 (1965) A796

The bridge between TD-DFT and BSE

TD-DFT	Connection	BSE
One-point density $\rho(1)$	$\rho(1) = -iG(11^+)$	Two-point Green's function $G(12)$
Two-point susceptibility $\chi(12) = \frac{\partial \rho(1)}{\partial U(2)}$	$\chi(12) = -iL(12;1^+2^+)$	Four-point susceptibility $L(12;34) = \frac{\partial G(13)}{\partial U(42)}$
Two-point kernel $K(12) = v(12) + \frac{\partial V^{xc}(1)}{\partial \rho(2)}$		Four-point kernel $i\Xi(1234) = v(13)\delta(12)\delta(34) - \frac{\partial \Sigma^{xc}(12)}{\partial G(34)}$

Recent Developments in Many-Body Perturbation Theory [JPCL 11 (2020) 7371]

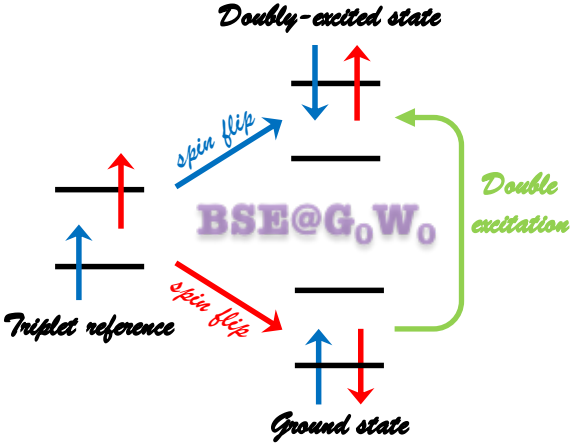
- scGW: Effect of self-consistency in *GW* methods [JCTC 14 (2018) 3071; 14 (2018) 5220; Front. Chem. 9 (2021) 751054]
- AC@BSE: Adiabatic connection formalism for total energies in BSE [JPCL 11 (2020) 3536; JCTC 17 (2021) 191]
- dBSE: Dynamical effects in BSE [JCP 153 (2020) 114120; 153 (2020) 184105; arXiv:2202.07936]
- sf-BSE: Spin-flip formalism for double excitations [JCTC 17 (2021) 2852]

Stefano Di Sabatino (Postdoc NanoX)

Roberto Orlando (PhD 80|PRIME)

Pina Romaniello (LPT)

Spin-flip BSE formalism



Monino & Loos, JCTC 17 (2021) 2852

Enzo Monino (PhD ERC)

Bethe-Salpeter for ground-state energies

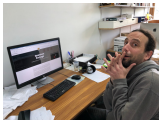
THE JOURNAL OF PHYSICAL CHEMISTRY Letters

pubs.acs.org/JPCL Letter

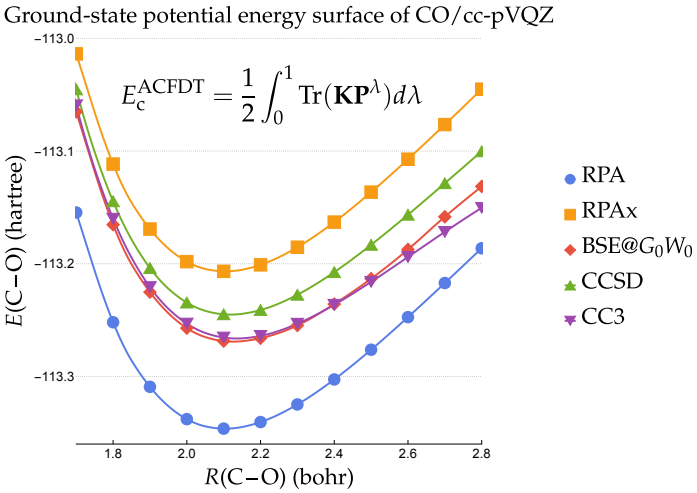
Pros and Cons of the Bethe–Salpeter Formalism for Ground-State Energies

Pierre-François Loos,* Anthony Scemama, Ivan Duchemin, Denis Jacquemin,* and Xavier Blase*

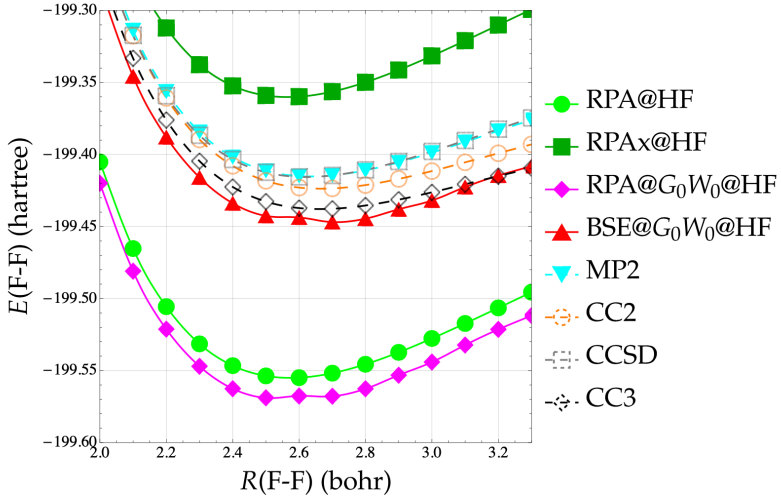
Cite This: *J. Phys. Chem. Lett.* 2020, 11, 3536–3545 Read Online



Bethe-Salpeter for ground-state energies



Bethe-Salpeter for ground-state energies



The elephant in the room of *GW*

JCTC Journal of Chemical Theory and Computation

Article

Cite This: *J. Chem. Theory Comput.* 2018, 14, 3071−3082

pubs.acs.org/JCTC

Green Functions and Self-Consistency: Insights From the Spherium Model

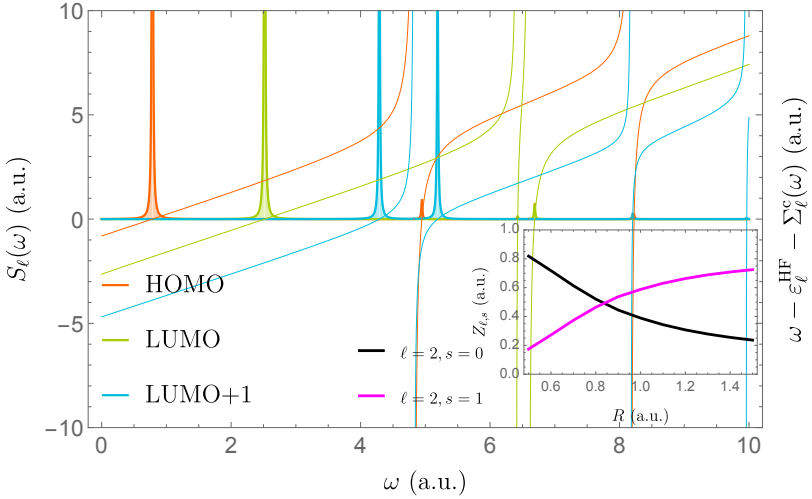
Pierre-François Loos,*[,†] Pina Romaniello,[‡,¶] and J. A. Berger[†,¶]

[†]Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, 31062 Toulouse, France

[‡]Laboratoire de Physique Théorique, Université de Toulouse, CNRS, UPS, 31062 Toulouse, France

[¶]European Theoretical Spectroscopy Facility (ETSF)

The elephant in the room of *GW*



The elephant in the room of *GW*

JCTC Journal of Chemical Theory and Computation

Article

Cite This: *J. Chem. Theory Comput.* 2018, 14, 5220−5228

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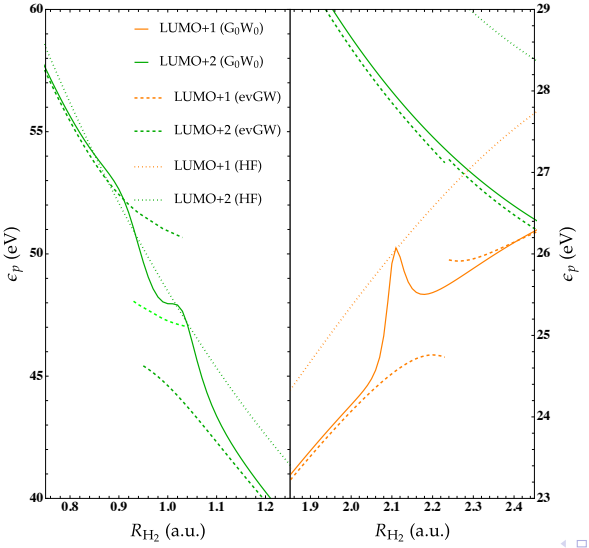
Unphysical Discontinuities in *GW* Methods

Mickaël Véril,[†] Pina Romaniello,[‡,¶] J. A. Berger,[†,¶] and Pierre-François Loos*[,†]

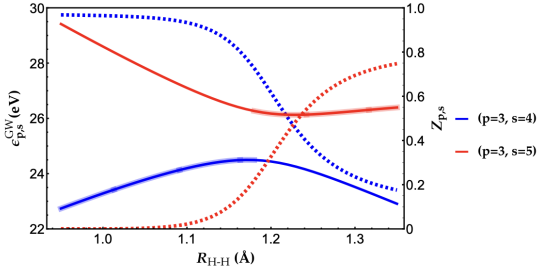
[†]Laboratoire de Chimie et Physique Quantiques, [‡]Laboratoire de Physique Théorique, and [¶]European Theoretical Spectroscopy Facility (ETSF), Université de Toulouse, CNRS, UPS, Toulouse, France

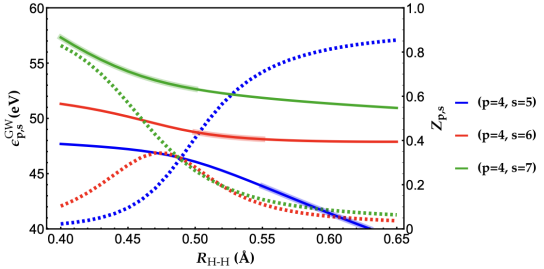


The elephant in the room of *GW* (H_2/6-31G)



Intruder States & Regularization

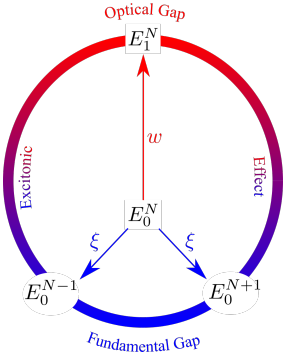




Monino & Loos, arXiv:2202.11589

Section 3

Density-functional theory for ensembles



© Bruno Senjean

eDFT for neutral excitations

A weight-dependent local correlation density-functional approximation for ensembles

Cite as: J. Chem. Phys. 152, 214101 (2020); doi: 10.1063/5.0007388
Submitted: 12 March 2020 • Accepted: 12 May 2020 •
Published Online: 1 June 2020

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Pierre-François Loos[1,a] and Emmanuel Fromager[2,b]

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[2]Laboratoire de Chimie Quantique, Institut de Chimie, CNRS, Université de Strasbourg, Strasbourg, France

Faraday Discussions
Cite this: *Faraday Discuss.*, 2020, **224**, 402

ROYAL SOCIETY OF CHEMISTRY

PAPER

Weight dependence of local exchange–correlation functionals in ensemble density-functional theory: double excitations in two-electron systems

Clotilde Marut, [a] Bruno Senjean, [bc] Emmanuel Fromager [d] and Pierre-François Loos [*a]



Gross-Oliveira-Kohn (GOK) DFT in a three-state ensemble

Ensemble energy:

$$\boxed{E^{\mathbf{w}} = (1 - w_1 - w_2)E^{(0)} + w_1 E^{(1)} + w_2 E^{(2)}}$$

Excitation energies:

$$\frac{\partial E^{\mathbf{w}}}{\partial w_1} = E^{(1)} - E^{(0)} = \Omega^{(1)} \qquad \frac{\partial E^{\mathbf{w}}}{\partial w_2} = E^{(2)} - E^{(0)} = \Omega^{(2)}$$

Ensemble energy in practice:

$$E^{\mathbf{w}} = \min_n \left\{ F^{\mathbf{w}}[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\} \qquad F^{\mathbf{w}}[n] = T_{\text{s}}^{\mathbf{w}}[n] + E_{\text{Hxc}}^{\mathbf{w}}[n]$$

Derivative discontinuity:

$$\boxed{\frac{\partial E^{\mathbf{w}}}{\partial w_I} = \mathcal{E}_I^{\mathbf{w}} - \mathcal{E}_0^{\mathbf{w}} + \left. \frac{\partial E_{\text{xc}}^{\mathbf{w}}[n]}{\partial w_I} \right|_{n=n^{\mathbf{w}}(\mathbf{r})} \qquad E_{\text{xc}}^{\mathbf{w}}[n] = \int \epsilon_{\text{xc}}^{\mathbf{w}}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}}$$

Construction of a weight-dependent LDA functional

Three-state ensemble exchange-correlation functional:

$$\tilde{\epsilon}_{\rm xc}^{w_1,w_2}(n) = (1-w_1-w_2)\epsilon_{\rm xc}^{(0)}(n) + w_1\epsilon_{\rm xc}^{(1)}(n) + w_2\epsilon_{\rm xc}^{(2)}(n)$$

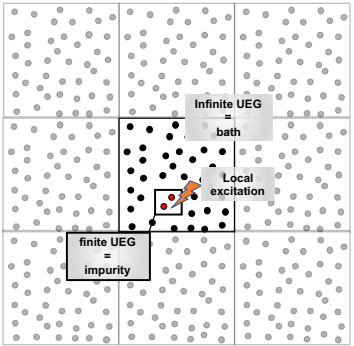
LDA-centered functionals:

$$\bar{\epsilon}_{\rm xc}^{(I)}(n) = \epsilon_{\rm xc}^{(I)}(n) + \epsilon_{\rm xc}^{\rm LDA}(n) - \epsilon_{\rm xc}^{(0)}(n)$$

$$\tilde{\epsilon}_{\rm xc}^{w_1,w_2}(n) \rightarrow \epsilon_{\rm xc}^{w_1,w_2}(n) = (1-w_1-w_2)\bar{\epsilon}_{\rm xc}^{(0)}(n) + w_1\bar{\epsilon}_{\rm xc}^{(1)}(n) + w_2\bar{\epsilon}_{\rm xc}^{(2)}(n)$$

Weight-dependent LDA functional for ensembles "eLDA":

$$\boxed{\epsilon_{\rm xc}^{w_1,w_2}(n) = \epsilon_{\rm xc}^{\rm LDA}(n) + w_1\left[\epsilon_{\rm xc}^{(1)}(n) - \epsilon_{\rm xc}^{(0)}(n)\right] + w_2\left[\epsilon_{\rm xc}^{(2)}(n) - \epsilon_{\rm xc}^{(0)}(n)\right]}$$



eDFT for charged excitations

PPLB formalism (fractional electrons) [Perdew, Parr, Levy & Balduz PRL 49 (1982) 1691]

$$E^{\boldsymbol{\alpha}} = (1-\alpha_1-\alpha_2)E^N + \alpha_1 E^{N-1} + \alpha_2 E^{N+1}$$
$$n^{\boldsymbol{\alpha}} = (1-\alpha_1-\alpha_2)n^N + \alpha_1 \Gamma^{N-1} + \alpha_2 n^{N+1} \quad \Rightarrow \quad \int n^{\boldsymbol{\alpha}} = N - \alpha_1 + \alpha_2$$

$\Rightarrow$ The exact xc functional does not need to be weight-dependent

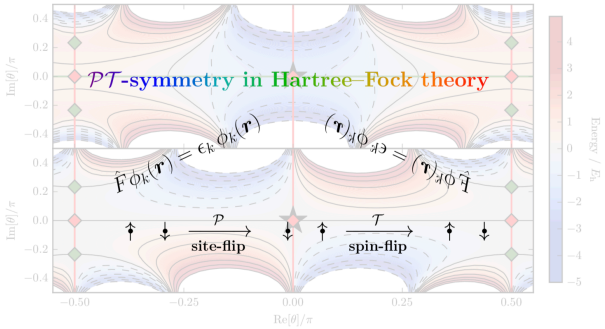
N-centered formalism [Senjean & Fromager PRA 98 (2018) 022513]

$$E^{\boldsymbol{\xi}} = \left(1 - \frac{N-1}{N}\xi_1 - \frac{N+1}{N}\xi_2\right)E^N + \xi_1 E^{N-1} + \xi_2 E^{N+1}$$
$$n^{\boldsymbol{\alpha}} = \left(1 - \frac{N-1}{N}\xi_1 - \frac{N+1}{N}\xi_2\right)n^N + \xi_1 n^{N-1} + \xi_2 n^{N+1} \quad \Rightarrow \quad \int n^{\boldsymbol{\xi}} = N$$

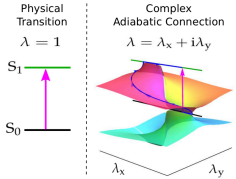
$\Rightarrow$ The exact xc functional must be weight-dependent

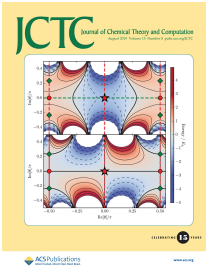
Section 4

Quantum Chemistry in the Complex Plane



Quantum Chemistry in the Complex Plane





Complex adiabatic connection: A hidden non-Hermitian path from ground to excited states

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Parity-Time Symmetry in Hartree–Fock Theory

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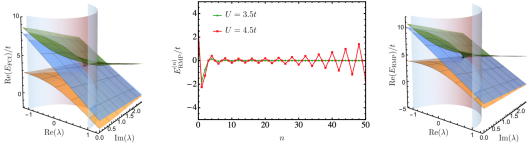
Hugh Burton (Oxford)

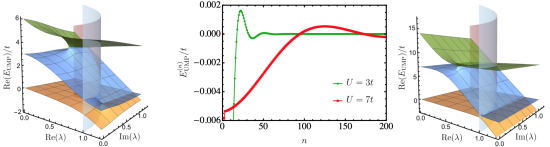
Perturbation Theory in the Complex Plane [JPCM 33 (2021) 283001]

Convergence of restricted Møller-Plesset perturbation theory



(a) $U/t = 3.5$ (b) (c) $U/t = 4.5$

Convergence of unrestricted Møller-Plesset perturbation theory



(a) $U/t = 3$ (b) (c) $U/t = 7$

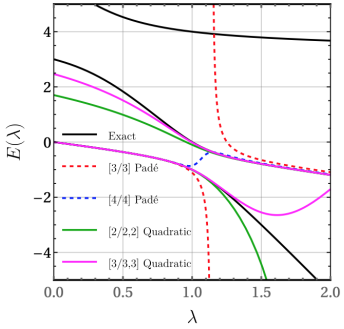
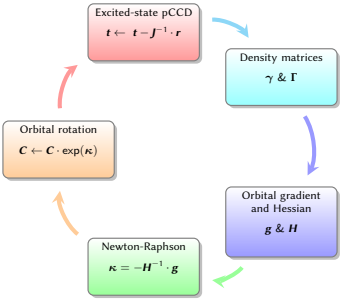


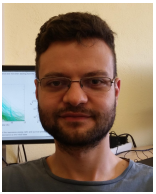
FIG. 12: UMP energies in the Hubbard dimer as a function of λ obtained using various approximants at $U/t = 3$.

Section 5

Coupled-cluster theory for excited states



Coupled-cluster theory for excited states



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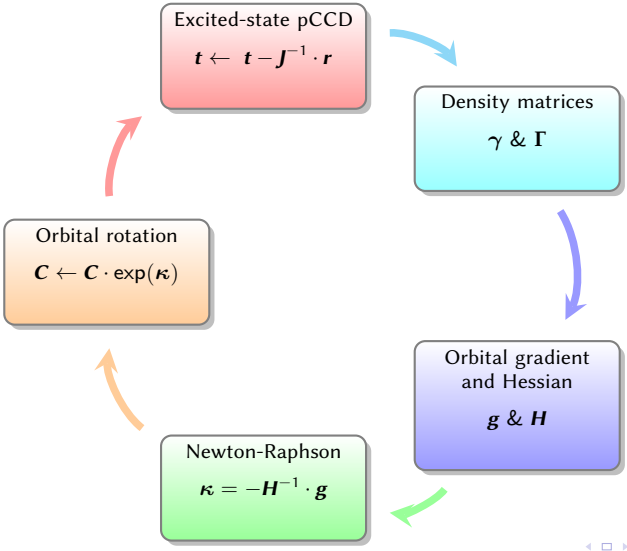
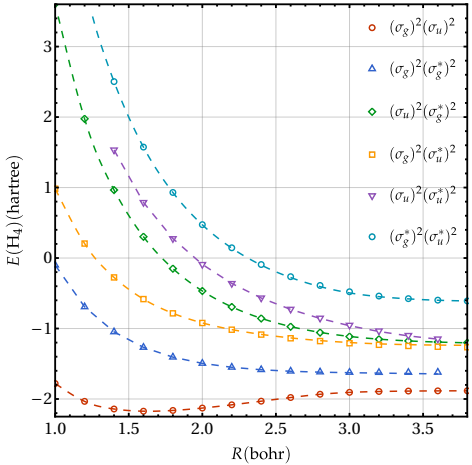
Michel Caffarel
(LCPQ)

State-specific orbital-optimized TpCCD (oo-TpCCD) for excited states



Stretching linear H_4/STO-6G: TpCCD vs DOCI with state-specific TpCCD reference



Lowest doubly-excited state of CH^+

molecule	method	ΔE (eV)	$\Delta\Delta E$ (eV)
CH^+[1]	Δoo-TpCCD	8.36	−0.19
	FCI[2]	8.55	0
	EOM-CCSDT[3]	8.62	+0.07
	EOM-CCSDt[3]	8.64	+0.09
	EOM-oo-pCCD-LCCSD[4]	8.84	+0.29
	EOM-pCCD-LCCSD[4]	7.61	−0.94
	CC3[5]	8.78	+0.23

[1] Basis set and geometry taken from Olsen et al. CPL 154 (1989) 380
[2] Results from Olsen et al. CPL 154 (1989) 380
[3] Results from Kowalski & Piecuch, CPL 347(2001) 237
[4] Results from Boguslawski, JCTC 15 (2019) 18
[5] Results from Christiansen et al. JCP 103 (1995) 7429

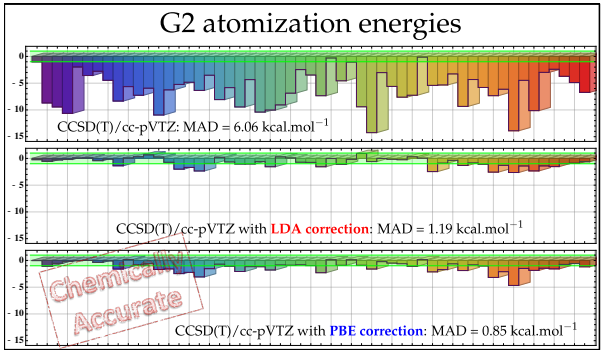
More doubly-excited states for molecules (6-31+G*)...

molecule	method	ΔE (eV)	$\Delta\Delta E$ (eV)
BH	Δoo-TpCCD	7.35	+0.24
	FCI	7.11	0
	EOM-CCSDTQ	7.12	+0.01
	EOM-CCSDT	7.15	+0.04
	CC3	7.30	+0.19
HNO	Δoo-TpCCD	4.49	−0.02
	FCI[1]	4.51	0
	EOM-CCSDTQ[1]	4.54	+0.03
	EOM-CCSDT[1]	4.81	+0.30
	CC3[1]	5.28	+0.77
H_3C-NO	Δoo-TpCCD	4.66	−0.20
	FCI[1]	4.86	0
	EOM-CCSDT[1]	5.26	+0.40
	CC3[1]	5.73	+0.87
$H_2C=O$	Δoo-TpCCD	11.26	+0.40
	FCI[1]	10.86	0
	EOM-CCSDTQ[1]	10.87	+0.01
	EOM-CCSDT[1]	11.10	+0.24
	CC3[1]	11.49	+0.63

[1] Results and geometries from Loos et al. JCTC 15 (2019) 1939

Section 6

Basis set incompleteness correction



Ground-state properties

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Letter

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A Density-Based Basis-Set Correction for Wave Function Theory

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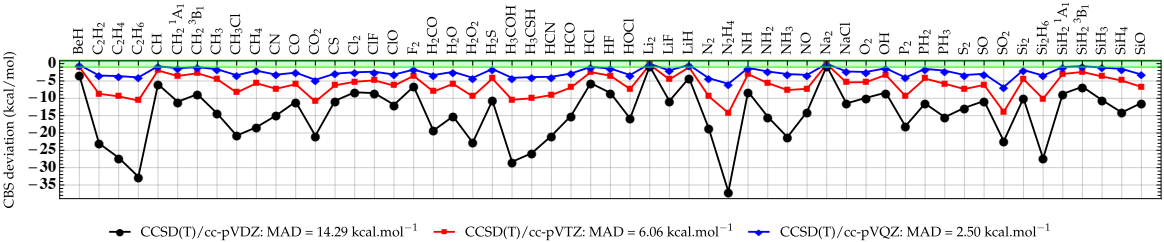
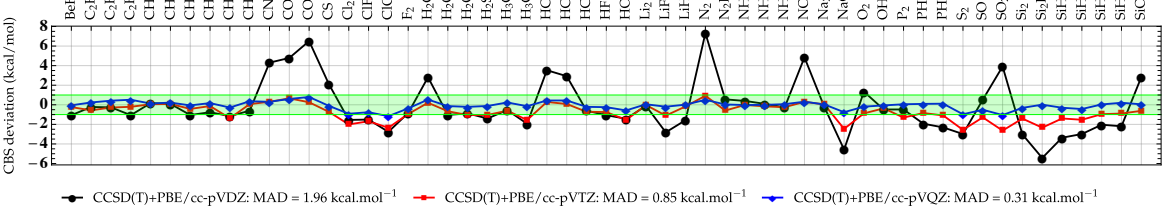
Ground-state properties





Neutral excitations

Chemically accurate excitation energies with small basis sets

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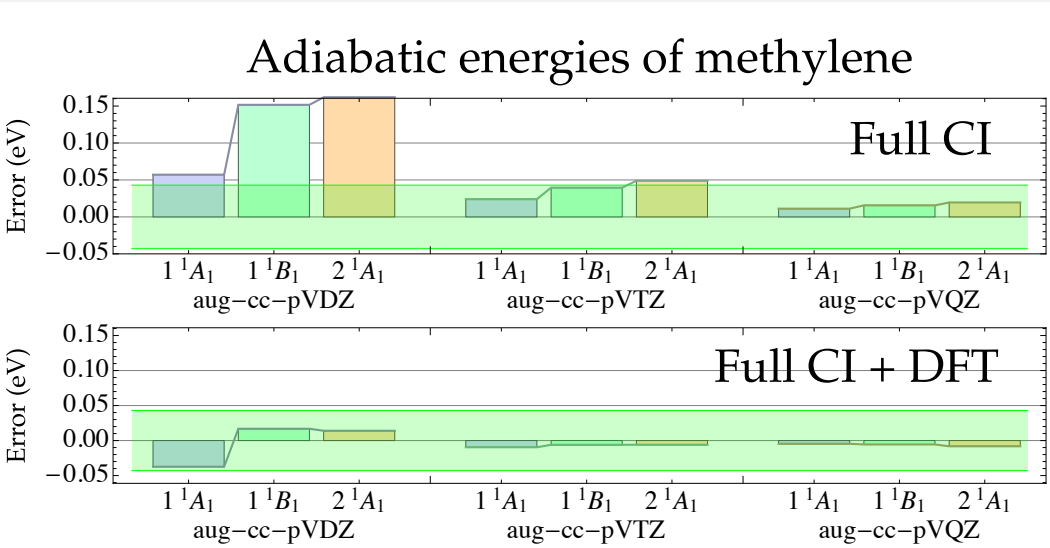
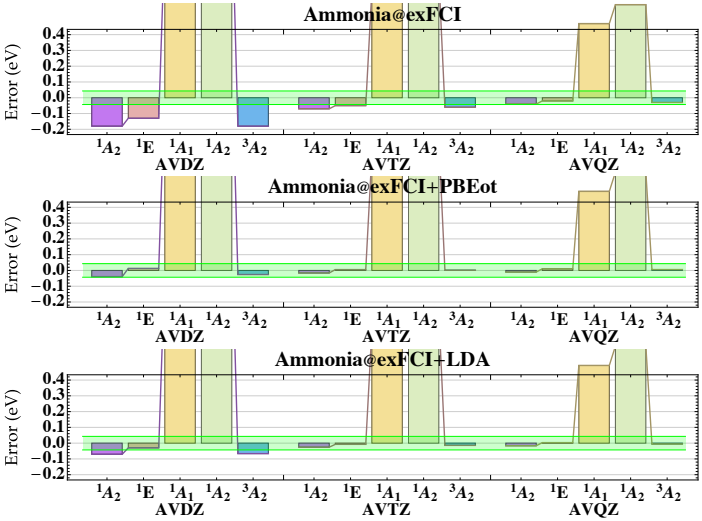
Neutral excitations



Neutral excitations



Charged excitations

JCTC Journal of Chemical Theory and Computation

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Density-Based Basis-Set Incompleteness Correction for *GW* Methods

Pierre-François Loos,* Barthélémy Pradines, Anthony Scemama, Emmanuel Giner, and Julien Toulouse*

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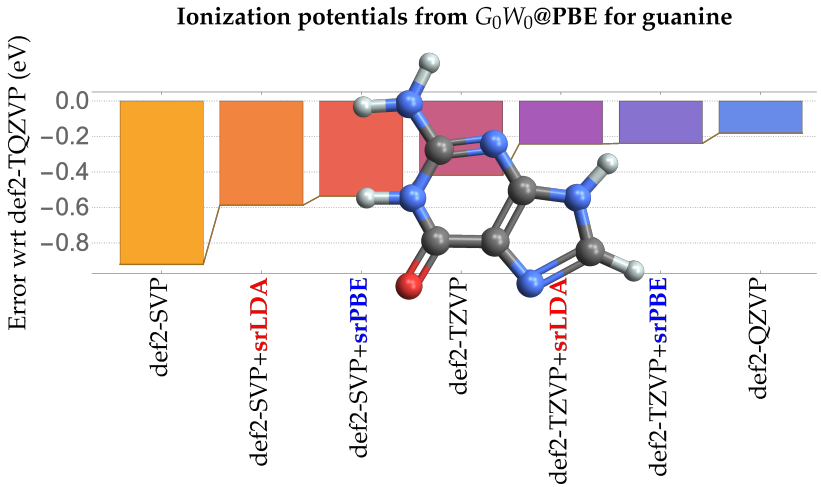
Charged excitations



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