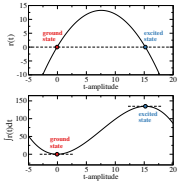
Higher roots of the Schrödinger equation

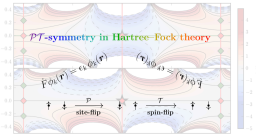
Pierre-François (Titou) LOOS & Friends

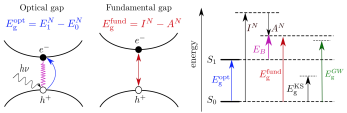
Laboratoire de Chimie et Physique Quantiques (UMR 5626),
Université de Toulouse, CNRS, UPS, Toulouse, France.

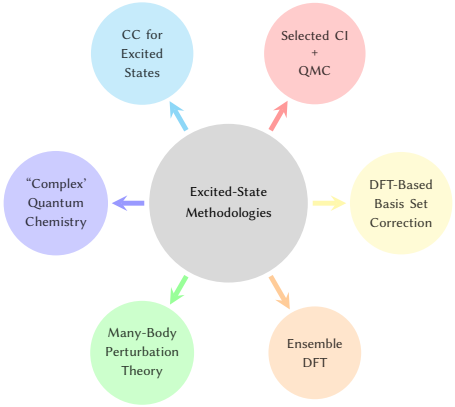
University of New Brunswick — Department of Chemistry

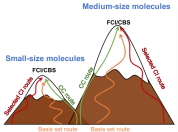
General overview of our research group

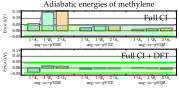


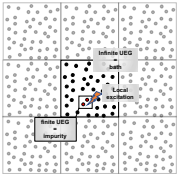






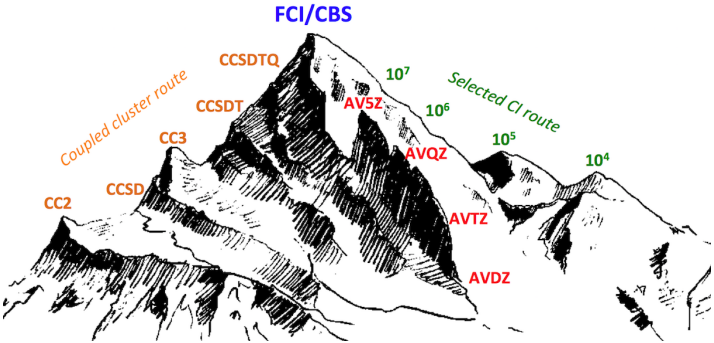






Section 1

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)
- ...

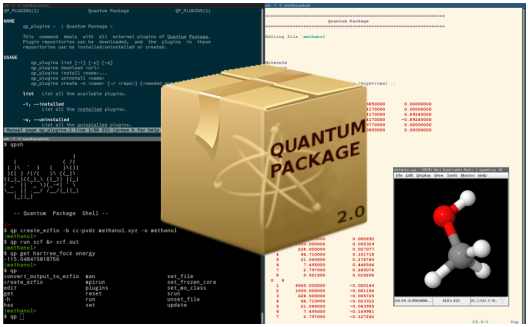
One selected CI (SCI) algorithm to rule them all

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"

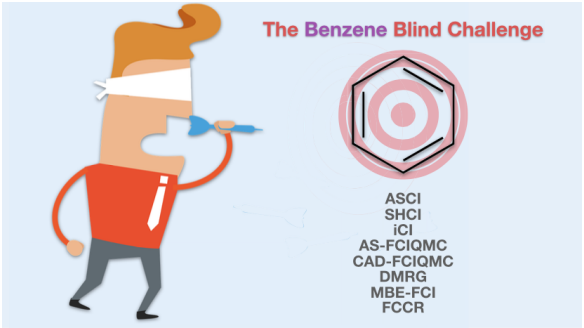


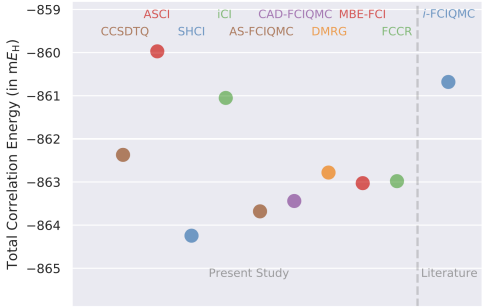
"Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs", Garniron et al., JCTC 15 (2019) 3591

Anthony Scemama

Michel Caffarel

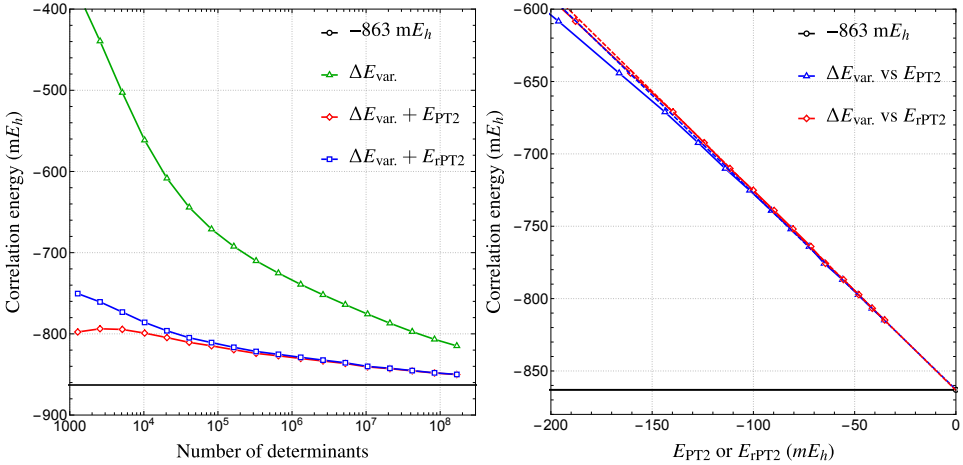
The Benzene Blind Challenge: Frozen-core correlation energy (cc-pVDZ)





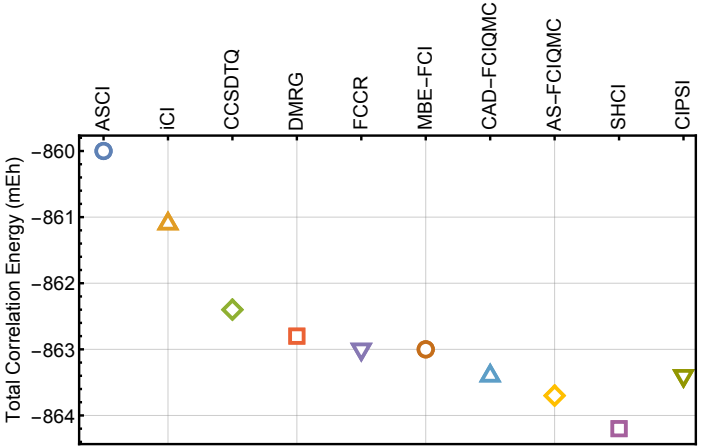
Eriksen et al. JPCL 11 (2020) 8922

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



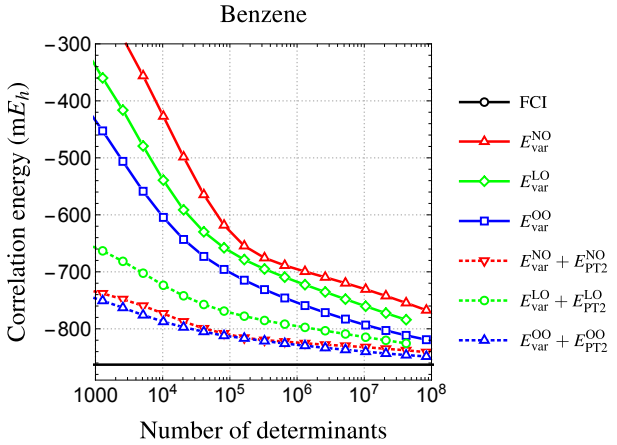
Loos, Damour & Scemama JCP 153 (2020) 176101

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)

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

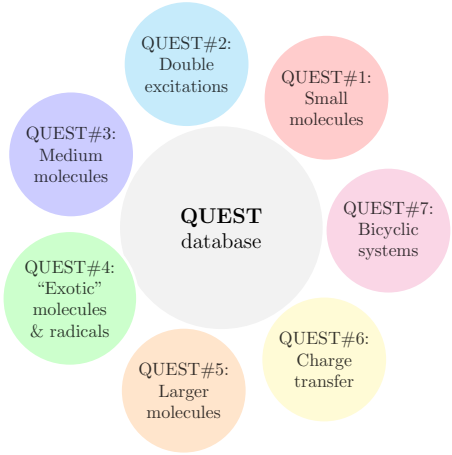
Cite as: J. Chem. Phys. **153**, 184111 (2020); https://doi.org/10.1063/5.0021036
Submitted: 06 July 2020 . Accepted: 12 October 2020 . Published Online: 11 November 2020

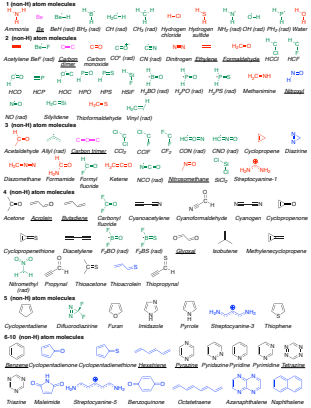
Anouar Benali, Kevin Gasperich, Kenneth D. Jordan, Thomas Applencourt, Ye Luo, M. Chandler Bennett, Jaron T. Krogel, Luke Shulenburger, Paul R. C. Kent, Pierre-François Loos, Anthony Scemama, and Michel Caffarel

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"





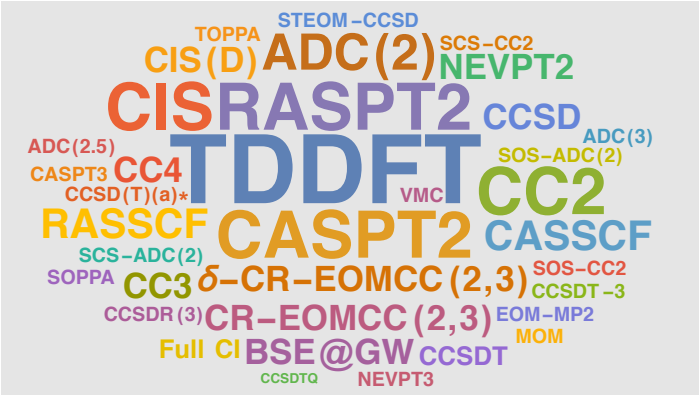
Mika Veril (PhD)

Martial Boggio-Pasqua

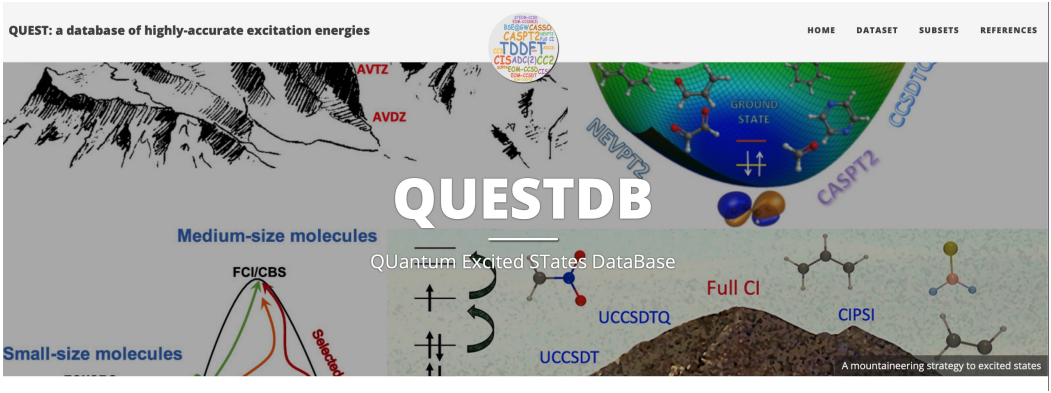
Denis Jacquemin

Electronic structure nightmare...

And this is just for excited states...



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

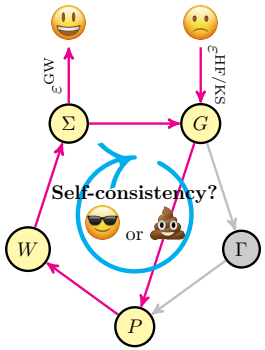


Véril et al. WIREs Comput. Mol. Sci. 11 (2021) e1517

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

Section 2

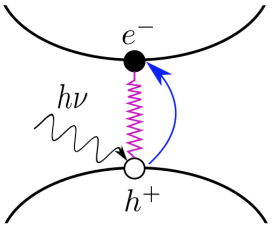
Many-body perturbation theory



Fundamental gap vs Optical gap

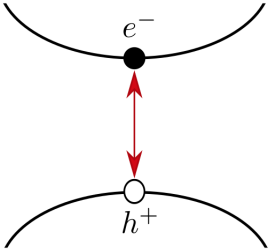
Optical gap

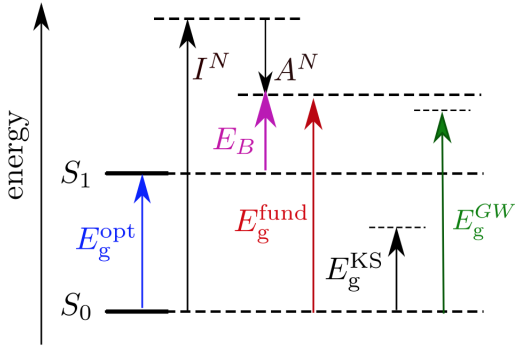
$$E_{\rm g}^{\rm opt} = E_1^N - E_0^N$$



Fundamental gap

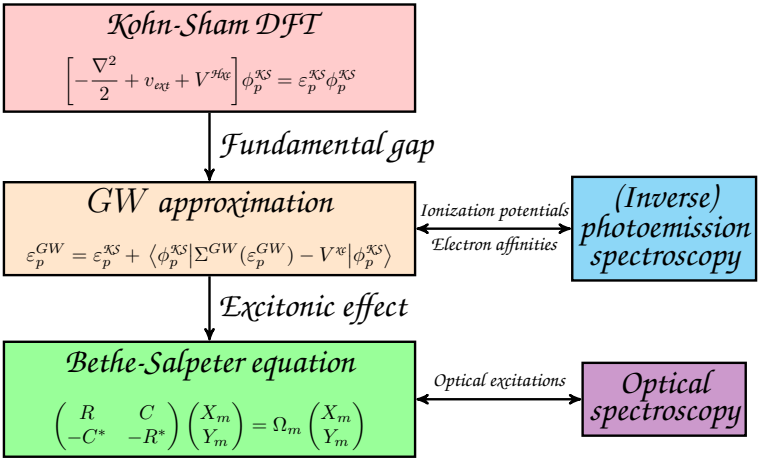
$$E_{\rm g}^{\rm fund} = I^N - A^N$$





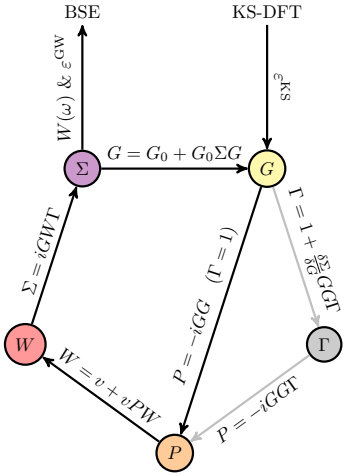
Blase, Duchemin, Jacquemin & Loos JPCL 11 (2020) 7371

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 $i\Xi(1234) = v(13)\delta(12)\delta(34) - \frac{\partial \Sigma^{xc}(12)}{\partial G(34)}$

TD-DFT and BSE in practice: Casida-like equations

Linear response problem

$$\begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix} \begin{pmatrix} X_m \\ Y_m \end{pmatrix} = \Omega_m \begin{pmatrix} X_m \\ Y_m \end{pmatrix}$$

Blue pill: TD-DFT within the adiabatic approximation

$$R_{ia,jb} = \left(\varepsilon_a^{\mathrm{KS}} - \varepsilon_i^{\mathrm{KS}}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) + f^{xc}_{ia,bj} \qquad C_{ia,jb} = 2(ia|jb) + f^{xc}_{ia,jb}$$

$$f^{xc}_{ia,bj} = \iint \phi_i(\mathbf{r})\phi_a(\mathbf{r}) \frac{\delta^2 E^{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \phi_b(\mathbf{r})\phi_j(\mathbf{r}) d\mathbf{r} d\mathbf{r}'$$

Red pill: BSE within the static approximation

$$R_{ia,jb} = \left(\varepsilon_a^{GW} - \varepsilon_i^{GW}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) - W^{\mathrm{stat}}_{ij,ba} \qquad C_{ia,jb} = 2(ia|jb) - W^{\mathrm{stat}}_{ib,ja}$$

$$W^{\mathrm{stat}}_{ij,ab} \equiv W_{ij,ab}(\omega = 0) = (ij|ab) - W^{c}_{ij,ab}(\omega = 0)$$

Dynamical BSE formalism

Dynamical correction to the Bethe–Salpeter equation beyond the plasmon-pole approximation

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Published Online: 21 September 2020

Pierre-François Loos[1,a] and **Xavier Blase**[2,b]

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[2] Université Grenoble Alpes, CNRS, Institut NEEL, F-38042 Grenoble, France

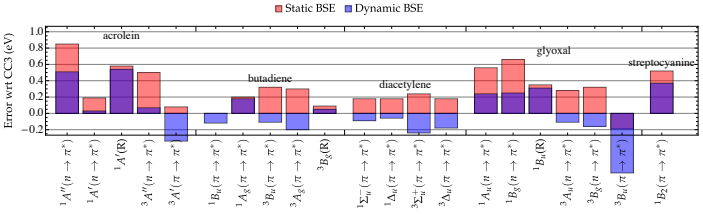
Dynamical correction to the BSE

Non-linear response problem

$$\begin{pmatrix} R(\Omega_S) & C(\Omega_S) \\ -C^*(-\Omega_S) & -R^*(-\Omega_S) \end{pmatrix} \begin{pmatrix} X_S \\ Y_S \end{pmatrix} = \Omega_S \begin{pmatrix} X_S \\ Y_S \end{pmatrix}$$

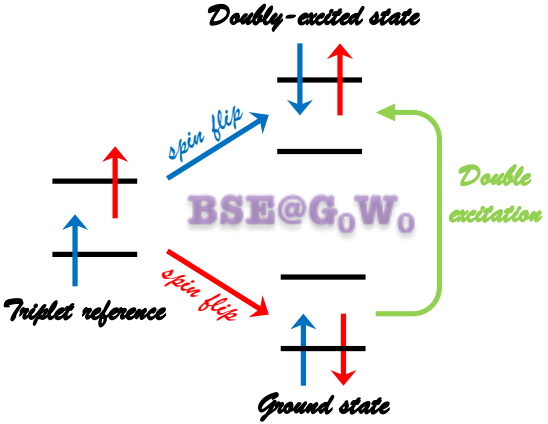
Dynamical BSE formalism [Strinati, Riv. Nuovo Cimento 11 (1988) 1]

$$R_{ia,jb}(\omega) = \left(\varepsilon_a^{GW} - \varepsilon_i^{GW}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) - \widetilde{W}_{ij,ba}(\omega) \qquad \widetilde{W}_{ij,ab}(\omega) = (ij|ab) - \widetilde{W}^c_{ij,ab}(\omega)$$



Loos & Blase, JCP 153 (2020) 114120; Authier & Loos, JCP 153 (2020) 184105

Spin-flip BSE formalism



Monino & Loos, JCTC 17 (2021) 2852

Bethe-Salpeter for ground-state energies

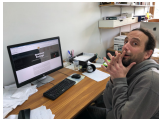
THE JOURNAL OF PHYSICAL CHEMISTRY Letters

pubs.acs.org/JPCL Letter

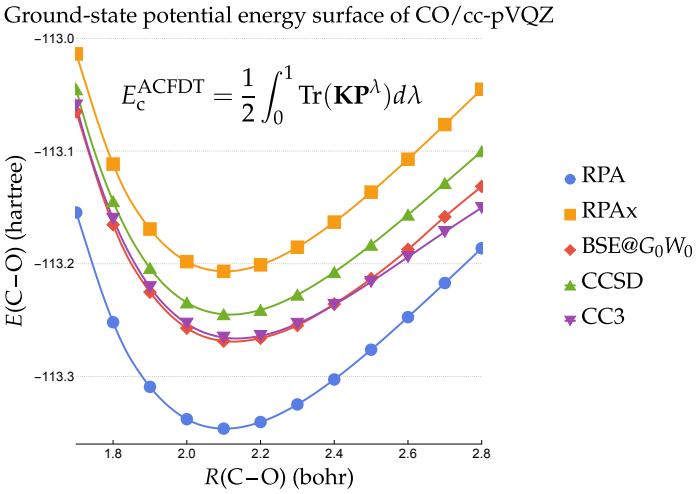
Pros and Cons of the Bethe–Salpeter Formalism for Ground-State Energies

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

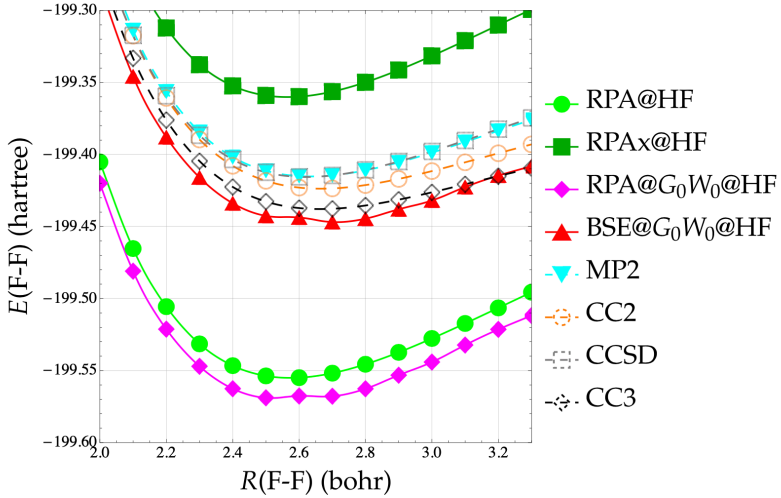
Cite This: *J. Phys. Chem. Lett.* 2020, 11, 3536–3545 Read Online



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

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

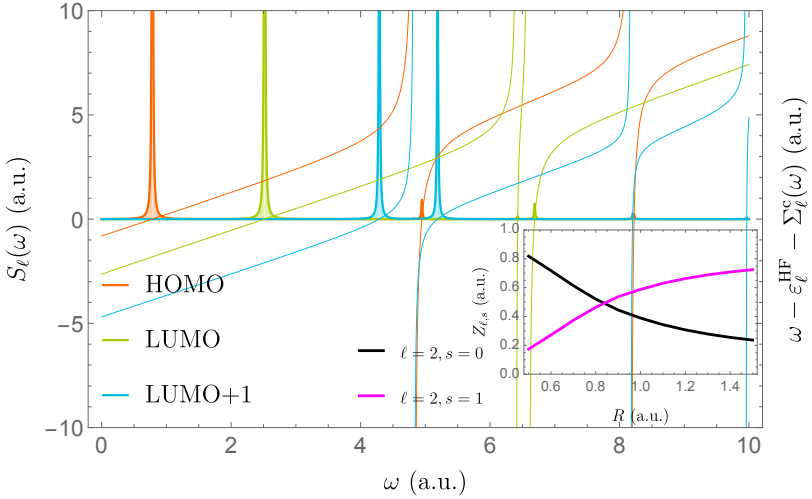
Pierre-François Loos,*[,†] Pina Romaniello,[‡,¶] and J. A. Berger[†,¶]

[†]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

pubs.acs.org/JCTC

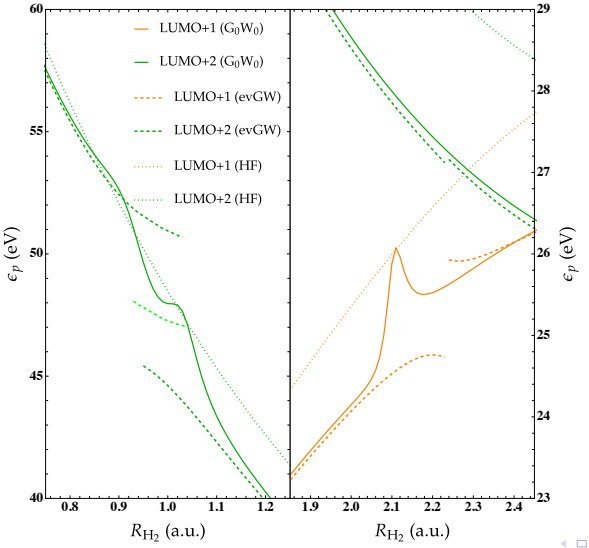
Unphysical Discontinuities in *GW* Methods

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)



The elephant in the room of GW

(Linearized) quasiparticle equation

$$\epsilon_p^{G_0W_0} = \epsilon_p^{\mathrm{HF}} + Z_p(\epsilon_p^{\mathrm{HF}})\,\mathrm{Re}[\Sigma_p^{\mathrm{c}}(\epsilon_p^{\mathrm{HF}})]$$

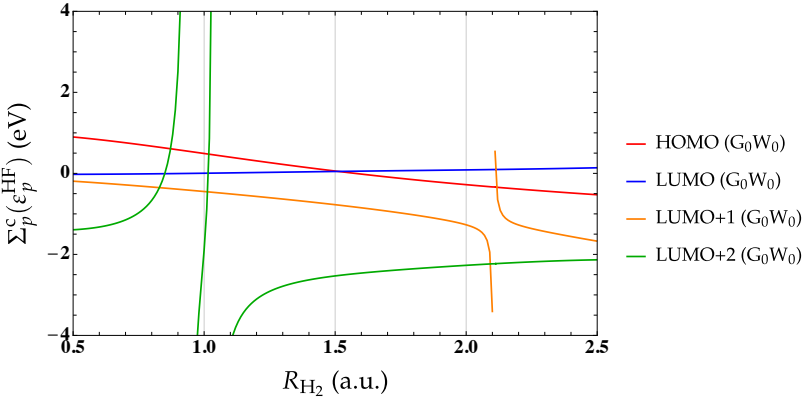
Correlation part of the self-energy:

$$\Sigma_p^{\mathrm{c}}(\omega) = 2\sum_{im} \frac{[pi|m]^2}{\omega - \epsilon_i^{\mathrm{HF}} + \Omega_m^{\mathrm{RPA}} - i\eta} + 2\sum_{am} \frac{[pa|m]^2}{\omega - \epsilon_a^{\mathrm{HF}} - \Omega_m^{\mathrm{RPA}} + i\eta}$$

Renormalization factor (or spectral weight):

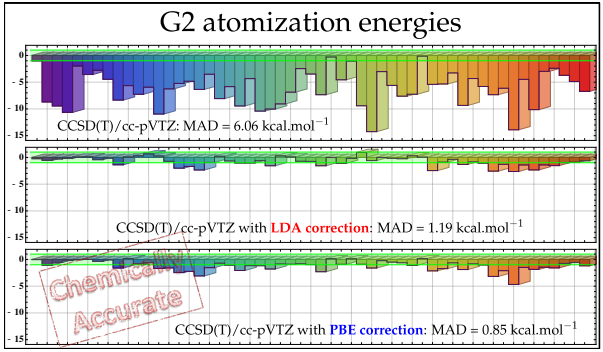
$$Z_p(\omega) = \left[1 - \frac{\partial\,\mathrm{Re}[\Sigma_p^{\mathrm{c}}(\omega)]}{\partial\omega}\right]^{-1}$$

The elephant in the room of GW



Section 3

Basis set incompleteness correction



Ground-state properties

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

Cite This: *J. Phys. Chem. Lett.* 2019, 10, 2931−2937

pubs.acs.org/JPCL

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

Pierre-François Loos,*[,†] Barthélémy Pradines,[‡,§] Anthony Scemama,[†] Julien Toulouse,*[,‡] and Emmanuel Giner*[,‡]

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[‡]Laboratoire de Chimie Théorique, Sorbonne Université, CNRS, 75005 Paris, France

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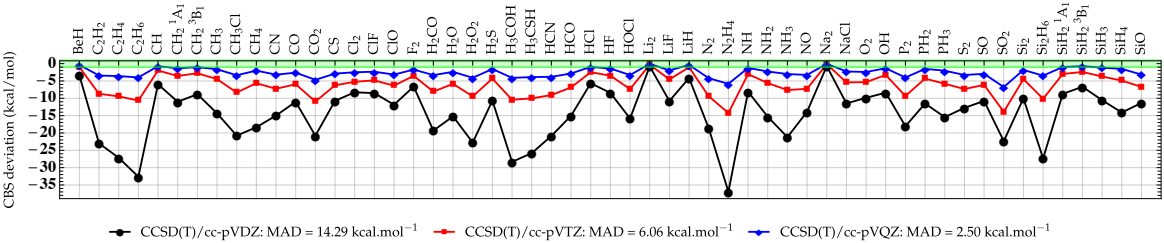
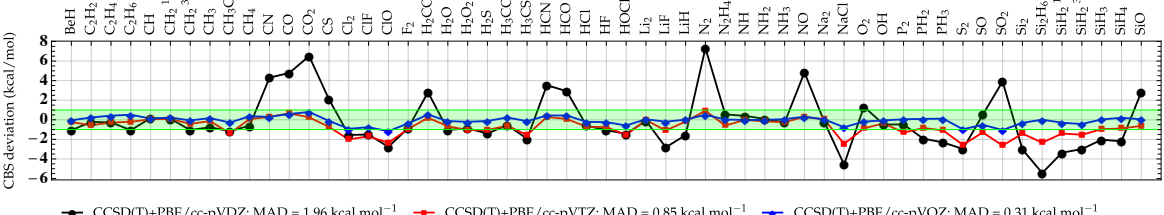
Ground-state properties





Neutral excitations

Chemically accurate excitation energies with small basis sets

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Submitted: 2 August 2019 • Accepted: 20 September 2019 •
Published Online: 14 October 2019

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Emmanuel Giner,[1,a)] Anthony Scemama,[2] Julien Toulouse,[1] and Pierre-François Loos[2,a)]

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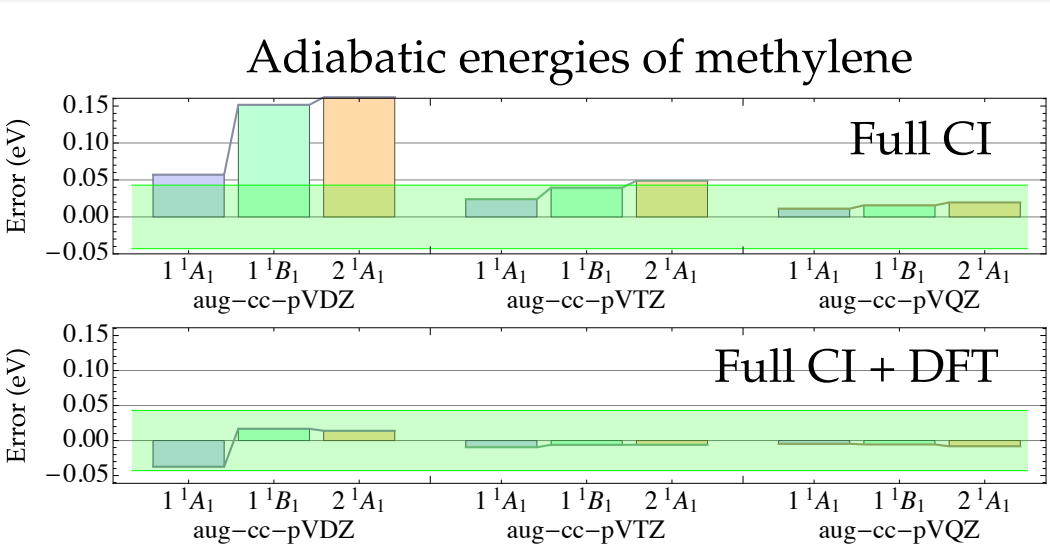
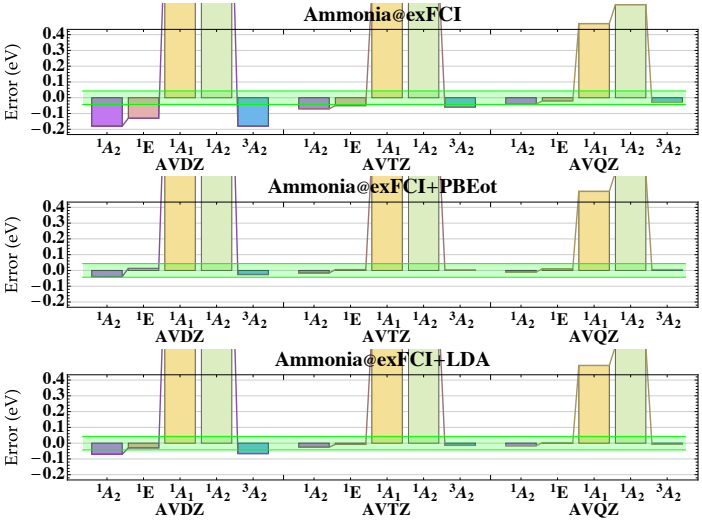
Neutral excitations



Neutral excitations



Charged excitations

JCTC Journal of Chemical Theory and Computation

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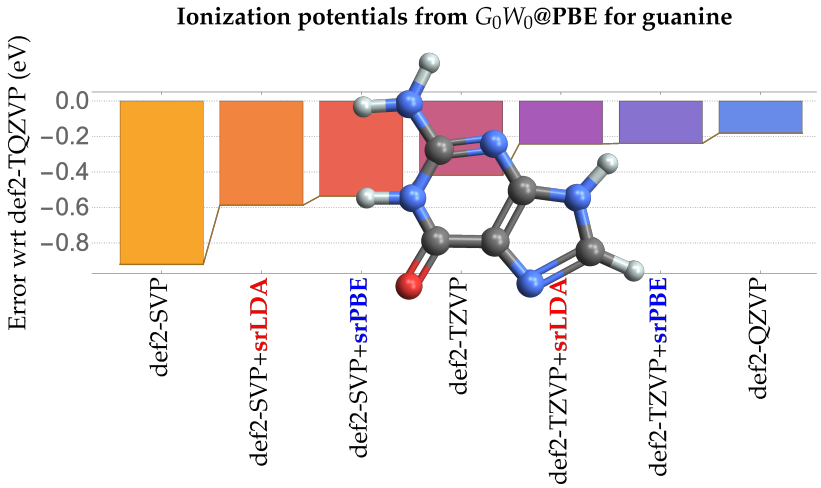
Density-Based Basis-Set Incompleteness Correction for *GW* Methods

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

Cite This: *J. Chem. Theory Comput.* 2020, 16, 1018–1028 Read Online

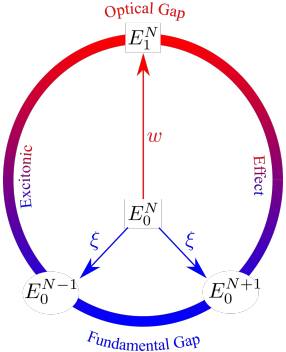



Charged excitations



Section 4

Density-functional theory for ensembles



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eDFT for neutral excitations

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

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Published Online: 1 June 2020

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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 [*d]



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:

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

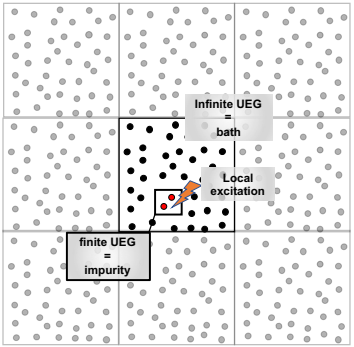
LDA-centered functionals:

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

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

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

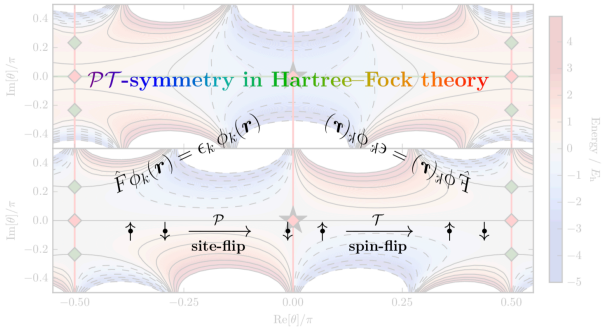
N-centered formalism [Senjean & Fromager PRA 98 (2018) 022513]

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

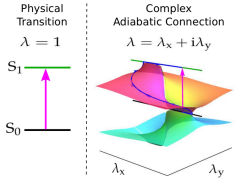
$\Rightarrow$ The exact xc functional must be weight-dependent

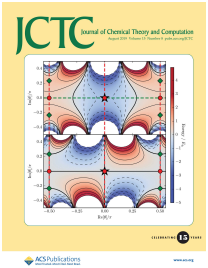
Section 5

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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Submitted: 9 December 2018 • **Accepted:** 11 January 2019 •
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JCTC Journal of Chemical Theory and Computation — Article
Cite This: J. Chem. Theory Comput. 2019, 15, 4374−4385 — pubs.acs.org/JCTC

Parity-Time Symmetry in Hartree−Fock Theory

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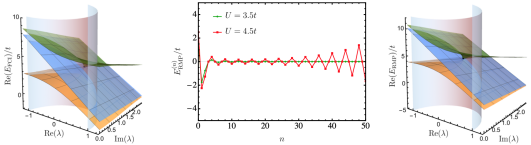
Antoine Marie (M2 ENS)

Hugh Burton (ECR Oxford)

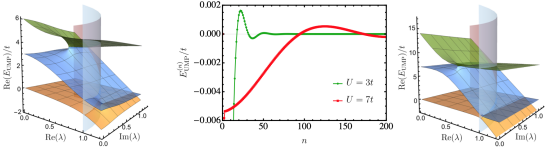
Perturbation Theory in the Complex Plane [JPCM 33 (2021) 283001]

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) $U/t = 7$

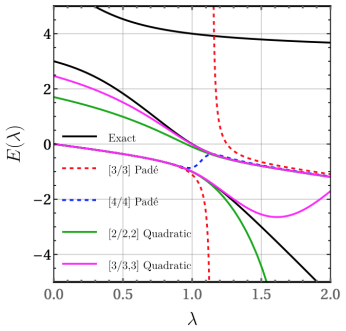
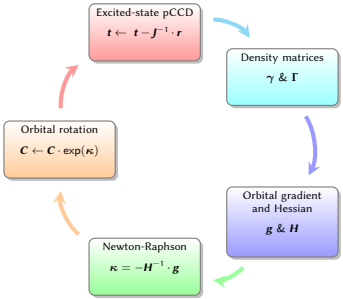


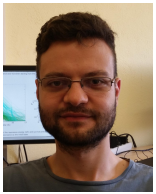
FIG. 12: UMP energies in the Hubbard dimer as a function of λ obtained using various approximants at $U/t = 3$.

Section 6

Coupled-cluster theory for excited states



Coupled-cluster theory for excited states



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(Postdoc)

Antoine Marie
(Master student)

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(CNRS)

Michel Caffarel
(CNRS)

Coupled-cluster theory

- Coupled-cluster (CC) wave function

$$\Psi_{\text{CC}} = e^{\hat{T}} \Psi_0 \quad \text{where } \Psi_0 \text{ is a reference wave function} \tag{1}$$

- Excitation operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_n \quad \text{where } n \text{ is the number of electrons} \tag{2}$$

- Exponential *ansatz*

$$\begin{aligned} e^{\hat{T}} &= \hat{1} + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \ldots \\ &= \hat{1} + \hat{T}_1 + \left(\underbrace{\hat{T}_2}_{\text{connected}} + \frac{1}{2} \underbrace{\hat{T}_1^2}_{\text{disconnected}} \right) + \left(\hat{T}_3 + \hat{T}_2\hat{T}_1 + \frac{1}{6}\hat{T}_3 \right) \\ &+ \left(\hat{T}_4 + \hat{T}_3\hat{T}_1 + \frac{1}{2} \underbrace{\hat{T}_2^2}_{\text{two pairs of electrons}} + \frac{1}{2}\hat{T}_2\hat{T}_1^2 + \frac{1}{24} \underbrace{\hat{T}_4}_{\text{four electrons}} \right) + \ldots \end{aligned} \tag{3}$$

Excitation operators

- Singles

$$\hat{T}_1\Psi_0 = \sum_i \sum_a \underbrace{t_i^a}_{\text{amplitudes}} \Psi_i^a \tag{4}$$

- Doubles

$$\hat{T}_2\Psi_0 = \sum_{i<j} \sum_{a<b} t_{ij}^{ab} \underbrace{\Psi_{ij}^{ab}}_{\text{excited determinants}} \tag{5}$$

- FCI wave function

$$\Psi_{\text{CI}} = (\hat{1} + \hat{T})\Psi_0 = (\hat{1} + \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_n)\Psi_0 \tag{6}$$

CC energies

- Schrödinger equation

$$\hat{H}\,|\Psi_{\rm CC}\rangle = E_{\rm CC}\,|\Psi_{\rm CC}\rangle \;\Rightarrow\; \hat{H}e^{\hat{T}}\,|\Psi_0\rangle = E_{\rm CC}\,e^{\hat{T}}\,|\Psi_0\rangle \;\Rightarrow\; \underbrace{e^{-\hat{T}}\,\hat{H}e^{\hat{T}}}_{\bar{H}\,=\,\text{similarity transform}}\,|\Psi_0\rangle = E_{\rm CC}\,|\Psi_0\rangle \tag{7}$$

- (Projected) Traditional CC energy (polynomial complexity)

$$\boxed{E_{\rm TCC} = \langle\Psi_0|\bar{H}|\Psi_0\rangle = \frac{\langle\Psi_0|e^{-\hat{T}}\,\hat{H}e^{\hat{T}}\,|\Psi_0\rangle}{\langle\Psi_0|e^{-\hat{T}}\,e^{\hat{T}}\,|\Psi_0\rangle} = \langle\Psi_0|e^{-\hat{T}}\,\hat{H}e^{\hat{T}}\,|\Psi_0\rangle} \tag{8}$$

- Variational CC energy (factorial complexity)

$$\boxed{E_{\rm VCC} = \frac{\langle\Psi_{\rm CC}|\hat{H}|\Psi_{\rm CC}\rangle}{\langle\Psi_{\rm CC}|\Psi_{\rm CC}\rangle} = \frac{\langle\Psi_0|e^{\hat{T}^\dagger}\,\hat{H}e^{\hat{T}}\,|\Psi_0\rangle}{\langle\Psi_0|e^{\hat{T}^\dagger}\,e^{\hat{T}}\,|\Psi_0\rangle} \geq E_{\rm FCI}} \tag{9}$$

Van Voorhis & Head-Gordon, JCP 113 (2000) 8873

Amplitude equations for TCC

- Amplitude equations for single amplitudes

$$\underbrace{r_i^a}_{\text{residual}} = \langle \Psi_i^a | \bar{H} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad t_i^a \tag{10}$$

- Amplitude equations for double amplitudes

$$r_{ij}^{ab} = \langle \Psi_{ij}^{ab} | \bar{H} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad t_{ij}^{ab} \tag{11}$$

- Amplitude equations for k-tuple amplitudes

$$r_{ij\ldots}^{ab\ldots} = \langle \Psi_{ij\ldots}^{ab\ldots} | \bar{H} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad t_{ij\ldots}^{ab\ldots} \tag{12}$$

Traditional pair CCD (TpCCD)

- We set $\hat{T} = \hat{T}_2$ (CCD) and we restrict the excitation manifold to electron pairs (p)

$$\hat{T}\,|\Psi_0\rangle = \sum_{ia} t_{i\bar{i}}^{a\bar{a}}\,|\Psi_{i\bar{i}}^{a\bar{a}}\rangle = \sum_{ia} t_i^a\,|\Psi_{i\bar{i}}^{a\bar{a}}\rangle \tag{13}$$

- TpCCD energy

$$E_{\text{TpCCD}} = \langle\Psi_0|\hat{H}|\Psi_0\rangle + \sum_{ia} t_i^a (ii|aa) \tag{14}$$

- TpCCD residual

$$\begin{aligned} r_i^a = {} & (ii|aa) + 2(f_a^a - f_i^i)t_i^a - 2\sum_j (jj|aa)t_j^a t_i^a - 2\sum_b (ii|bb)t_i^b t_i^a \\ & - 2(2(ia|ia) - (ia|ai))t_i^a + 2(ii|aa)t_i^a t_i^a \\ & + \sum_b (aa|bb)t_i^b + \sum_j (ii|jj)t_j^a + \sum_{jb} (jj|bb)t_j^a t_i^b \end{aligned} \tag{15}$$

- Update amplitudes

$$t_i^a \leftarrow t_i^a - \frac{r_i^a}{2f_a^a - 2f_i^i} \quad \text{quasi-Newton algorithm} \tag{16}$$

Henderson et al. JCP 141 (2014) 244104; Limacher et al. JCTC 9 (2013) 1394

TpCCD vs DOCI: Ground state with HF reference [Henderson et al. JCP 141 (2014) 244104]

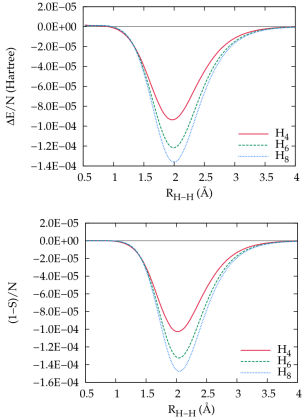


FIG. 3. Dissociation of equally spaced hydrogen chains. Top panel: Differences between DOCI and pCCD energies (ΔE, defined in Eq. (27)) per electron pair. Bottom panel: Deviations in the overlap ($1 - S$, with S defined in Eq. (28)) per electron pair.

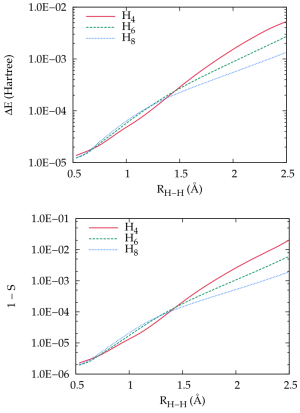


FIG. 4. Dissociation of equally spaced hydrogen chains in the canonical RHF basis rather than the pCCD-optimized basis used elsewhere. Top panel: Differences between DOCI and pCCD energies (ΔE, defined in Eq. (27)). Bottom panel: Deviations in the overlap ($1 - S$, with S defined in Eq. (28)).

Targeting excited states at the CC level

Does the similarity between TpCCD and DOCI still hold for excited states?

Equation-of-motion (EOM) formalism

$$\bar{\boldsymbol{H}} = \begin{pmatrix} E_{\text{CC}} & \langle \Psi_0 | \bar{H} | \Psi_i^a \rangle & \langle \Psi_0 | \bar{H} | \Psi_{ij}^{ab} \rangle \\ \mathbf{0} & \langle \Psi_i^a | \bar{H} | \Psi_i^a \rangle & \langle \Psi_i^a | \bar{H} | \Psi_{ij}^{ab} \rangle \\ \mathbf{0} & \langle \Psi_{ij}^{ab} | \bar{H} | \Psi_i^a \rangle & \langle \Psi_{ij}^{ab} | \bar{H} | \Psi_{ij}^{ab} \rangle \end{pmatrix}$$

Krylov, Annu Rev Phys 59 (2008) 433

"Ground state" formalism

There is more than one solution!!

$$r_i^a = \langle \Psi_i^a | \bar{H} | \Psi_0 \rangle = 0$$
$$r_{ij}^{ab} = \langle \Psi_{ij}^{ab} | \bar{H} | \Psi_0 \rangle = 0$$

Piecuch & Kowalski, in Computational Chemistry: Reviews of Current Trends, Vol. 5 (2000) 1

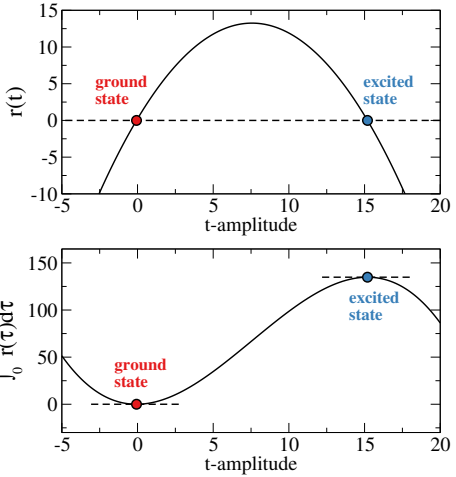
Example: TpCCD for He/6-31G with h = HOMO and l = LUMO

We're looking for the roots of $r(t)$...

Residual and curvature

$$r(t) = (hh|ll) + \Big(2f_l^l - 2f_h^h - 4(hl|hl) + 2(lh|hl) + (ll|ll) + (hh|hh)\Big)t - (ll|hh)t^2 \quad (17)$$

$$r'(t) = 2f_l^l - 2f_h^h - 4(hl|hl) + 2(lh|hl) + (ll|ll) + (hh|hh) - 2(ll|hh)t \quad (18)$$



Newton-Raphson algorithm to target excited states

$$\boxed{t_i^a \leftarrow t_i^a - \sum_{jb} (\boldsymbol{J}^{-1})_{ia,jb} r_j^b \quad \text{Newton-Raphson algorithm}} \tag{19}$$

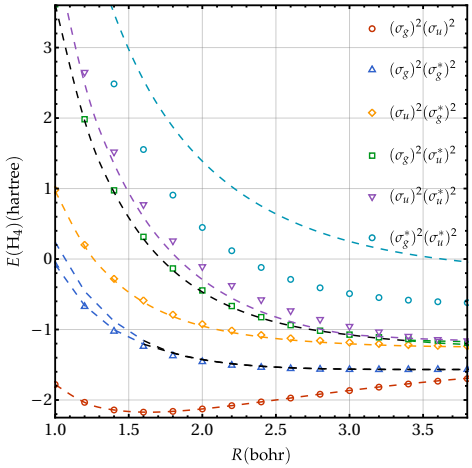
Elements of the exact Jacobian matrix for TpCCD

$$\begin{aligned} J_{ia,jb} = \frac{\partial r_i^a}{\partial t_j^b} &= \left[2f_a^a - 2f_i^i - 4(ia|ia) + 2(ia|ai) \right] \delta_{ij}\delta_{ab} \\ &+ \left[(aa|bb) - (jj|aa)\, t_i^a + (1 - 2\delta_{ab}) \sum_{k \neq i} (kk|bb)\, t_k^a \right] \delta_{ij} \\ &+ \left[(ii|jj) - (ii|bb)\, t_i^a + (1 - 2\delta_{ij}) \sum_{c \neq a} (jj|cc)\, t_i^c \right] \delta_{ab}. \end{aligned} \tag{20}$$

Kossoski, Marie, Scemama, Caffarel & Loos JCTC 17 (2021) 4756

NB: Same strategy works for VCC [Marie, Kossoski & Loos JCP 155 (2021) 104105]

Stretching linear H_4/STO-6G: pCCD vs DOCI with HF ground-state reference



Orbital optimization

Orbital rotations via unitary transformation

$$\tilde{E}(\hat{T},\hat{\kappa}) = \langle \Psi_0 | \underbrace{(\hat{1}+\hat{Z})}_{\text{de-excitation operator}} e^{-\hat{T}} e^{-\hat{\kappa}} \hat{H} e^{\hat{\kappa}} e^{\hat{T}} | \Psi_0 \rangle \tag{21}$$

NB: pCCD is not invariant wrt orbital rotations...

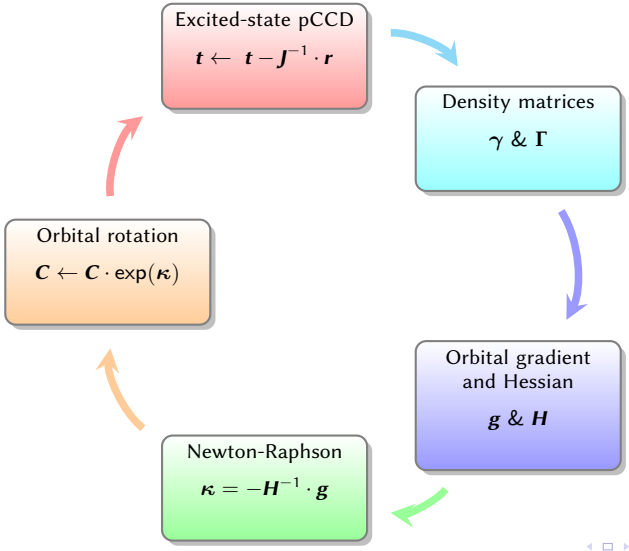
Updating the orbital coefficients

$$\tilde{E}(\boldsymbol{\kappa}) \approx \tilde{E}(\mathbf{0}) + \boldsymbol{g}\cdot\boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^{\dagger}\cdot\boldsymbol{H}\cdot\boldsymbol{\kappa} \quad \Rightarrow \quad \boxed{\underbrace{\boldsymbol{C}}_{\text{new coefficients!}} \leftarrow \boldsymbol{C}\cdot e^{\boldsymbol{\kappa}} \quad \text{with} \quad \boldsymbol{\kappa} = -\boldsymbol{H}^{-1}\cdot\boldsymbol{g}} \tag{22}$$

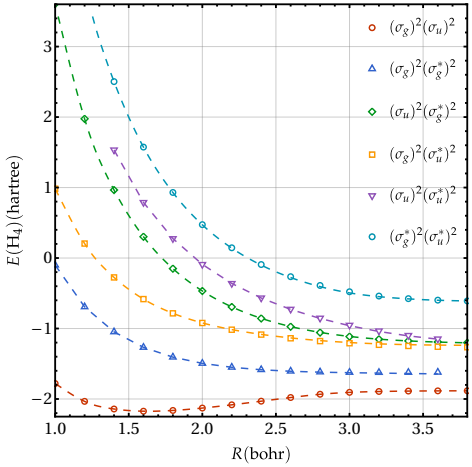
$$\text{Density matrices } \boldsymbol{\gamma} \ \& \ \boldsymbol{\Gamma} \quad \Rightarrow \quad \underbrace{g_{pq}}_{\text{gradient}} = \left.\frac{\partial \tilde{E}(\boldsymbol{\kappa})}{\partial \kappa_{pq}}\right|_{\boldsymbol{\kappa}=\mathbf{0}} \qquad \underbrace{H_{pq,rs}}_{\text{Hessian}} = \left.\frac{\partial^2 \tilde{E}(\boldsymbol{\kappa})}{\partial \kappa_{pq}\partial \kappa_{rs}}\right|_{\boldsymbol{\kappa}=\mathbf{0}} \tag{23}$$

Henderson et al. JCP 141 (2014) 244104

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	$+0.23$

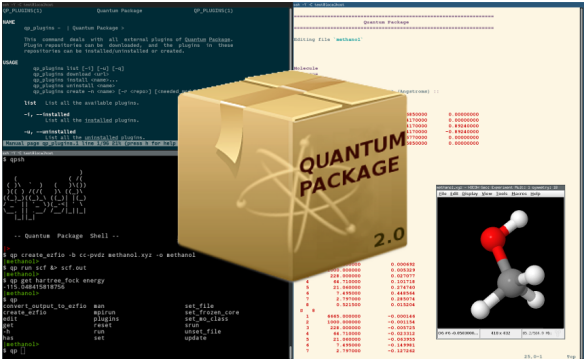
[1] Basis set and geometry taken from Olsen et al. CPL 154 (1989) 380
[2] Results from Olsen et al. CPL 154 (1989) 380
[3] Results from Kowalski & Piecuch, CPL 347(2001) 237
[4] Results from Boguslawski, JCTC 15 (2019) 18
[5] Results from Christiansen et al. JCP 103 (1995) 7429

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

Quantum Package 2.0: https://github.com/QuantumPackage/qp2



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

Fábris' repo: https://github.com/kossoski/qp_plugins_kossoski

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