Higher roots of the Schrödinger equation

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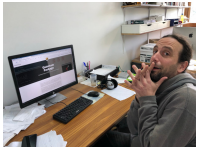
JTMS 2020: Journées “Théorie, Modélisation et Simulation”

Section 1

Selected Configuration Interaction

Collaborators



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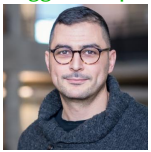


Anouar Benali

One selected CI (SCI) algorithm to rule them all

CIPSI = CI using a Perturbative Selection made Iteratively

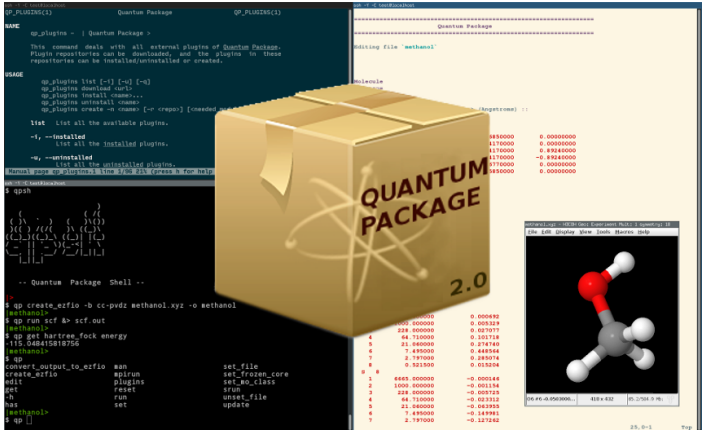
- Developed in Toulouse many (many) years ago
  Huron, Malrieu & Rancurel, JCP 58 (1973) 5745
- Based on old idea by Bender and Davidson, and Whitten and Hackmeyer
  Bender & Davidson, Phys. Rev. 183 (1969) 23
  Whitten & Hackmeyer, JCP 51 (1969) 5584
- CIPSI (and SCI methods in general) has been recently 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 or how to create new methods with new acronyms

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

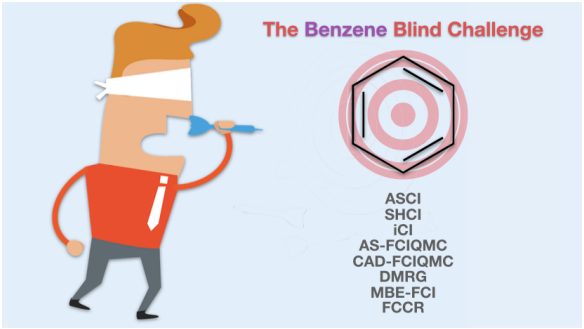
- CIPSI (Malrieu, Evangelisti, Angeli, Spiegelman, Giner, Caffarel, Scemama, etc)
- Semistochastic Heat-bath CI (Sharma & Umrigar)
- Adaptive sampling CI (Evangelista & Tubman)
- Incremental CI (Zimmerman)
- Iterative CI (Liu & Hoffmann)
- FCIQMC (Alavi & Booth)
- ...

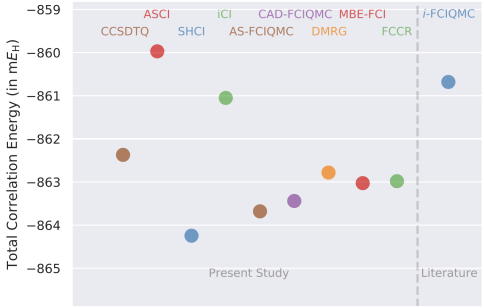
Quantum Package 2.0: https://github.com/QuantumPackage/qp2



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

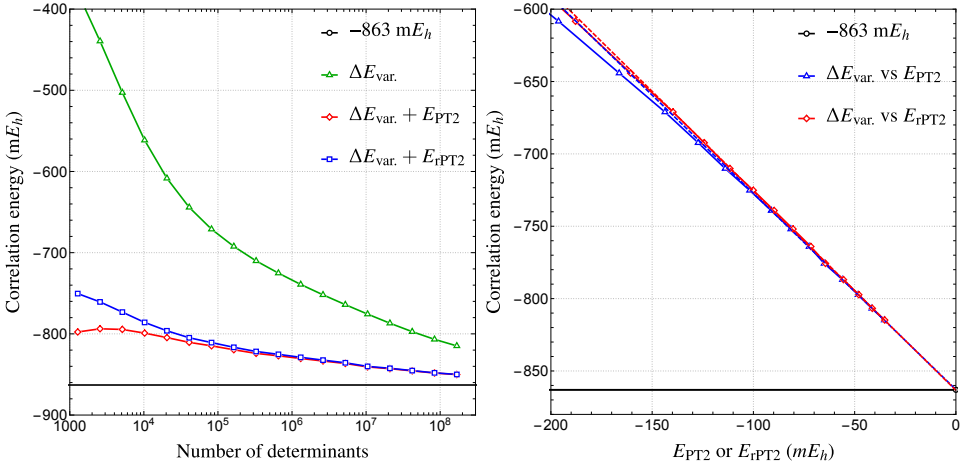
The Benzene Blind Challenge: Frozen-core correlation energy (cc-pVDZ)





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)

TABLE I. The frozen-core correlation energy ΔE (in mE_h) of benzene in the cc-pVDZ basis set using various methods.

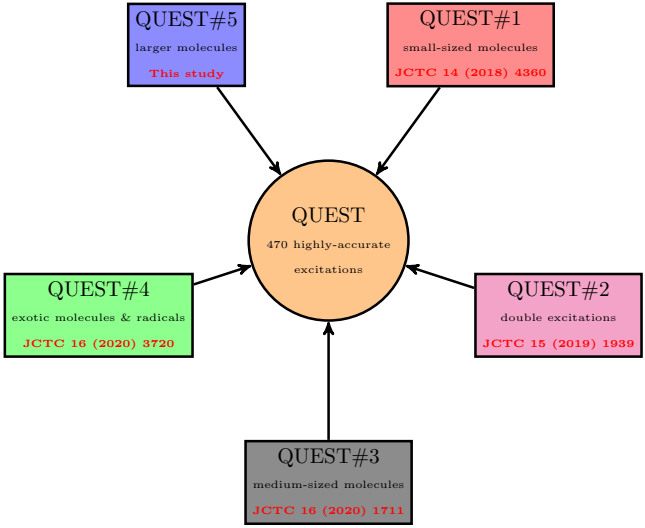
Method	ΔE	Ref.
ASCI	−860.0	17
iCI	−861.1	17
CCSDTQ	−862.4	17
DMRG	−862.8	17
FCCR	−863.0	17
MBE-FCI	−863.0	17
CAD-FCIQMC	−863.4	17
AS-FCIQMC	−863.7	17
SHCI	−864.2	17
ph-AFQMC	−864.3(4)	45
CIPSI	−863.4	This work

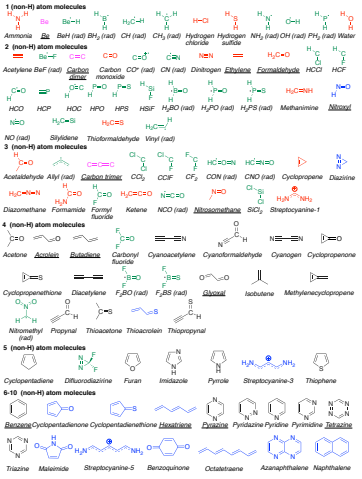
TABLE III. Extrapolation distances, ΔE_{dist}, defined as the difference between the final computed energy, ΔE_{final}, and the extrapolated energy, $\Delta E_{\text{extrap.}}$ associated with ASCI, iCI, SHCI, DMRG, and CIPSI for the best blind-test and post-blind-test estimates of the correlation energy of benzene in the cc-pVDZ basis. The final variational energies $\Delta E_{\text{var.}}$ are also reported. See Ref. 17 for more details. All correlation energies are given in mE_h.

Method	$\Delta E_{\text{var.}}$	ΔE_{final}	$\Delta E_{\text{extrap.}}$	ΔE_{dist}
Best blind-test estimates				
ASCI	−737.1	−835.4	−860.0	−24.6
iCI	−730.0	−833.7	−861.1	−27.4
SHCI	−827.2	−852.8	−864.2	−11.4
DMRG	−859.2	−859.2	−862.8	−3.6
Best post-blind-test estimates				
ASCI	−772.4	−835.2	−861.3	−26.1
iCI	−770.7	−842.8	−864.2	−21.3
SHCI	−835.2	−854.9	−863.6	−8.7
CIPSI	−814.8	−850.2	−863.4	−13.2

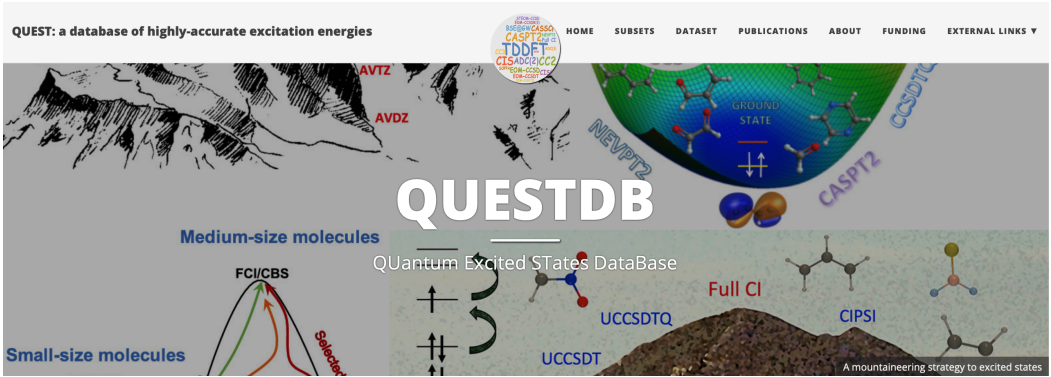
Loos, Damour & Scemama JCP 153 (2020) 176101

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





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



Véril et al. WIREs Comput. Mol. Sci. (in preparation)

https://github.com/mveril/QUESTDB_website

CIPSI trial wave functions for periodic solids

The Journal of Chemical Physics | ARTICLE | scitation.org/journal/jcp

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

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See also Scemama et al. JCP (in press) arXiv:2008.10088 for a range-separated approach in molecules

Section 2

Many-Body Perturbation Theory: *GW* and Bethe-Salpeter equation

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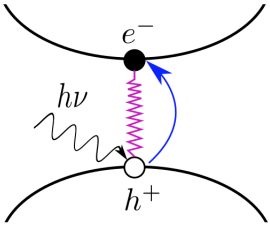
Xavier Blase

Fundamental gap vs Optical gap

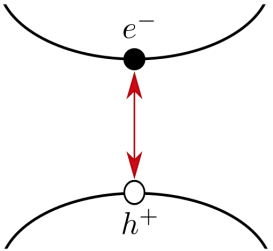
Optical gap

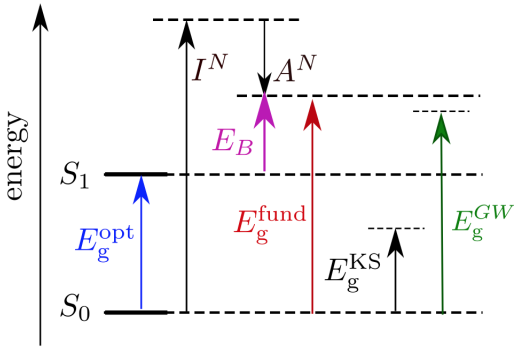
$$E_{\rm g}^{\rm opt} = E_1^N - E_0^N$$



Fundamental gap

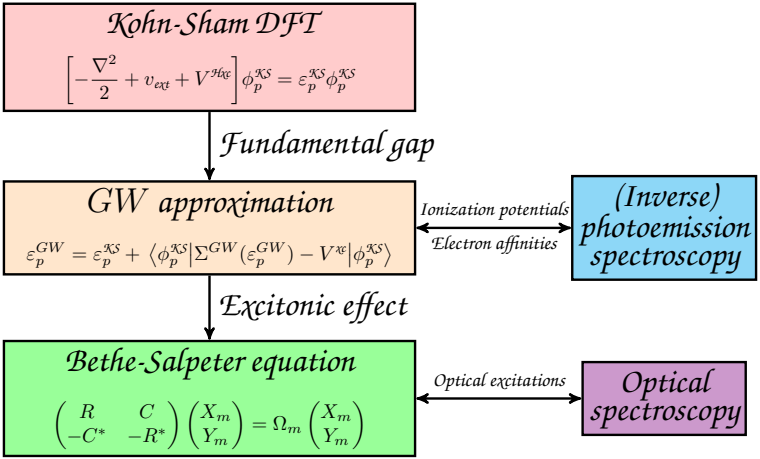
$$E_{\rm g}^{\rm fund} = I^N - A^N$$





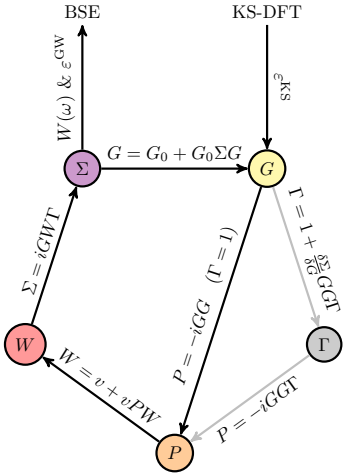
Bredas, Mater. Horiz. 1 (2014) 17

The MBPT chain of actions



Blase et al. 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

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

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

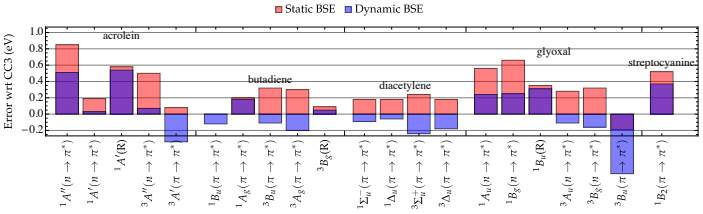
Dynamical correction to the BSE

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 (in press) arXiv:2008.13143

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