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Laboratoire de Chimie et Physique Quantiques

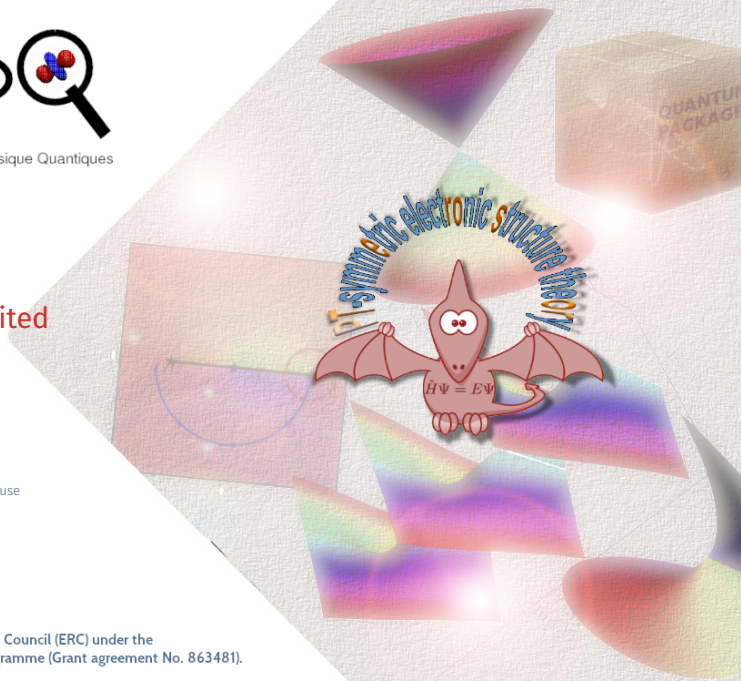
New Electronic Structure Methodologies for Electronic Excited States

Pierre-François Loos & Friends

12th March 2024

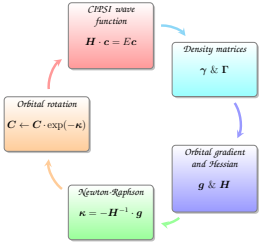
Laboratoire de Chimie et Physique Quantiques, IRSAMC, UPS/CNRS, Toulouse

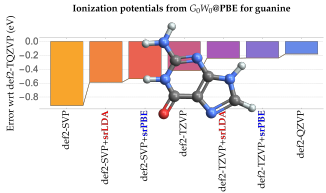
https://lcpq.github.io/pterosor

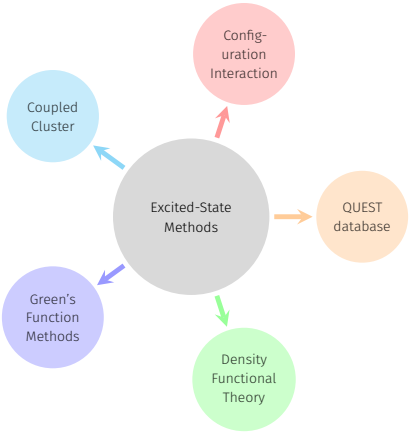


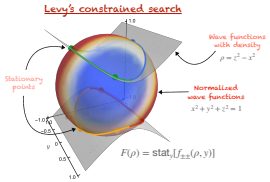
PTEROSOR has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 863481).

General Overview of our Research Group



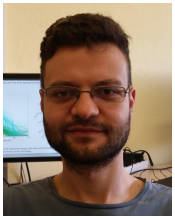




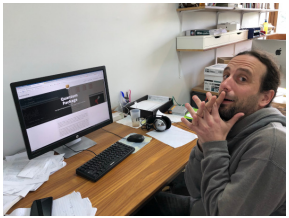


https://lcpq.github.io/PTEROSOR/

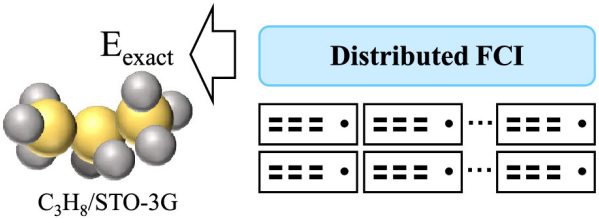
Yann Damour (PhD)



Fábris Kossoski (Postdoc)



Anthony Scemama (Toulouse)



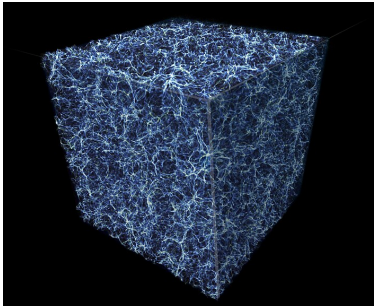
- FCI energy of propane (C_3H_8) in STO-3G
- Active space of 26 electrons in 23 orbitals $\Rightarrow 1.3 \times 10^{12}$ determinants!
- 512 processes on 256 nodes (40 cores each) for a total wall time of 113.6 hours.
- 19 TB of memory required!

Gao et al. JCTC 20 (2024) 1185

$$\frac{1}{\sqrt{2}}|\text{🌿}\rangle + \frac{1}{\sqrt{2}}|\text{🍂}\rangle$$

What do we know?

- Size of Hilbert space increases exponentially fast with system size
- FCI matrix is (very) large but full of zeros!
- Only a tiny fraction of the determinants significantly contributes to the energy
- SCI performs a sparse exploration of the FCI space



What do we know?

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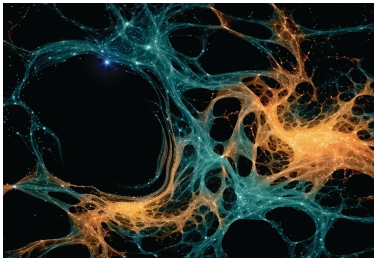
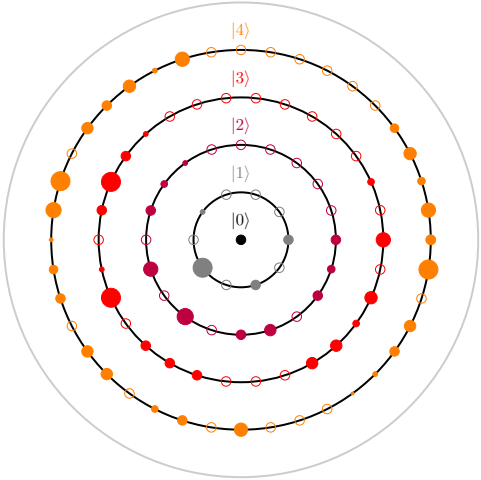


Lemonick, *"Cosmic Nothing"*, Scientific American, 330 (2024) 20

Hilbert Space “Onion”



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

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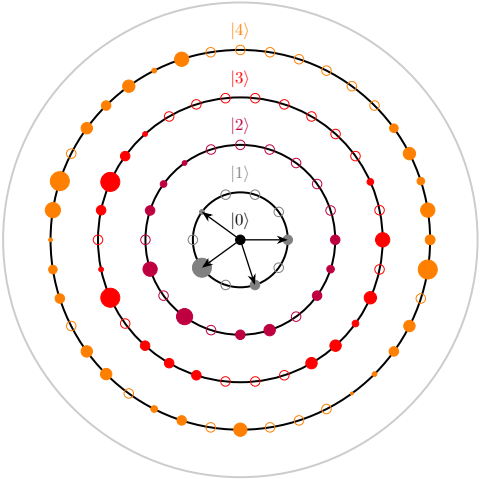

“Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs”, Garniron et al, JCTC 15 (2019) 3591

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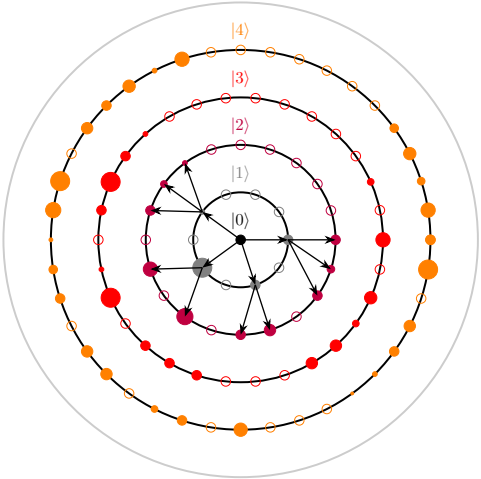

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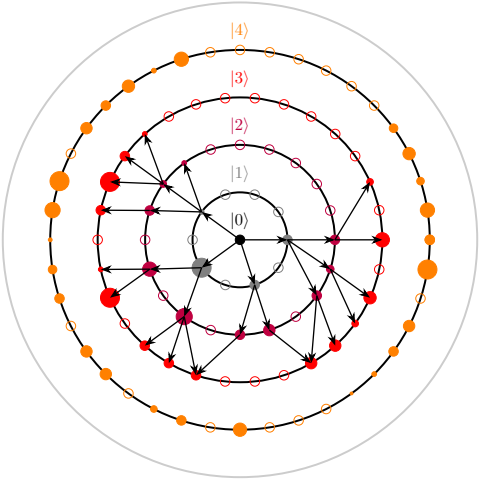

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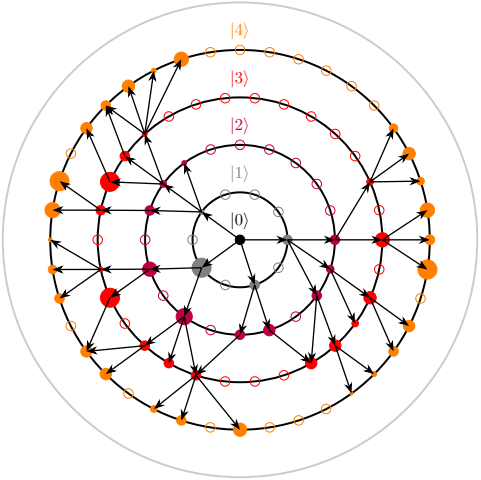
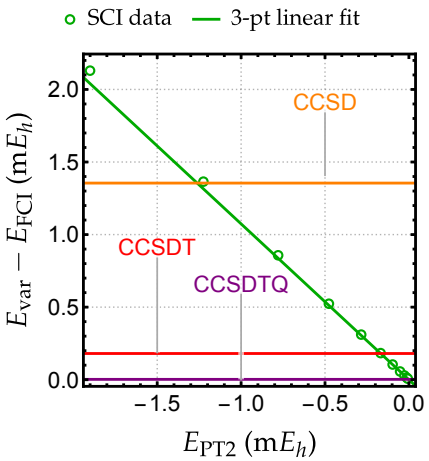


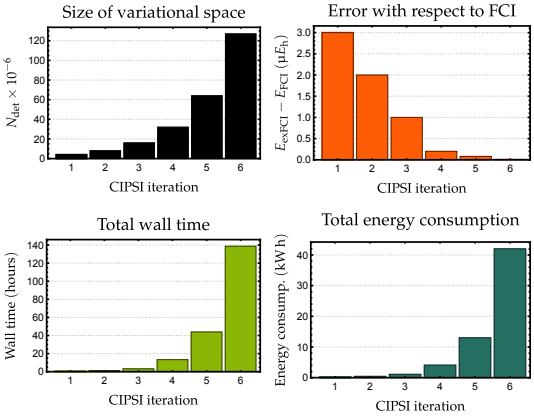
“Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs”, Garniron et al, JCTC 15 (2019) 3591

Method	Energy (E_h)	Error wrt FCI
FCI[1]	−117.100 122 681 461	
CCSD	−117.098 767	1.355 mE_h
CCSD(T)	−117.099 708	0.414 mE_h
CCSDT	−117.099 942 158	0.181 mE_h
CCSDTQ	−117.100 120 230	2.451 μE_h
SCI[2]	−117.100 093 52	0.029 mE_h
SCI+PT2[3]	−117.100 120 66	2.021 μE_h
exFCI[4]	−117.100 122 89(6)	−0.21(6) μE_h



[1] Gao et al. JCTC 20 (2024) 1185
[2] Variational energy obtained with $N_{\mathrm{det}} = 32 \times 10^6$
[3] Perturbatively-corrected variational energy obtained with $N_{\mathrm{det}} = 32 \times 10^6$
[4] Extrapolated FCI value obtained via a 3-point linear fit using $N_{\mathrm{det}} = 32 \times 10^6$ as the largest variational space

Memory, CPU & Energy Consumptions



N_{det}	Wall time (hh:mm)	Memory consump.	Energy consump.	Error wrt FCI
2×10^6	00:14	5.3 GB	74 W h	3 μE_h
4×10^6	00:33	8.1 GB	176 W h	3 μE_h
8×10^6	01:19	15 GB	438 W h	2 μE_h
16×10^6	03:12	25 GB	1.1 kW h	1 μE_h
32×10^6	13:16	47 GB	4.1 kW h	0.2 μE_h
64×10^6	43:54	83 GB	13 kW h	0.08 μE_h
127×10^6	138:44	138 GB	42 kW h	0.01 μE_h

Loos et al, arXiv:2402.13111[1]

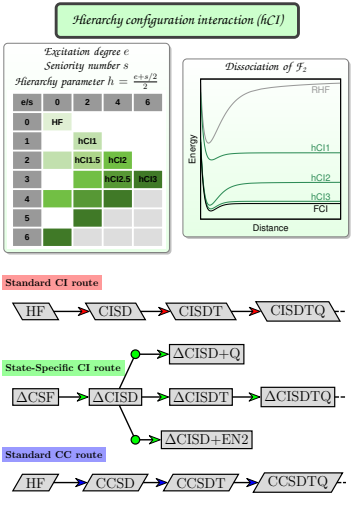
[1]Single-node calculation (dual-socket Intel Skylake 6140 CPU@2.3 Ghz with 192 GB of memory and 36 physical CPU cores)

Recent developments

- Seniority & Hierarchy CI
  [Kossoski et al, JPCL 13 (2022) 4342; JCTC 19 (2023) 8654]
- State-specific CI for excited states
  [Kossoski & Loos, JCTC 19 (2023) 2258]
- State-specific CC for excited states
  [Damour et al, arXiv:2401.05048]

Future developments

- Selected CI for resonant states (complex absorbing potential)
  [Damour, Kossoski et al, in preparation]



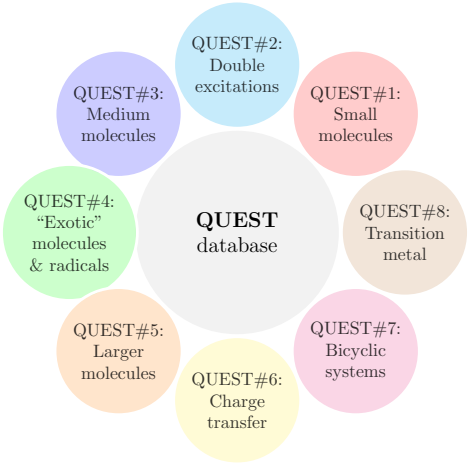
Fábris Kossoski (Postdoc)

Martial Boggio-Pasqua (Toulouse)

Denis Jacquemin (Nantes)

Highly-accurate excitation energies: The QUEST project

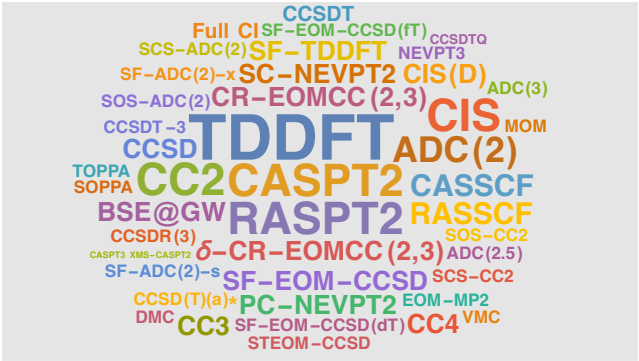
"The QUEST project aims to provide to the community a large set of highly-accurate excitation energies for various types of excited states"



- #1: JCTC 14 (2018) 4360
- #2: JCTC 15 (2019) 1939
- #3: JCTC 16 (2020) 1711
- #4: JCTC 16 (2020) 3720
- #5: WIREs 11 (2021) e1517
- #6: JCTC 17 (2021) 3666
- #7: JPCA 125 (2021) 10174
- #8: JCTC 19 (2023) 8782

Zoo of functionals...

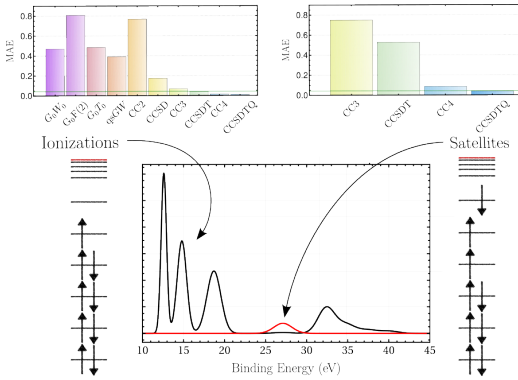
And this is just for excited states...



Other research groups using QUEST

- Head-Gordon's group: orbital-optimized DFT for double excitations [JCTC 16 (2020) 1699; JPCL 12 (2021) 4517] and TD-DFT benchmark [JCTC 18 (2022) 3460]
- Kaupp's group: assessment of hybrid functionals [JCP 155 (2021) 124108]
- Kallay's and Goerigk's groups: double hybrids [JCTC 15 (2019) 4735; JCTC 17 (2021) 927; JCTC 17 (2021) 5165; JCTC 17 (2021) 4211]
- Truhlar/Gagliardi's group: p-DFT [JCTC 18 (2022) 6065]
- Bartlett's group: Variants of EOM-CC for doubly-excited states [JCP 156 (2022) 201102; JPCA 127 (2023) 828; JCP 159 (2023) 094101]
- Neuscamman's group: QMC for doubly-excited states [JCP 153 (2022) 234105]
- Filippi's group: QMC for excited states [JCTC 15 (2019) 4889; JCTC 17 (2021) 3426; JCTC 18 (2022) 1089; JCTC 18 (2022) 6722]
- Gould's group: ensemble DFT [JPCL 13 (2022) 2452]

Antoine's new layer: charged excitations



Marie & Loos, arXiv:2402.13877

Fábris' new layer: double excitations

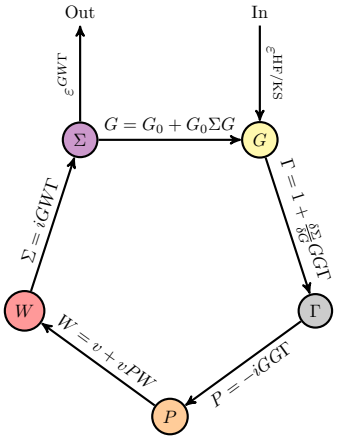
- Double excitations are hard!
- The concept of excitation is relative
- Improvement of reference data
- Extension of our previous set

Kossoski et al, in preparation

Antoine Marie (PhD)

Abdallah Ammar (Postdoc)

Pina Romaniello (Toulouse)



Hedin, Phys Rev 139 (1965) A796

The wonderful equations of Hedin

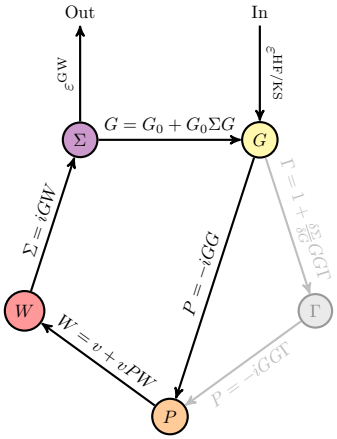
$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(673)d(4567)$$

$$\underbrace{P(12)}_{\text{polarizability}} = -i\int G(13)\Gamma(342)G(41)d(34)$$

$$\underbrace{W(12)}_{\text{screening}} = v(12) + \int v(13)P(34)W(42)d(34)$$

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = i\int G(14)W(13)\Gamma(423)d(34)$$



Hedin, Phys Rev 139 (1965) A796

The *GW* approximation

$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(673)d(4567)$$

$$\underbrace{P(12)}_{\text{polarizability}} = -i\int G(12)\Gamma(342)G(21)d(34) = -iG(12)G(21)$$

$$\underbrace{W(12)}_{\text{screening}} = v(12) + \int v(13)P(34)W(42)d(34)$$

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = i\int G(12)W(12)\Gamma(423)d(34) = iG(12)W(12)$$

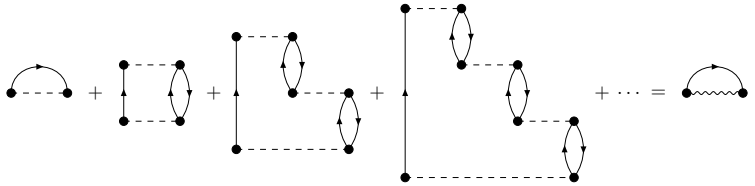
Recent developements

- Improve self-consistent *GW* calculations via similarity renormalization group
  [Marie & Loos, JCTC 19 (2023) 3943]
- Connections between Green's function methods and coupled-cluster theory
  [Quintero-Monsebaiz et al, JCP 157 (2022) 231102]

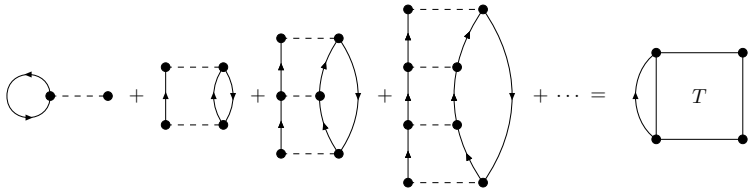
Future developments

- Hedin's equations and vertex corrections for the particle-particle channel
  [Marie & Loos, in preparation]
- Combination of "correlation" channels via anomalous propagators
  [Marie & Loos, in preparation]
- Multireference version of *GW*
  [Ammar et al, JCP (in press)]

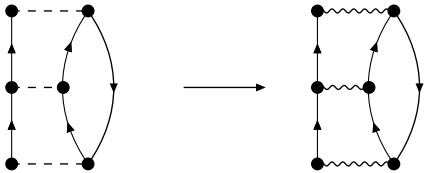
Bubble diagrams of *GW*



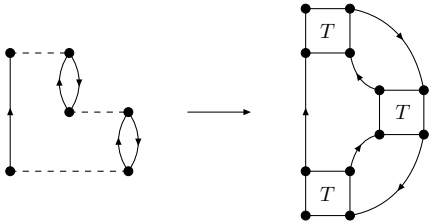
Ladder diagrams of *T*-matrix



Vertex corrections on top of GW



Vertex corrections on top of T-matrix



Sara Giarrusso (Postdoc)

Levy-Lieb constrained search

Ground-state energy

External potential

$$E = \min_{\rho} \left\{ F[\rho] + \int v(\mathbf{r})\, \rho(\mathbf{r}) \mathrm{d}\mathbf{r} \right\}$$

Ground-state Functional

$$F[\rho] = \min_{\substack{\Psi \\ \rho_\Psi = \rho}} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ee}} | \Psi \rangle$$

Kinetic

Repulsion

Levy PNAS 76 (1979) 6062; Lieb IJQC 24 (1983) 243

Generalized constrained search for excited states

$$E_m = \operatorname*{stat}_{\rho} \left\{ F_m[\rho] + \int v(\mathbf{r})\, \rho(\mathbf{r}) \mathrm{d}\mathbf{r} \right\}$$

*m*th excited-state energy

External potential

Excited-state functional

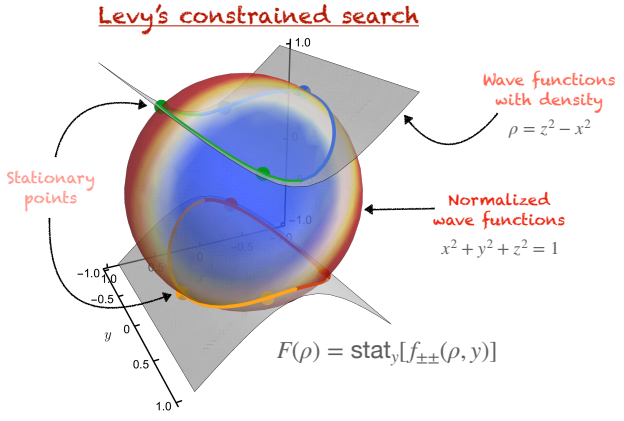
$$F_m[\rho] = \operatorname*{stat}_{\substack{\Psi \\ \rho_\Psi = \rho}} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ee}} | \Psi \rangle$$

Kinetic

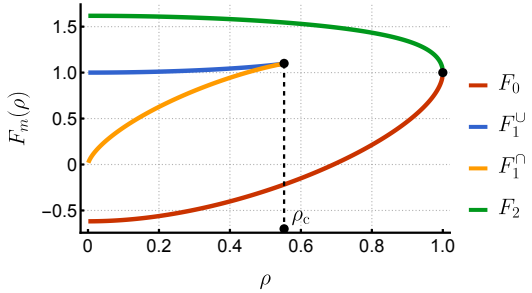
Repulsion

Görling PRA 54 (1996) 3912

Functional manifold in the asymmetric Hubbard dimer



Exact Functionals of asymmetric Hubbard dimer



Giarrusso & Loos, JPCL 14 (2023) 8780

Future developments

- Practical Kohn-Sham scheme [Giarrusso & Loos, in preparation]
- State-specific functionals for realistic systems at the TD-DFT & ΔSCF levels

Acknowledgements & Funding

- Antoine Marie, Enzo Monino, Roberto Orlando, Yann Damour & Mika Véril
- Sara Giarrusso, Raúl Quintero-Monsebaiz & Fábris Kossoski
- Anthony Scemama
- Denis Jacquemin
- Martial Boggio-Pasqua
- Michel Caffarel

https://pfloos.github.io/WEB_LOOS

https://lcpq.github.io/PTEROSOR