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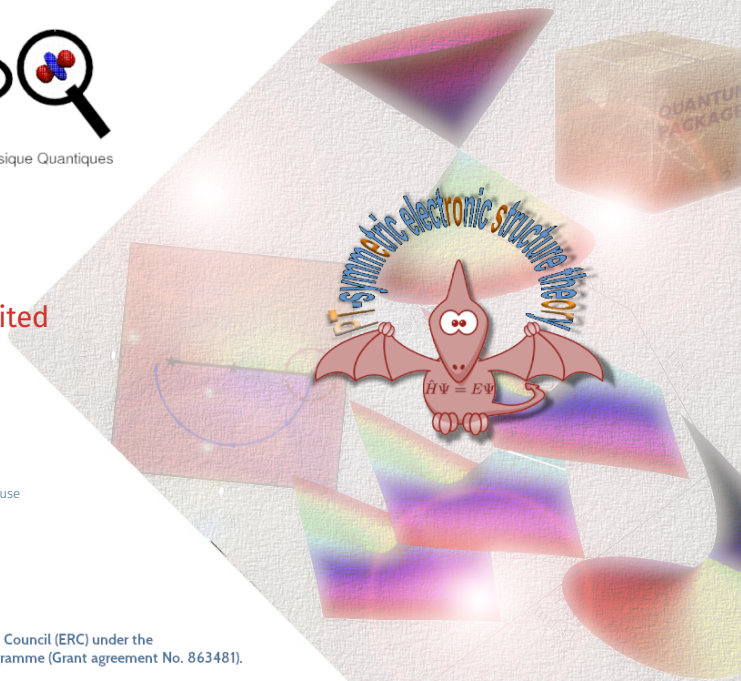
Laboratoire de Chimie et Physique Quantiques

New Electronic Structure Methodologies for Electronic Excited States

Pierre-François Loos & Friends

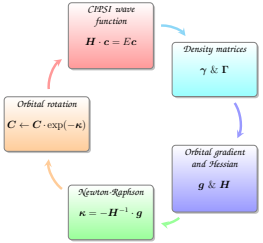
24th April 2024

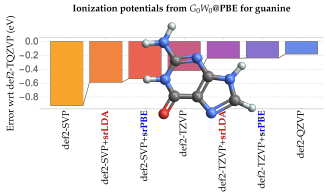
Laboratoire de Chimie et Physique Quantiques, IRSAMC, UPS/CNRS, Toulouse
https://lcpq.github.io/pterosor

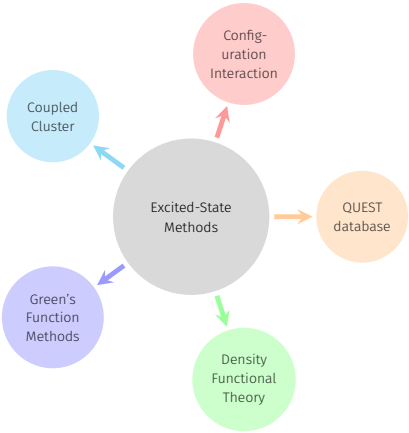


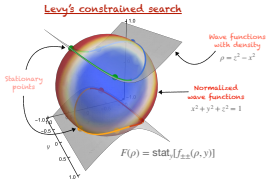
PTEROSOR has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 863481).

General Overview of our Research Group



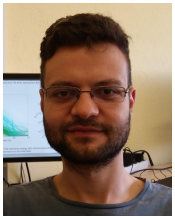




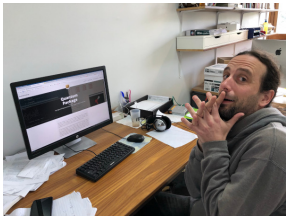


https://lcpq.github.io/PTEROSOR/

Yann Damour (PhD)



Fábris Kossoski (Postdoc)



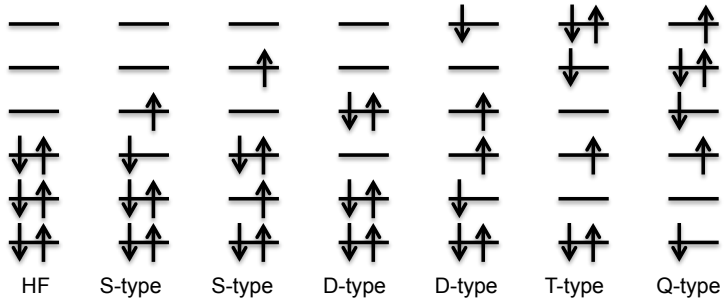
Anthony Scemama (Toulouse)

- This is the oldest and perhaps the easiest method to understand
- The CI wave function is a linear combination of Slater determinants
- CI methods use excited determinants to “improve” the reference wave function

$$|\Phi_{\mathrm{CI}}\rangle = \underbrace{c_0\,|\Psi_0\rangle}_{\text{reference}} + \underbrace{\sum_{\substack{i\\a}} c_i^a\,|\Psi_i^a\rangle}_{\text{singles}} + \underbrace{\sum_{\substack{i<j\\a<b}} c_{ij}^{ab}\,|\Psi_{ij}^{ab}\rangle}_{\text{doubles}} + \underbrace{\sum_{\substack{i<j<k\\a<b<c}} c_{ijk}^{abc}\,|\Psi_{ijk}^{abc}\rangle}_{\text{triples}} + \underbrace{\sum_{\substack{i<j<k<l\\a<b<c<d}} c_{ijkl}^{abcd}\,|\Psi_{ijkl}^{abcd}\rangle}_{\text{quadruples}} + \cdots$$

- CI is based on the variational principle

Excited determinants



CI wave function

$$|\Phi_{\mathrm{CI}}\rangle = c_0\,|0\rangle + c_{\mathrm{S}}\,|\mathrm{S}\rangle + c_{\mathrm{D}}\,|\mathrm{D}\rangle + c_{\mathrm{T}}\,|\mathrm{T}\rangle + c_{\mathrm{Q}}\,|\mathrm{Q}\rangle + \cdots$$

- When $|S\rangle$ (singles) are taken into account: **CIS**

$$|\Phi_{CIS}\rangle = c_0 |0\rangle + c_S |S\rangle$$

- When $|S\rangle$ and $|D\rangle$ (doubles) are taken into account: **CISD**

$$|\Phi_{CISD}\rangle = c_0 |0\rangle + c_S |S\rangle + c_D |D\rangle$$

- When $|S\rangle$, $|D\rangle$ and $|T\rangle$ (triples) are taken into account: **CISDT**

$$|\Phi_{CISDT}\rangle = c_0 |0\rangle + c_S |S\rangle + c_D |D\rangle + c_T |T\rangle$$

- **CISDTQ**, etc.

- When all possible excitations are taken into account, this is called a Full CI calculation (**FCI**)

$$|\Phi_{\text{FCI}}\rangle = c_0 |0\rangle + c_S |S\rangle + c_D |D\rangle + c_T |T\rangle + c_Q |Q\rangle + \dots$$

- FCI gives the exact solution of the Schrödinger equation within a given basis
- So, why do we care about other methods?
- Because FCI is super computationally expensive!

"Assume we have 10 electrons in 38 spin orbitals: 10 are occupied and 28 are empty"

- There is C_{10}^k possible ways of selecting k electrons out of the 10 occupied orbitals

$$C_n^k = \binom{n}{k} = \frac{n!}{k!(n-k)!}$$

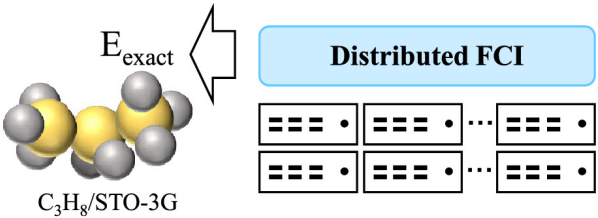
- There is C_{28}^k ways of distributing them out in the 28 virtual orbitals
- For a given excitation level k, there is $C_{10}^k C_{28}^k$ excited determinants
- The total number of possible excited determinant is

$$\sum_{k=0}^{10} C_{10}^k C_{28}^k = C_{38}^{10} = 472,733,756$$

- This is a lot...

For $N = 10$ and $K = 38$:

k	Num. of excitations
0	1
1	280
2	17,010
3	393,120
4	4,299,750
5	24,766,560
6	79,115,400
7	142,084,800
8	139,864,725
9	69,069,000
10	13,123,110
Tot.	472,733,756



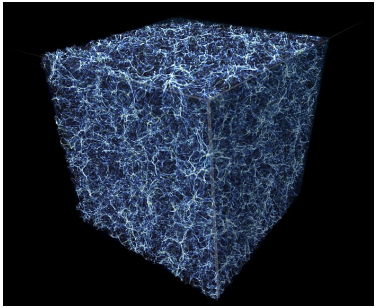
- FCI energy of propane (C_3H_8) in STO-3G
- Active space of 26 electrons in 23 orbitals $\Rightarrow 1.3 \times 10^{12}$ determinants!
- 512 processes on 256 nodes (40 cores each) for a total wall time of 113.6 hours
  $\Rightarrow \approx 10^6$ CPU hours $\Rightarrow \approx 10$ MW h $\Rightarrow \approx 2$ household years
- 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



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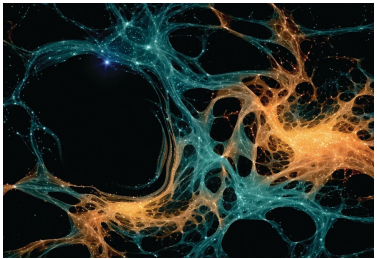
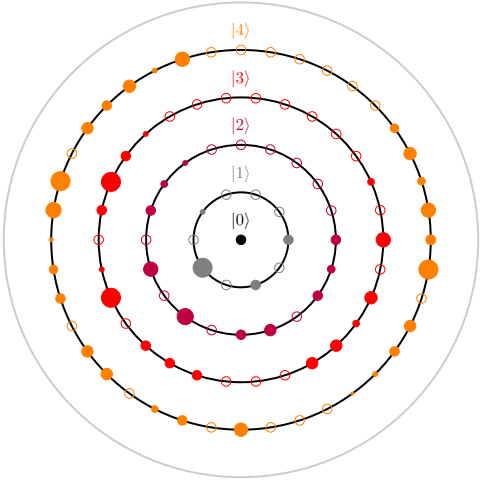


Lemonick, *"Cosmic Nothing"*, Scientific American, 330 (2024) 20

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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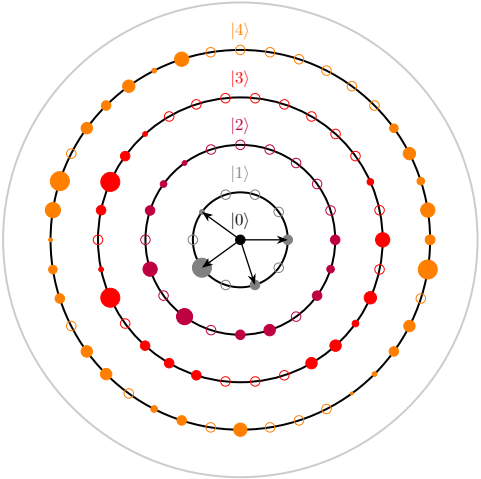

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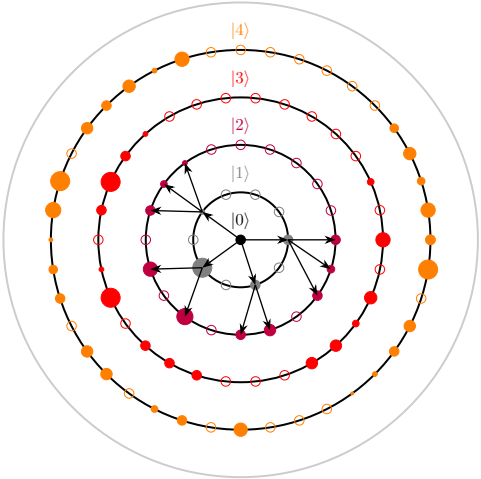

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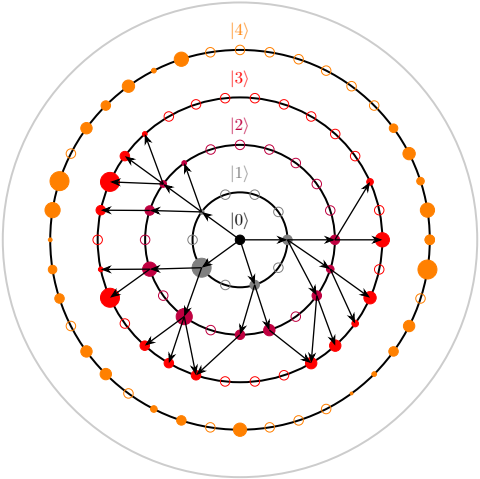

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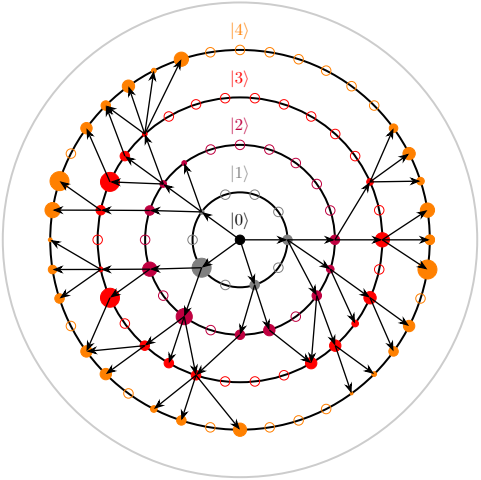
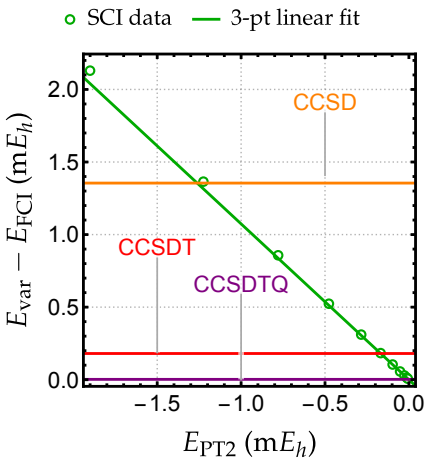


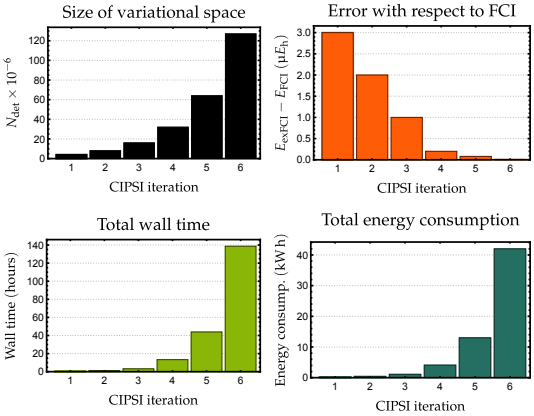
“Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs”, Garniron et al, JCTC 15 (2019) 3591

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)

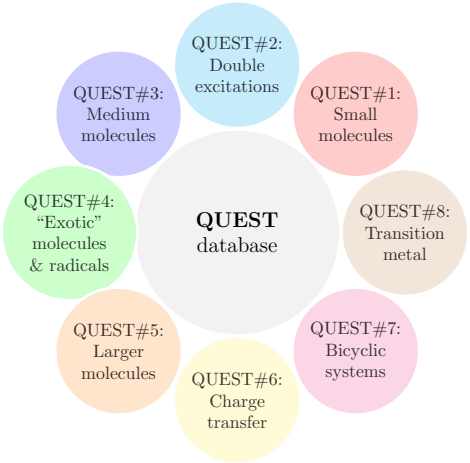
Fábris Kossoski (Postdoc)

Martial Boggio-Pasqua (Toulouse)

Denis Jacquemin (Nantes)

Highly-accurate excitation energies: The QUEST project

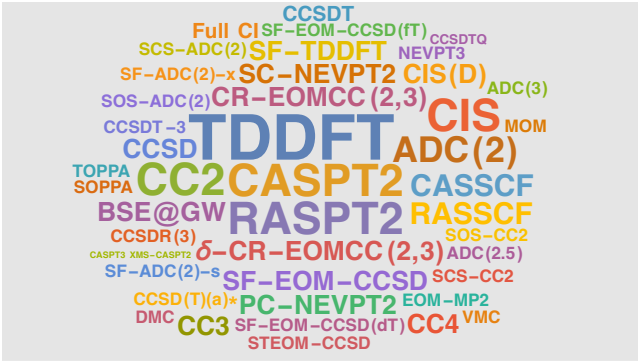
"The QUEST project aims to provide to the community a large set of highly-accurate excitation energies for various types of excited states"



- #1: JCTC 14 (2018) 4360
- #2: JCTC 15 (2019) 1939; arXiv:2403.19597
- #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...

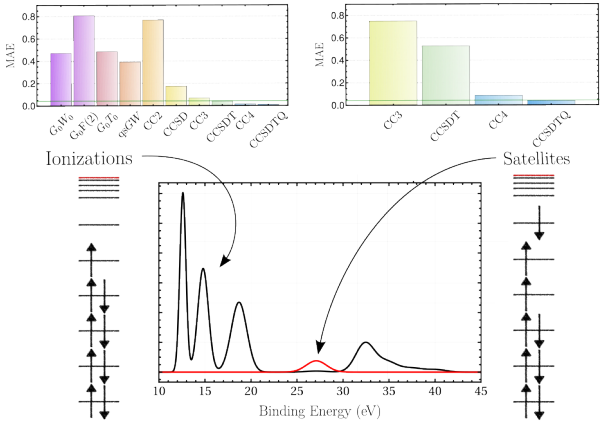
And this is just for excited states...



Other research groups using QUEST

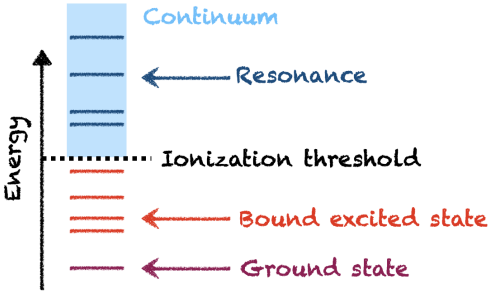
- Head-Gordon's group: orbital-optimized DFT for double excitations [JCTC 16 (2020) 1699; JPCL 12 (2021) 4517] and TD-DFT benchmark [JCTC 18 (2022) 3460]
- Kaupp's group: assessment of hybrid functionals [JCP 155 (2021) 124108]
- Kallay's and Goerigk's groups: double hybrids [JCTC 15 (2019) 4735; JCTC 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]

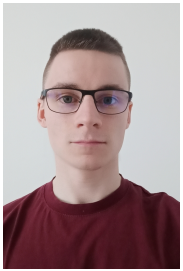
Extension to Charged Excitations



Marie & Loos, arXiv:2402.13877

Antoine Marie (PhD)





Yann Damour (PhD)

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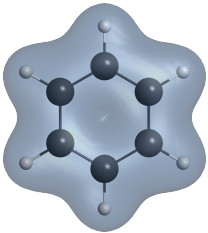
Photochemistry

$$h\nu + AB \rightarrow AB^* \rightarrow A + B$$



Bound state

Photochemistry

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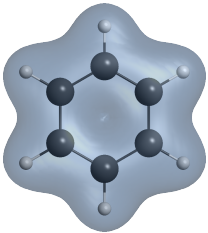
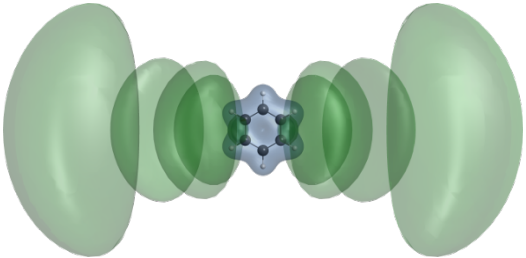


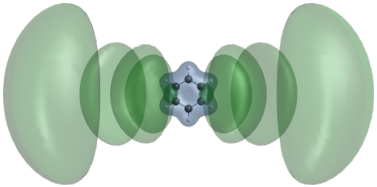
Bound state

Low-energy electron-induced chemistry

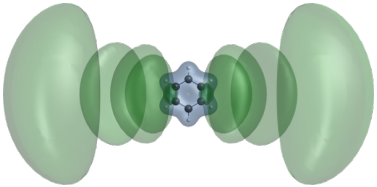
$$e^- + AB \rightarrow AB^- \rightarrow A^- + B$$
$$\rightarrow e^- + AB^*$$

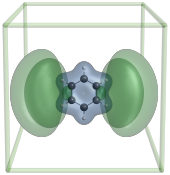


Resonance

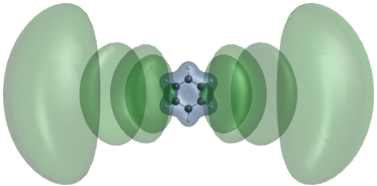


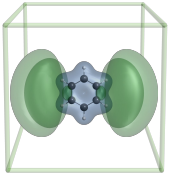
Jagau, Chem. Comm. 58 (2022) 5205



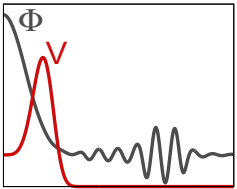


Jagau, Chem. Comm. 58 (2022) 5205

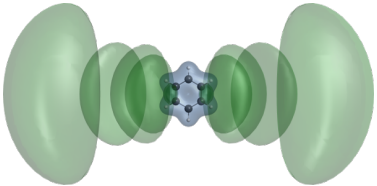




$H = T + V$



Jagau, Chem. Comm. 58 (2022) 5205



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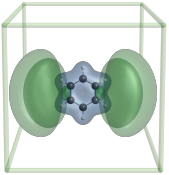
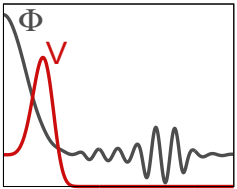
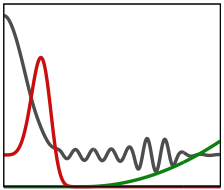


$H(\eta) = T + V - i\eta W$





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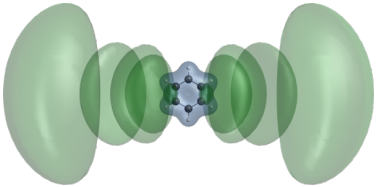

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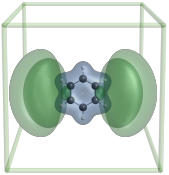
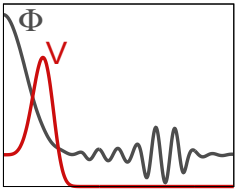
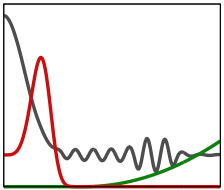
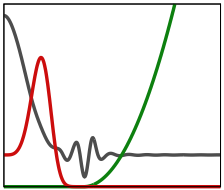


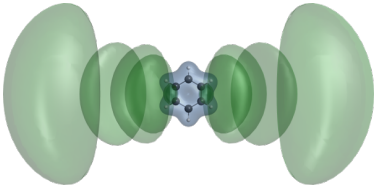
$H(\eta) = T + V - i\eta W$



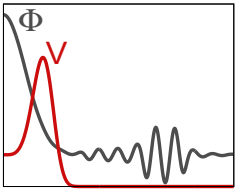


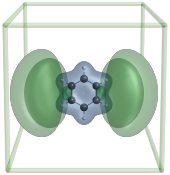


Jagau, Chem. Comm. 58 (2022) 5205

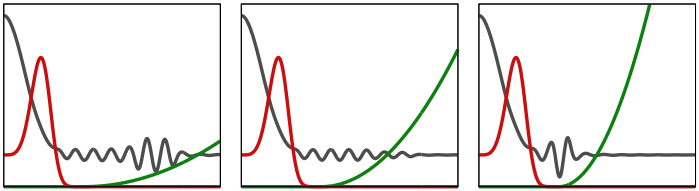


$H = T + V$





$H(\eta) = T + V - i\eta W$



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Sara Giarrusso (Postdoc)

Levy-Lieb constrained search

Ground-state energy

External potential

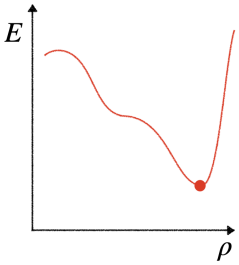
$$E = \min_{\rho} \left\{ F[\rho] + \int v(\boldsymbol{r})\, \rho(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \right\}$$

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

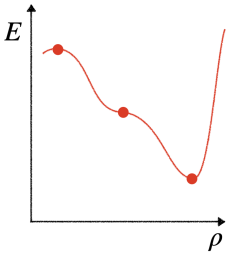
mth excited-state energy

External potential

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

Excited-state functional

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



Görling PRA 54 (1996) 3912

Generic wave function

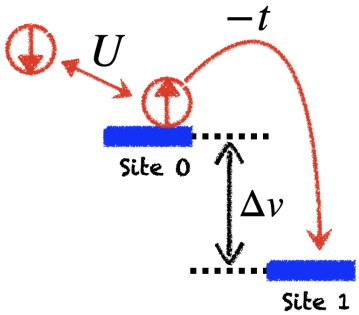
$$|\Psi\rangle = x\,|0_\uparrow 0_\downarrow\rangle + y\,\frac{|0_\uparrow 1_\downarrow\rangle - |0_\downarrow 1_\uparrow\rangle}{\sqrt{2}} + z\,|1_\uparrow 1_\downarrow\rangle$$

Energy

Total: E — Repulsion: V_{ee} — Kinetic: T — External: V_{ext}

$$E = T + V_{ee} + V_{ext}$$

$$T = -2\sqrt{2}\,t\,y\,(x+z) \qquad V_{ee} = U\left(x^2+z^2\right) \qquad V_{ext} = \rho\,\Delta v$$



Carrascal et al. JPCM 27 (2015) 393001

Normalization

$x^2 + y^2 + z^2 = 1 \quad \Rightarrow$ This is a sphere!

Density

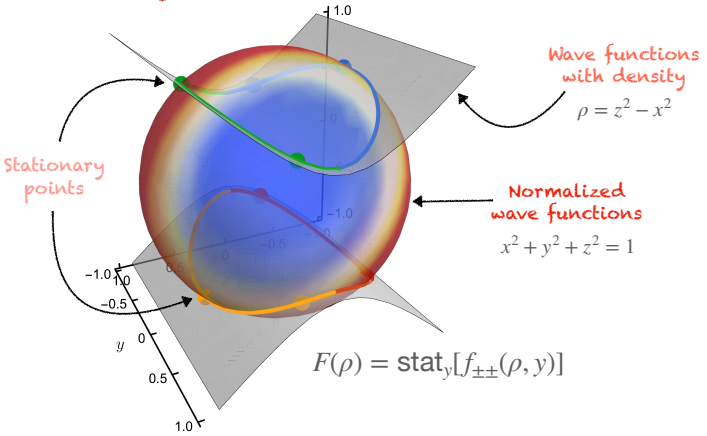
$\rho = z^2 - x^2 \quad \Rightarrow$ This is a parabola!

Stationary condition

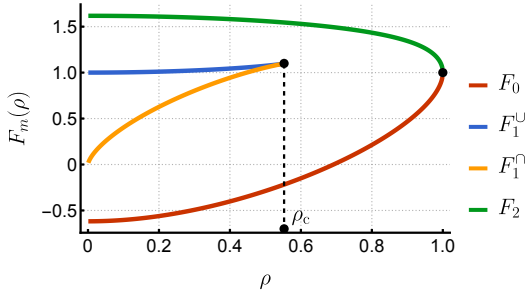
$$F(\rho) = \underset{\substack{\Psi \\ \rho_\Psi = \rho}}{\text{stat}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \underset{\substack{\Psi \\ \rho_\Psi = \rho}}{\text{stat}} \left[-2\sqrt{2}\, t\, y\, (x+z) + U\left(x^2 + z^2\right) \right] = \underset{y}{\text{stat}} [f_{\pm\pm}(\rho, y)]$$

$$f_{\pm\pm}(\rho, y) = -2ty\left(\pm\sqrt{1 - y^2 - \rho} \pm \sqrt{1 - y^2 + \rho} \right) + U\left(1 - y^2\right)$$

Levy's constrained search



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

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- Denis Jacquemin
- Martial Boggio-Pasqua
- Michel Caffarel

https://pfloos.github.io/WEB_LOOS

https://lcpq.github.io/PTEROSOR