Quantum Chemistry in the Complex Domain

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Collaborators and Funding

- Selected CI and QMC

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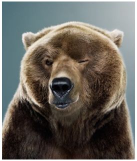

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Michel Caffarel

Denis Jacquemin

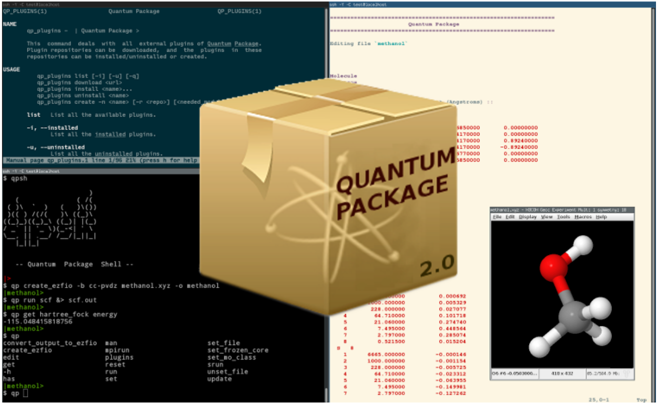
- Green function methods

Arjan Berger

Pina Romaniello

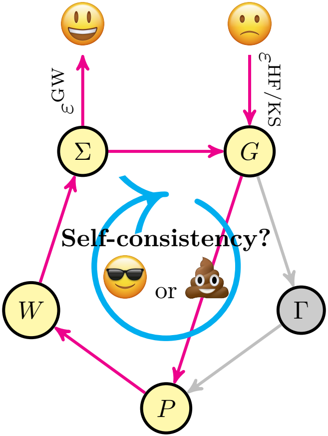
Mika Véril

Selected CI methods + range-separated hybrids



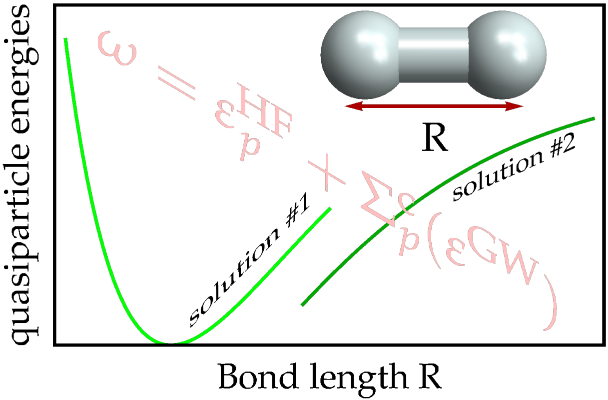
"Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs",
Garniron et al. , JCTC (submitted) arXiv:1902.08154

Green functions & self-consistency: an unhappy marriage?



"Green functions and self-consistency: insights from the spherium model",
Loos, Romaniello & Berger, JCTC 14 (2018) 3071

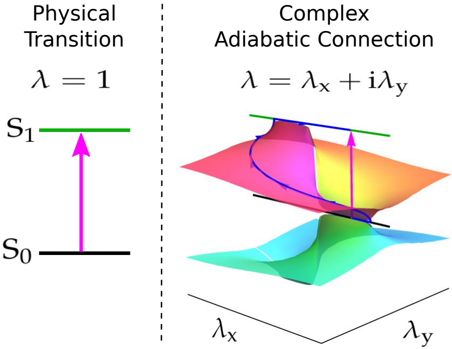
There's a glitch in GW



"Unphysical discontinuities in GW methods",
Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

How to morph ground state into excited state?

$$\hat{H} = -\frac{1}{2}\hat{\nabla}^2 + \lambda \sum_{i<j} \frac{1}{r_{ij}}$$



"Complex Adiabatic Connection: a Hidden Non-Hermitian Path from Ground to Excited States",
Burton, Thom & Loos, JCP *Comm.* 150 (2019) 041103

Section 2

$\mathcal{PT}$-symmetric Quantum Mechanics

Carl Bender

- Professor of Physics at Washington University in St. Louis:
  Expert in Mathematical Physics
- Homepage:
  https://web.physics.wustl.edu/cmb/
- Book:
  "Advanced Mathematical Methods for Scientists and Engineers"
- Series of 15 lectures (can be found on YouTube) on Mathematical Physics:
  - summation of divergent series
  - perturbation theory
  - asymptotic expansion
  - WKB approximation
- He will be lecturing at the 3rd Mini-school on Mathematics (19th-21st Jun, Jussieu)
  https://wiki.lct.jussieu.fr/gdrnbody

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Real Spectra in Non-Hermitian Hamiltonians Having $\mathcal{PT}$ Symmetry

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The condition of self-adjointness ensures that the eigenvalues of a Hamiltonian are real and bounded below. Replacing this condition by the weaker condition of $\mathcal{PT}$ symmetry, one obtains new infinite classes of complex Hamiltonians whose spectra are also real and positive. These $\mathcal{PT}$ symmetric theories may be viewed as analytic continuations of conventional theories from real to complex phase space. This paper describes the unusual classical and quantum properties of these theories. [S0031-9007(98)06371-6]

The spectrum of the Hamiltonian

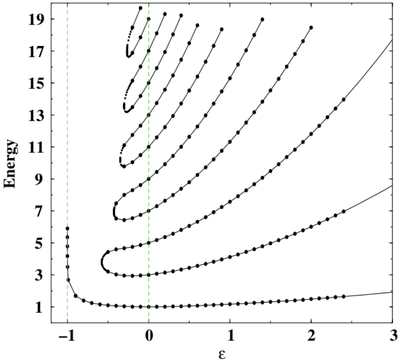
$$\hat{H} = p^2 + i\,x^3$$

is *real and positive*.

Why? Because it is $\mathcal{PT}$ symmetric, i.e. invariant under the *combination* of

- parity $\mathcal{P}$: $p \to -p$ and $x \to -x$
- time reversal $\mathcal{T}$: $p \to -p$, $x \to x$ and $i \to -i$

$$\hat{H} = p^2 + x^2(ix)^\epsilon$$



- $\epsilon \geq 0$: unbroken $\mathcal{PT}$-symmetry region
- $\epsilon = 0$: $\mathcal{PT}$ boundary
- $\epsilon < 0$: broken $\mathcal{PT}$-symmetry region
  (eigenfunctions of $\hat{H}$ aren't eigenfunctions of $\mathcal{PT}$ simultaneously)

Hermitian vs $\mathcal{PT}$-symmetric

$\mathcal{PT}$-symmetric QM is an extension of QM into the complex plane

- Hermitian: $\hat{H} = \hat{H}^\dagger$ where $\dagger$ means transpose + complex conjugate
- $\mathcal{PT}$-symmetric: $\hat{H} = \hat{H}^{\mathcal{PT}}$, i.e. $\hat{H} = \mathcal{PT}\hat{H}(\mathcal{PT})^{-1}$
- Hermiticity is very powerful as it guarantees real energies and conserves probability
- (unbroken) $\mathcal{PT}$ symmetry is a *weaker* condition which still ensure real energies and probability conservation

Hermitian vs $\mathcal{PT}$-symmetric vs Non-Hermitian

Hermitian $\hat{H}$	$\mathcal{PT}$-symmetric $\hat{H}$	non-Hermitian $\hat{H}$
$\hat{H}^\dagger = \hat{H}$	$\hat{H}^{\mathcal{PT}} = \hat{H}$	$\hat{H}^\dagger \neq \hat{H}$
Closed systems	$\mathcal{PT}$-symmetric systems	Open systems
$\langle a\|b\rangle = a^\dagger \cdot b$	$\langle a\|b\rangle = a^{\mathcal{CPT}} \cdot b$	(scattering, resonances, etc)

$\mathcal{PT}$-symmetric QM is a genuine quantum theory

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Complex Extension of Quantum Mechanics

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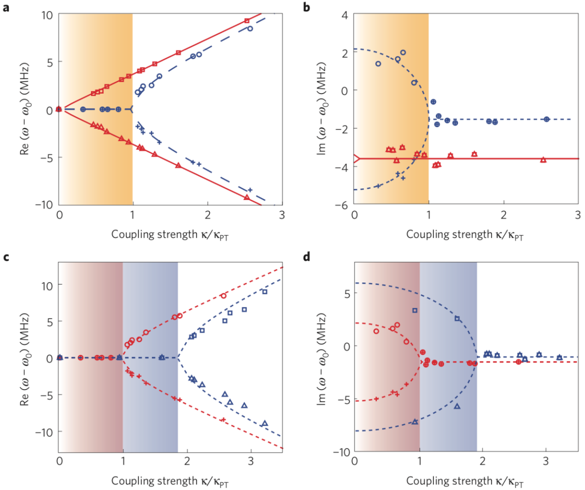
(Received 12 August 2002; published 16 December 2002)

Requiring that a Hamiltonian be Hermitian is overly restrictive. A consistent physical theory of quantum mechanics can be built on a complex Hamiltonian that is not Hermitian but satisfies the less restrictive and more physical condition of space-time reflection symmetry ($\mathcal{PT}$ symmetry). One might expect a non-Hermitian Hamiltonian to lead to a violation of unitarity. However, if $\mathcal{PT}$ symmetry is not spontaneously broken, it is possible to construct a previously unnoticed symmetry C of the Hamiltonian. Using C, an inner product whose associated norm is positive definite can be constructed. The procedure is general and works for any $\mathcal{PT}$-symmetric Hamiltonian. Observables exhibit $C\mathcal{PT}$ symmetry, and the dynamics is governed by unitary time evolution. This work is not in conflict with conventional quantum mechanics but is rather a complex generalization of it.

Take-home message:

$\mathcal{PT}$-symmetric Hamiltonian can be seen as analytic continuation of Hermitian Hamiltonian from real to complex space. [1]

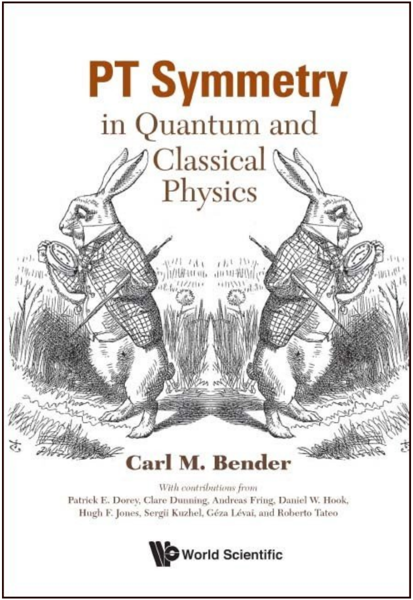
[1] The relativistic version of $\mathcal{PT}$-symmetric QM does exist.



"Parity-time-symmetric whispering-gallery microcavities"
Peng et al. *Nature Physics* 10 (2014) 394

Highlight in Nature Physics (2015)

$\mathcal{PT}$-symmetry in Quantum and Classical Physics



Section 3

Non-Hermitian quantum chemistry

Hermitian Hamiltonian going complex

Let's consider the Hamiltonian for two electrons on a unit sphere

$$\boldsymbol{H} = -\frac{\nabla_1^2 + \nabla_2^2}{2} + \frac{\lambda}{r_{12}}$$

The CID/CCD Hamiltonian for 2 states reads

$$\boldsymbol{H} = \boldsymbol{H}^{(0)} + \lambda\, \boldsymbol{H}^{(1)} = \begin{pmatrix} \lambda & \lambda/\sqrt{3} \\ \lambda/\sqrt{3} & 2 + 7\lambda/5 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 2 \end{pmatrix} + \lambda \begin{pmatrix} 1 & 1/\sqrt{3} \\ 1/\sqrt{3} & 7/5 \end{pmatrix}$$

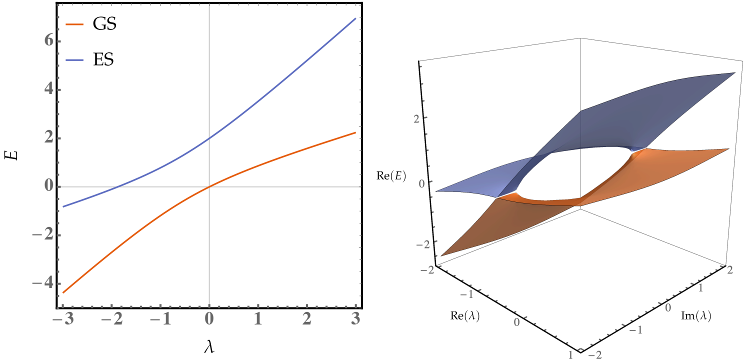
The eigenvalues are

$$E_{\pm} = 1 + \frac{18\lambda}{15} \pm \sqrt{1 + \frac{2\lambda}{5} + \frac{28\lambda^2}{75}}$$

For complex λ, the Hamiltonian becomes non Hermitian.
There is a (square-root) singularity in the complex-λ plane at

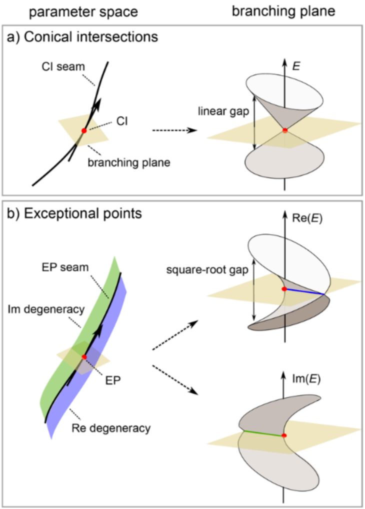
$$\lambda_{\text{EP}} = -\frac{15}{28}\left(1 \pm i\,\frac{5}{\sqrt{3}}\right) \qquad \text{(Exceptional points)}$$

Hermitian Hamiltonian going complex



- There is an avoided crossing at $\text{Re}(\lambda_{\text{EP}})$
- The smaller $\text{Im}(\lambda_{\text{EP}})$, the sharper the avoided crossing is
- Square-root branch cuts from λ_{EP} running parallel to the Im axis towards $\pm i\infty$
- (non-Hermitian) exceptional points $\equiv$ (Hermitian) conical intersection
- $\text{Im}(\lambda_{\text{EP}})$ is linked to the radius of convergence of PT

Conical intersection (CI) vs exceptional point (EP)



Benda & Jagau, JPCL 9 (2018) 6978

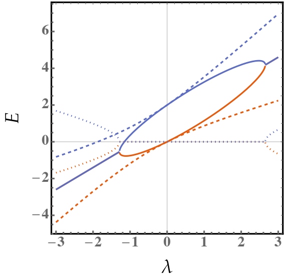
- At CI, the eigenvectors stay orthogonal
- At EP, both eigenvalues and eigenvectors coalesce (self-orthogonal state)
- Encircling a CI, states do not interchange but wave function picks up geometric phase
- Encircling a EP, states can interchange and wave function picks up geometric phase
- encircling a EP clockwise or anticlockwise yields different states

Hermitian Hamiltonian going $\mathcal{PT}$-symmetric

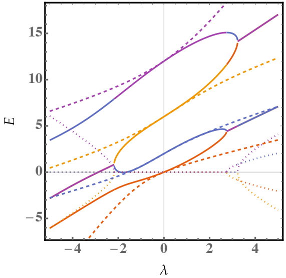
How to $\mathcal{PT}$-symmetrize a CI matrix?

$$\boldsymbol{H} = \begin{pmatrix} \lambda & i\lambda/\sqrt{3} \\ i\lambda/\sqrt{3} & 2 + 7\lambda/5 \end{pmatrix}$$

It is definitely not Hermitian but the $\mathcal{PT}$-symmetry is not obvious...



$$\begin{aligned}\boldsymbol{H} &= \begin{pmatrix} \epsilon_1 & i\lambda \\ i\lambda & \epsilon_2 \end{pmatrix} \\ &= \begin{pmatrix} (\epsilon_1+\epsilon_2)/2 & 0 \\ 0 & (\epsilon_1+\epsilon_2)/2 \end{pmatrix} \\ &+ i \begin{pmatrix} i(\epsilon_2-\epsilon_1)/2 & \lambda \\ \lambda & -i(\epsilon_2-\epsilon_1)/2 \end{pmatrix}\end{aligned}$$



$\mathcal{PT}$-symmetry projects exceptional points on the real axis

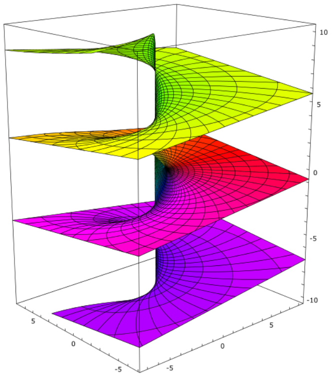
Section 4

non-Hermitian Quantum Chemistry

- Quantum mechanics is quantized because we're looking at it in the real plane (Reimann sheets or parking garage)
- If you extend real numbers to complex numbers you lose the *ordering* property of real numbers
- So, can we interchange ground and excited states away from the real axis?
- How do we do it (in practice)?

The basic idea

- Quantum mechanics is quantized because we're looking at it in the real plane (Reimann sheets or parking garage)
- If you extend real numbers to complex numbers you lose the *ordering* property of real numbers
- So, can we interchange ground and excited states away from the real axis?
- How do we do it (in practice)?



Holomorphic HF = analytical continuation of HF

Let's consider (again) the Hamiltonian for two electrons on a unit sphere

$$\hat{H} = -\frac{\nabla_1^2 + \nabla_2^2}{2} + \frac{\lambda}{r_{12}}$$

We are looking for a UHF solution of the form

$$\Psi_{\text{UHF}}(\theta_1, \theta_2) = \varphi(\theta_1)\varphi(\pi - \theta_2)$$

where the spatial orbital is $\varphi = s \cos\chi + p_z \sin\chi$.

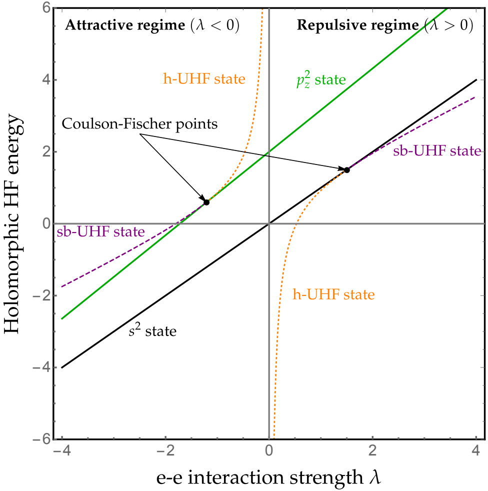
Ensuring the stationarity of the UHF energy, i.e., $\partial E_{\text{UHF}} / \partial \chi = 0$

$$\sin 2\chi \, (75 + 6\lambda - 56\lambda \cos 2\chi) = 0$$

or

$$\chi = 0 \text{ or } \pi/2 \qquad\qquad \chi = \pm \arccos\left(\frac{3}{28} + \frac{75}{56\lambda}\right)$$

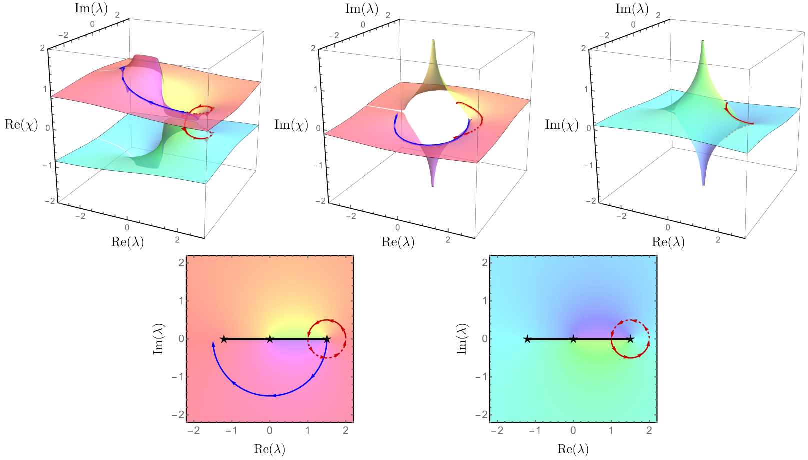
HF energy landscape



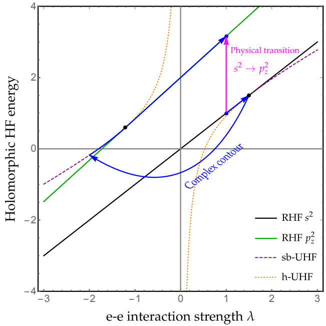
$$E_{\text{RHF}}^{s^2}(\lambda) = \lambda \quad E_{\text{RHF}}^{p_z^2}(\lambda) = 2 + \frac{29\lambda}{25} \quad E_{\text{UHF}}(\lambda) = -\frac{75}{112\lambda} + \frac{25}{28} + \frac{59\lambda}{84}$$

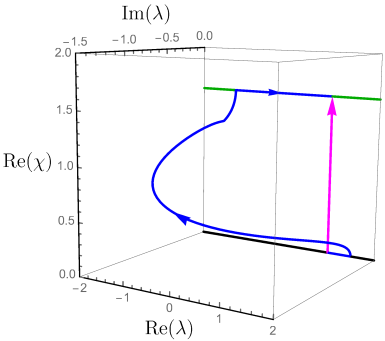
Analytical continuation and state interconversion

$$\arccos(z) = \pi/2 + i\log\left(i\,z + \sqrt{1 - z^2}\right) \qquad z = 3/28 + 75/(56\lambda)$$



Complex adiabatic connection path





Coulson-Fisher points ≈ exceptional points ⇒ quasi-exceptional points

That's (almost) the end...

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