Quantum Chemistry in the Complex Domain

Pierre-François (Titou) Loos

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

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Students, postdocs & colleagues

- Selected CI and QMC

Anthony Scemama

Michel Caffarel

Mika Véril

Clotilde Marut

- Green's function methods

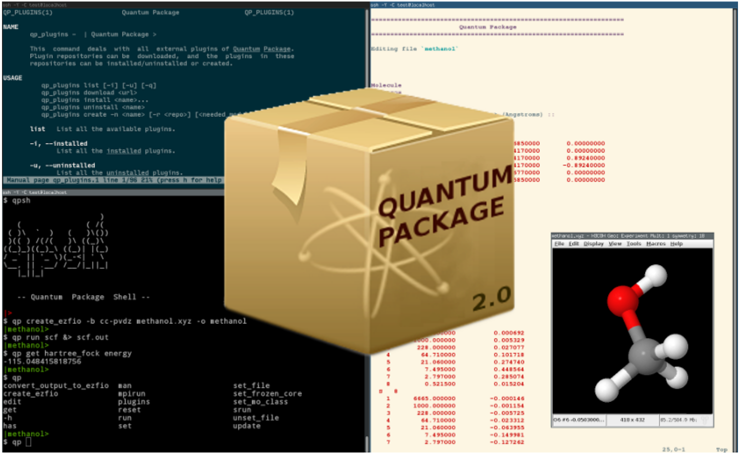
Arjan Berger

Pina Romaniello

Mr/Ms Postdoc

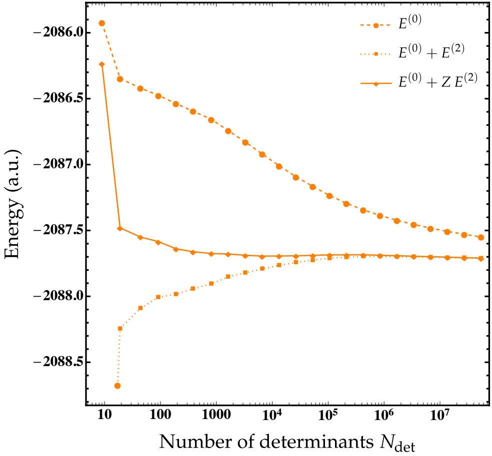
Loos, Romaniello & Berger, JCTC 14 (2018) 3071

Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220



"Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs",
Garniron et al., JCTC (ASAP) 10.1021/acs.jctc.9b00176

Ground state of Cr_2 in cc-pVQZ: full-valence CAS(28,198)



Garniron et al., JCTC (ASAP) 10.1021/acs.jctc.9b00176

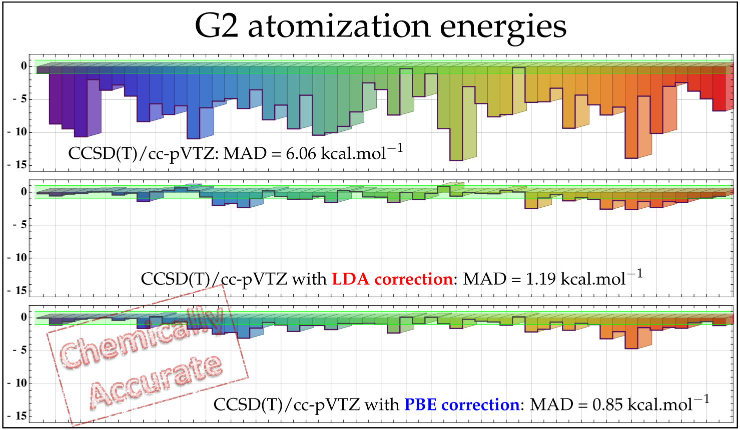
What can you do with QP2? (Basically everything but here's a short list...)

Applications

- sCI+PT2: Benchmarking excited-state methods
  Loos, Scemama, Blondel, Garniron, Caffarel & Jacquemin, JCTC 14 (2018) 4360
- sCI+PT2: Double excitations
  Loos, Boggio-Pasqua, Scemama, Caffarel & Jacquemin, JCTC 15 (2019) 1939
- sCI+QMC: "Challenging" case of FeS
  Scemama, Garniron, Caffarel & Loos, JCTC 14 (2018) 1395
- sCI+QMC: Excitation energies with "deterministic" nodes
  Scemama, Benali, Jacquemin, Caffarel & Loos, JCP 149 (2019) 064103

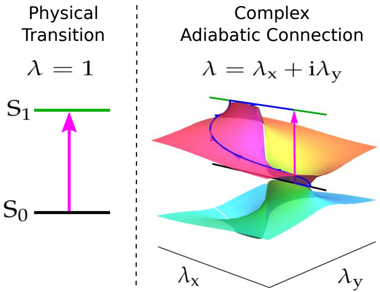
Developments

- Semi-stochastic PT2
  Garniron, Scemama, Loos & Caffarel, JCP 147 (2017) 034101
- Renormalized PT2 & stochastic selection
  Garniron et al., JCTC (ASAP) 10.1021/acs.jctc.9b00176
- Internally-decontrated version (shifted-Bk)
  Garniron, Scemama, Giner, Caffarel & Loos, JCP 149 (2018) 064103



"A Density-Based Basis-Set Correction for Wave Function Theory",
Loos, Pradines, Scemama, Toulouse & Giner JPCL 10 (2019) 2931

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



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

"$\mathcal{PT}$-Symmetry in Hartree-Fock Theory",
Burton, Thom & Loos, JCTC (revised) arXiv:1903.08489

Section 2

Non-Hermitian quantum chemistry

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

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

Loos & Gill, PRL 103 (2009) 123008

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

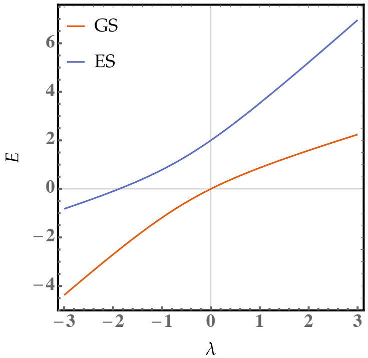
$$\boxed{E_{\pm} = 1 + \frac{18\lambda}{15} \pm \sqrt{1 + \frac{2\lambda}{5} + \frac{28\lambda^2}{75}}}$$

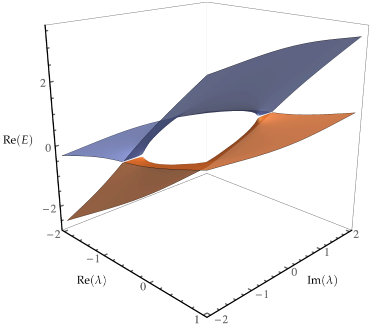
For complex λ, the Hamiltonian becomes non Hermitian.

There is a (square-root) singularity in the complex-λ plane at

$$\lambda_{\text{EP}} = -\frac{15}{28}\left(1 \pm i\frac{5}{\sqrt{3}}\right) \qquad \text{(Exceptional points)} \qquad |\lambda_{\text{EP}}| \approx 1.64 > 1$$

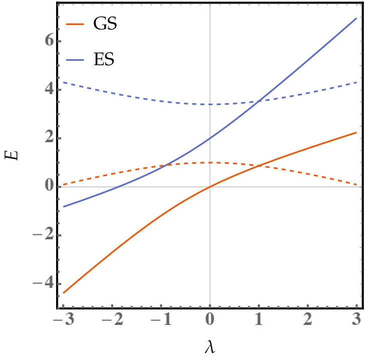
Moiseyev, *Non-Hermitian Quantum Mechanics*, Cambridge University Press, 2011

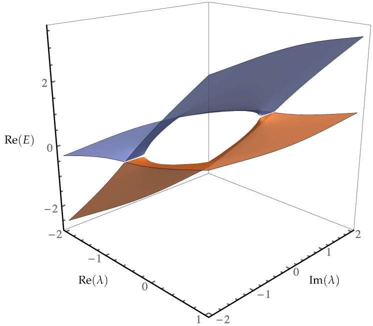




- There is an avoided crossing at $\mathrm{Re}(\lambda_{\mathrm{EP}})$
- Square-root branch cuts from λ_{EP} running parallel to the Im axis towards $\pm i\infty$
- (non-Hermitian) exceptional points $\equiv$ (Hermitian) conical intersection
- $\mathrm{Im}(\lambda_{\mathrm{EP}})$ is linked to the radius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

Hermitian Hamiltonian going complex





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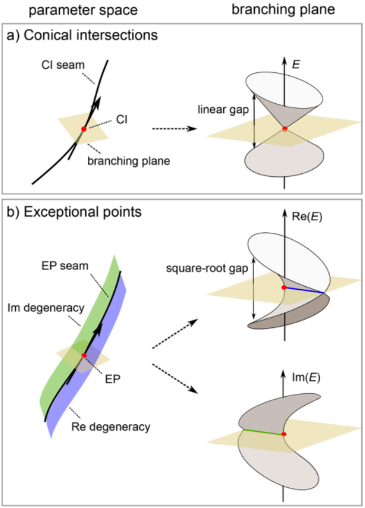
Conical intersection (CI) vs exceptional point (EP)



Benda & Jagau, JPCL 9 (2018) 6978

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

- Quantum mechanics is quantized because we're looking at it in the real plane (Riemann 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)?

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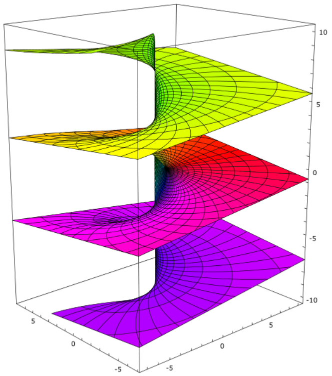


Let's consider (again) the Hamiltonian for two electrons on a unit sphere

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

We are looking for a UHF solution of the form

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

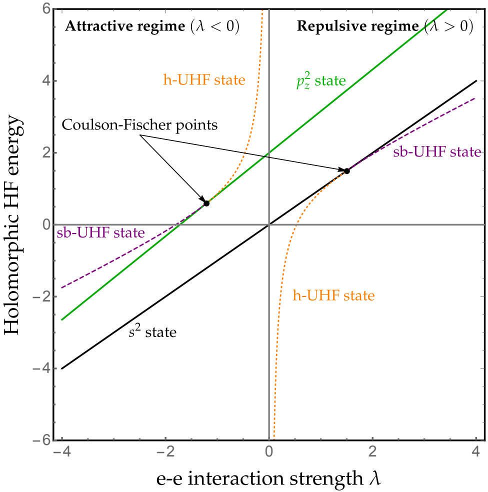
where the spatial orbital is $\varphi = s \cos\chi + p_z \sin\chi$.

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

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

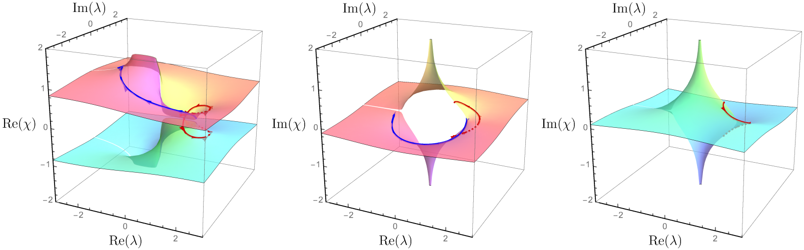
or

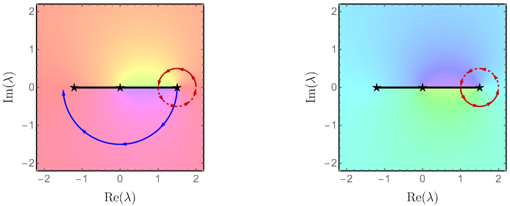
$$\chi = 0 \text{ or } \pi/2 \qquad\qquad \chi = \pm \arccos\left(\frac{3}{28} + \frac{75}{56\lambda}\right)$$

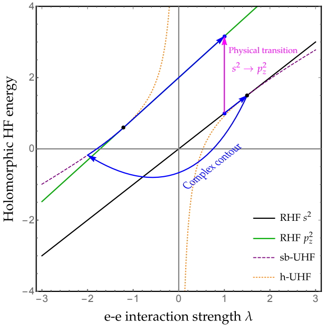


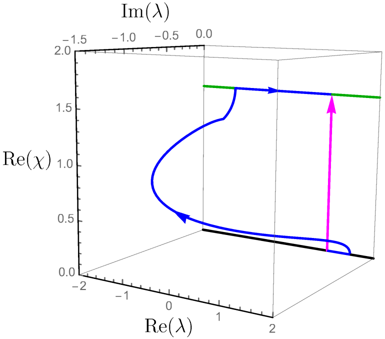
$$E_{\text{RHF}}^{s^2}(\lambda) = \lambda \qquad E_{\text{RHF}}^{p_z^2}(\lambda) = 2 + \frac{29\lambda}{25} \qquad E_{\text{UHF}}(\lambda) = -\frac{75}{112\lambda} + \frac{25}{28} + \frac{59\lambda}{84}$$

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









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

Section 3

$\mathcal{PT}$-symmetric Quantum Mechanics

VOLUME 80, NUMBER 24 PHYSICAL REVIEW LETTERS 15 JUNE 1998

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

Carl M. Bender[1] and Stefan Boettcher[2,3]
[1]*Department of Physics, Washington University, St. Louis, Missouri 63130*
[2]*Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
[3]*CTSPS, Clark Atlanta University, Atlanta, Georgia 30314*
(Received 1 December 1997; revised manuscript received 9 April 1998)

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?

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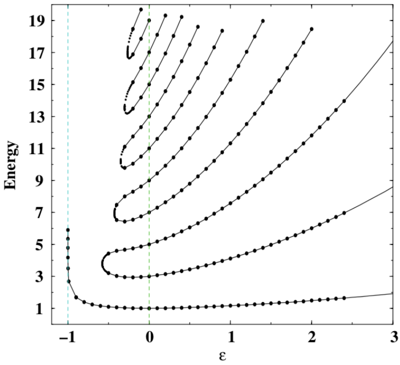
Why?

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 $i \to -i$
- Combined $\mathcal{PT}$: $p \to p$, $x \to -x$ and $i \to -i$

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

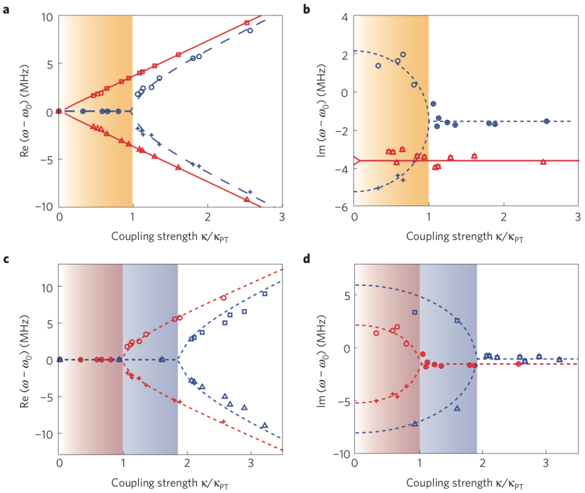


- $\epsilon \geq 0$: unbroken $\mathcal{PT}$-symmetry region
- $\epsilon = 0$: $\mathcal{PT}$ boundary
- $\epsilon < 0$: broken $\mathcal{PT}$-symmetry region
  (eigenfunctions of $\hat{H}$ aren't eigenfunctions of $\mathcal{PT}$ simultaneously)

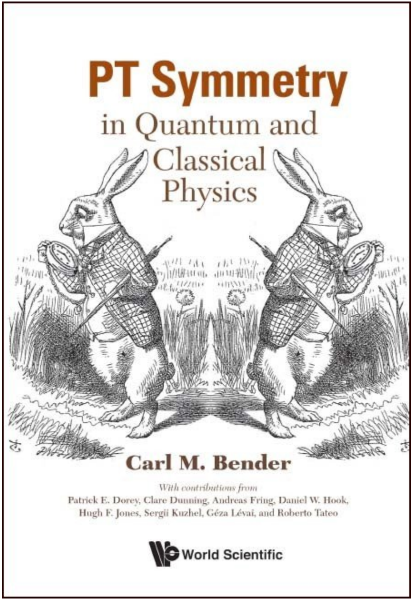
$\mathcal{PT}$-symmetric QM is an extension of QM into the complex plane

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



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


PT Symmetry
in Quantum and
Classical
Physics
Carl M. Bender
With contributions from
Patrick E. Dorey, Clare Dunning, Andreas Fring, Daniel W. Hook,
Hugh F. Jones, Sergii Kuzhel, Géza Lévai, and Roberto Tateo
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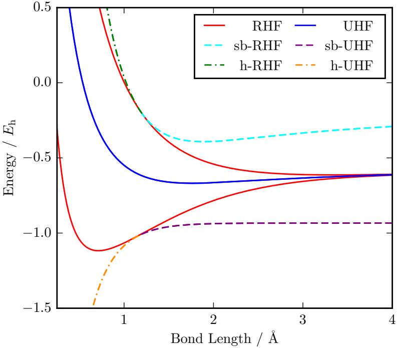
$\mathcal{PT}$-symmetry in Hartree-Fock theory: minimal basis H_2



Real UHF solution $\equiv$ covalent configuration

Real RHF solution $\equiv$ ionic configuration

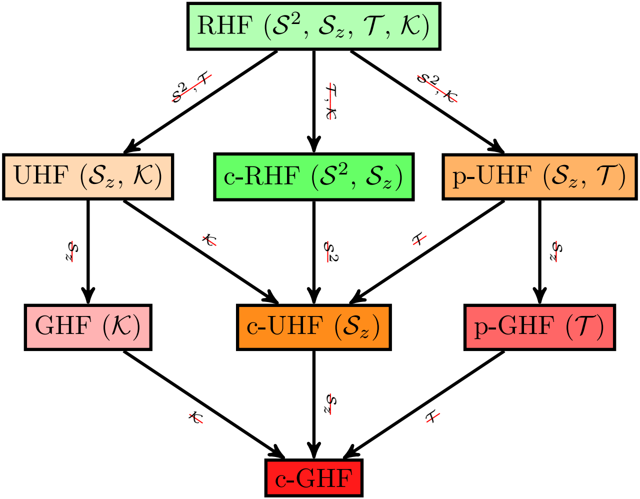
Burton, Thom & Loos, JCTC (revised) arXiv:1903.08489

$\mathcal{PT}$-HF theory

- MOs are $\mathcal{PT}$-symmetric iff Fock operator is $\mathcal{PT}$-symmetric (and vise-versa)
- Like other symmetries, $\mathcal{PT}$-symmetry "propagates" during SCF process
- If MOs are $\mathcal{PT}$-symmetric then MOs energies and HF energy are real
- $\mathcal{PT}$-symmetry can be ensured by constructing $\mathcal{PT}$-doublets

$\mathcal{PT}$-symmetry is a new type of symmetry

The seven families of HF solutions



That's (almost) the end...

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NEXT
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