Diving into the continuum with resonances

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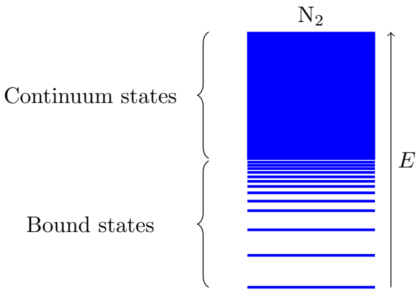
Resonances

Electronic spectrum of molecular systems:



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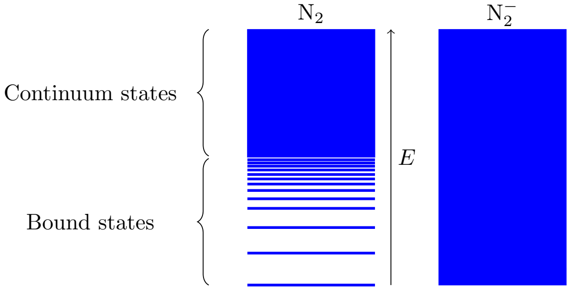

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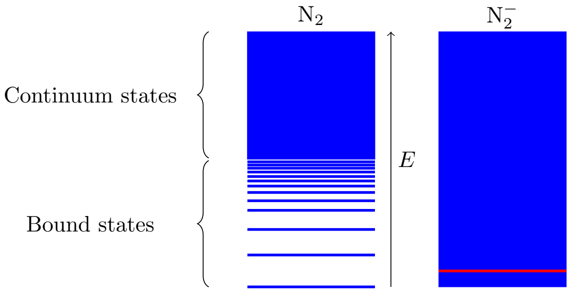

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Metastable states embedded in the continuum that can decay by losing one electron.
ex: $N_2{}^- \rightarrow N_2 + e^-$

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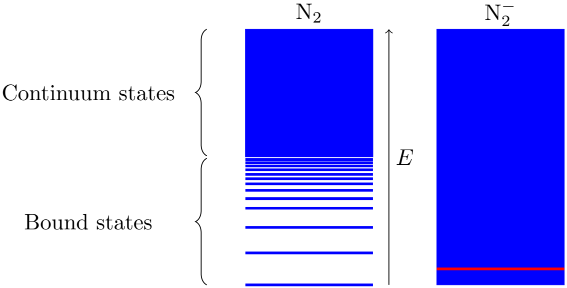

Temporary anions

- Electron attachment on a molecule:
  $A + e^- \rightarrow A^-$
- Photoexcitation of a bound anion:
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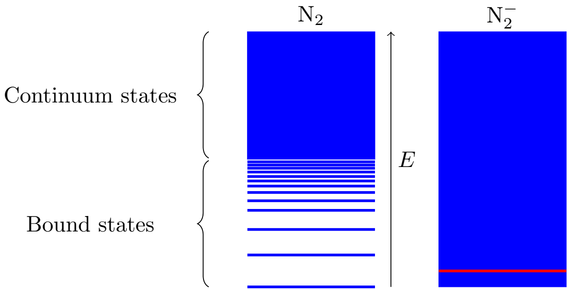

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Applications

- DNA damage induced by ionizing radiation
- Radiosensitizers for cancer
- Chemistry of interstellar medium
- ...

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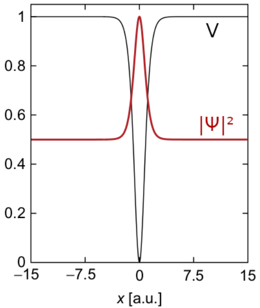

S. Klaiman and I. Gilary, in Advances in Quantum Chemistry, Vol. 63, 1–31 (2012)

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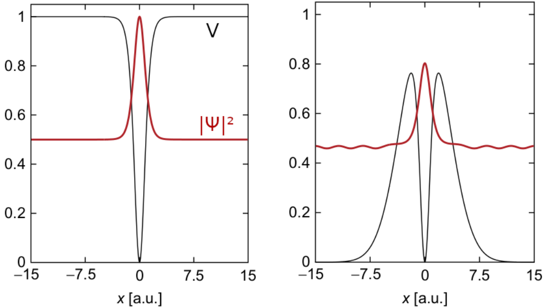

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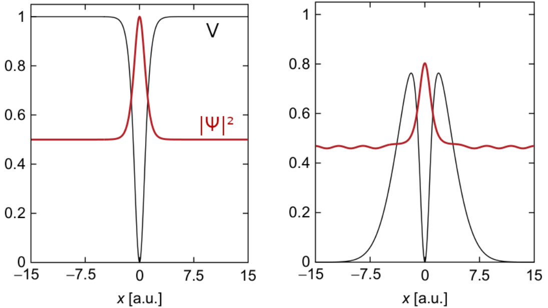

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Solutions

- Scattering methods
- Adaptation of quantum chemistry methods
  - Complex-absorbing potential, ...

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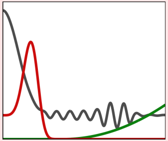

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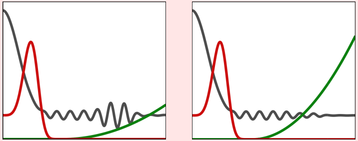

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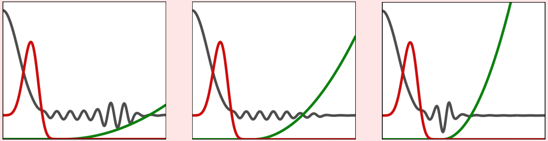

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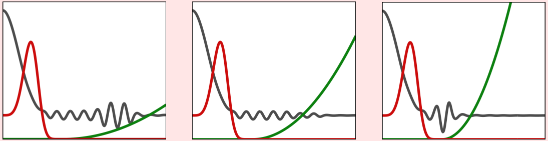

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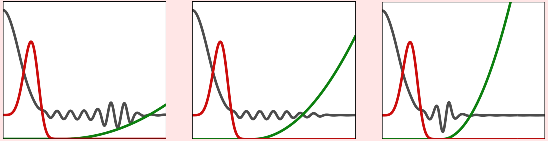

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Complete basis set

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Finite basis set

$\Rightarrow$ Optimal value η_{opt}

$$E_R = \text{Re}[E(\eta_{\text{opt}})] \qquad \Gamma = -2\,\text{Im}[E(\eta_{\text{opt}})]$$

CAP-CIPSI

Configuration Interaction using a Perturbative Selection made Iteratively (CIPSI)

- Accurately approach the FCI energy of usual bound states
- Required to benchmark methods
- CIPSI adaptation to do CAP-CIPSI
- Relatively small systems

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- Iterative algorithm
- At each iteration:
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  - Energy $E(\eta)$
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For a sufficiently large Ψ

- $E_{\text{FCI}}(\eta) \approx E(\eta) + E_{\text{PT2}}(\eta)$
- Evolution of $E(\eta)$ as a function of $E_{\text{PT2}}(\eta)$ to estimate $E_{\text{FCI}}(\eta)$

Application

N_2^-

- CAP-EA-EOM-CCSD / aug-cc-pVTZ+3s3p3d[a]
- η_{opt} from their work

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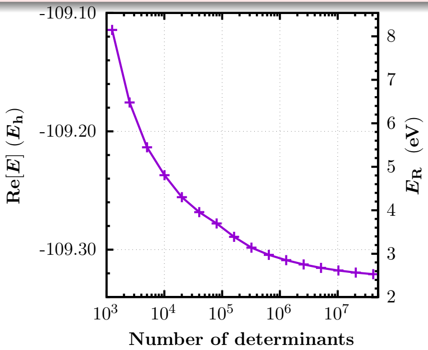

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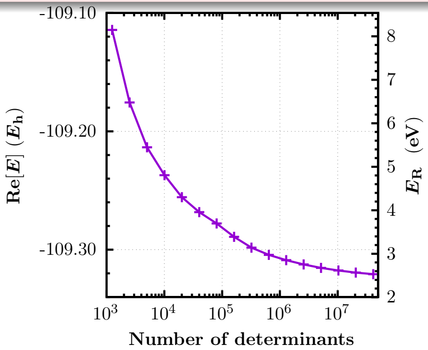

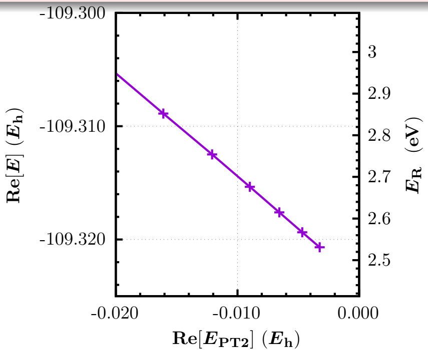

$1\ \text{kcal mol}^{-1} = 1.6 \times 10^{-3}\ E_h$

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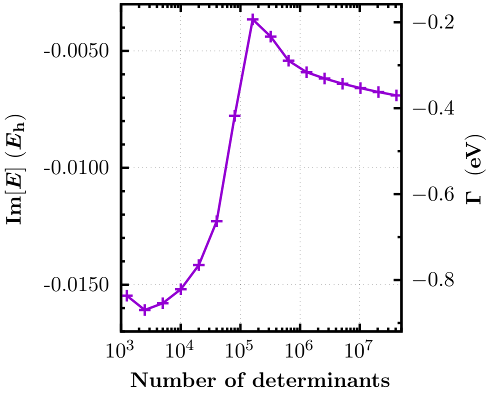

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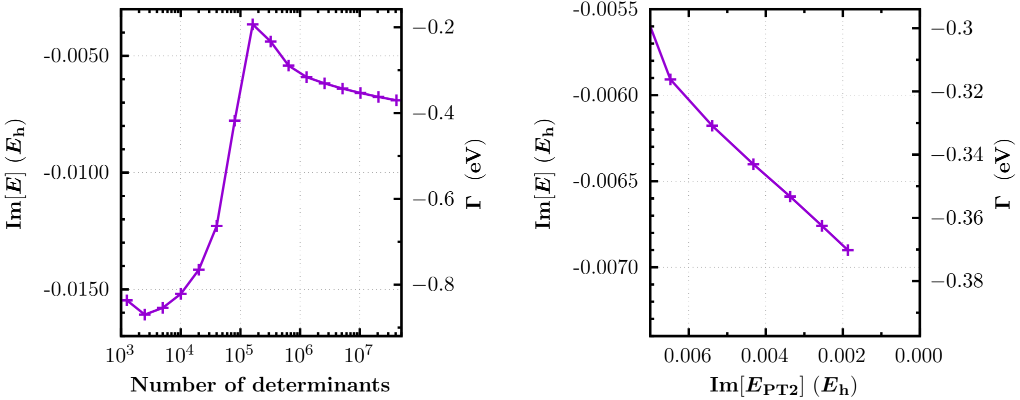

Results

N_2^-/aug-cc-pVTZ+3s3p3d

Method	E_R (eV)	Γ (eV)
Experiment[a]	2.316	0.414
CAP-EA-EOM-CCSD[b]	2.487	0.417
CAP-CIPSI	2.45	0.39

[a] Berman *et al.*, Phys. Rev. A 28, 1363 (1983)
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$N_2{}^-$/aug-cc-pVQZ+3s3p3d

Method	E_R (eV)	Γ (eV)
CAP-EA-EOM-CCSD[a]	2.508	0.364

[a]Zuev *et al.* , J. Chem. Phys. 141, 024102 (2014)

Perspectives

- Reference values for E_R and Γ with CAP-CIPSI
- η_{opt} with CAP-CIPSI
- Complex-basis functions

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cnrs

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LCPQ

Laboratoire de Chimie et Physique Quantiques

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