Resonances from density functional theory with complex scaling

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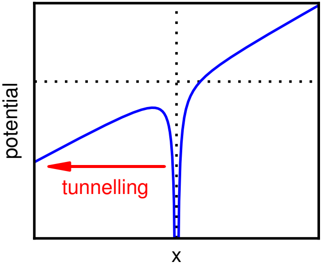
Examples of resonances

Negatively charged molecules

- Electrons may be locally bound by exchange/correlation, but be repelled once they escape beyond a certain radius
- Autoionization: N_2^-, Be^-, ...

Molecules/atoms in electric fields

- Right: atom + static E-field
- Molecules in strong adiabatic laser fields



Resonances may be long-lived and have important properties

Trouble with ordinary DFT

- DFT calculates the ground state density
- A "resonant state" is by definition not the ground state

Complex scaling

- Method to calculate "resonant states"
- Involves non-Hermitian "Hamiltonian"
- Resonances become eigenstates with complex energy
- Combine with DFT → DFRT,
  "density functional resonance theory"

The complex-scaling method

- Initial work by Aguilar, Balslev, Combes (1971) on operators under the "dilation" $\hat{R}_\theta \psi(\mathbf{r}) = \mathrm{e}^{iN\theta/2}\psi(\mathbf{r}\mathrm{e}^{i\theta})$,
- Original Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r})\right]\psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r})$$

- Complex-scaled by some fixed angle θ: $\hat{H}(\mathbf{r}) \rightarrow \hat{H}^\theta(\mathbf{r}) \equiv \hat{R}_\theta \hat{H} \hat{R}_\theta^{-1} = \hat{H}(\mathbf{r}\mathrm{e}^{i\theta})$ and

$$\left[-\mathrm{e}^{-i2\theta}\frac{1}{2}\nabla^2 + v(\mathbf{r}\mathrm{e}^{i\theta})\right]\psi_n^\theta(\mathbf{r}) = \epsilon_n^\theta \psi_n^\theta(\mathbf{r})$$

- Transformation differently affects eigenvalues of discrete versus continuous spectrum.

The complex-scaling method

- The complex Hamiltonian $\hat{H}^{\theta}(\mathbf{r})$ is non-Hermitian
- A “Resonant” eigenstate with energy $\epsilon_R + i\epsilon_I$ is characterized by uniform decay under time propagation
- Decay rate is $\Gamma = -2\epsilon_I$
- Let us diagonalize some complex-scaled Hamiltonians and see what happens

The free particle in one dimension

- Form of equation is effectively unchanged by complex scaling:

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi_\theta(x)}{\mathrm{d}x^2}\mathrm{e}^{-i2\theta} = \epsilon_\theta\psi_\theta(x)$$

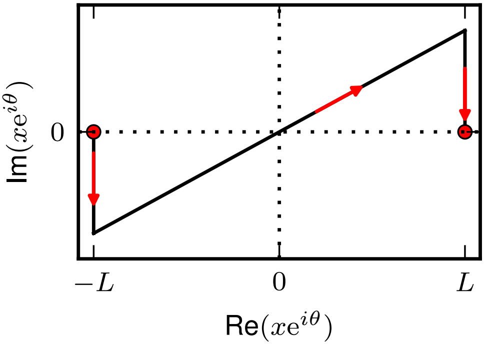
- Solve equation in box with zero boundary conditions to obtain same free-particle solutions but different energies $\epsilon_\theta = \epsilon_0 \exp(-i2\theta)$
- The continuum has “rotated down” by an angle of -2θ.
- Back-rotated states diverge exponentially:

$$\hat{R}_{-\theta}\psi_\theta(x) = \mathrm{e}^{-i\theta/2}\left(A\mathrm{e}^{ikx\cos\theta}\mathrm{e}^{kx\sin\theta} + B\mathrm{e}^{-ikx\cos\theta}\mathrm{e}^{-kx\sin\theta}\right)$$

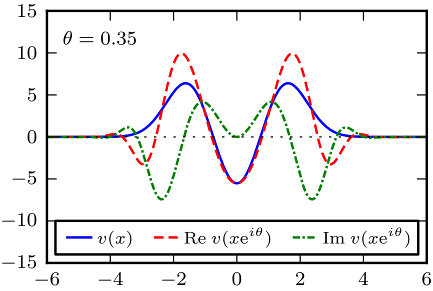
- The back-rotated states (almost) have outgoing character
- Suggestion: Square-integrable complex-scaled states can correspond to outgoing waves

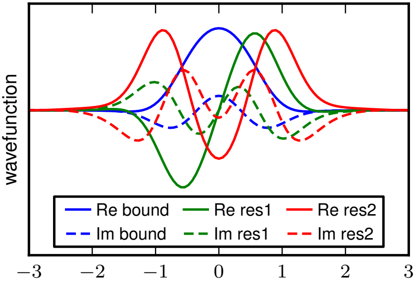
Effect on bounded states

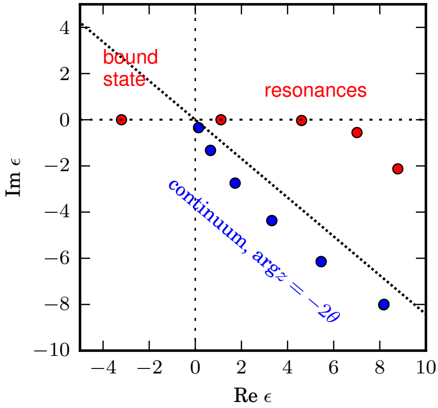
or: why this would ever work



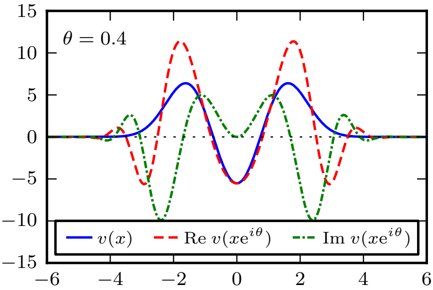
- Transformation corresponds to change of integration contour
- Integrals of analytic functions are contour-independent
- Thus: matrix elements of nice localized states unaffected by θ

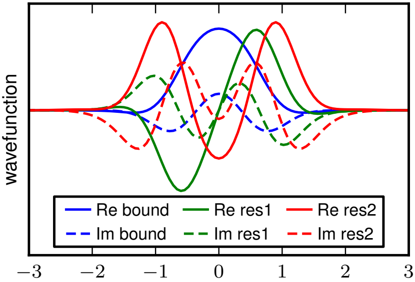


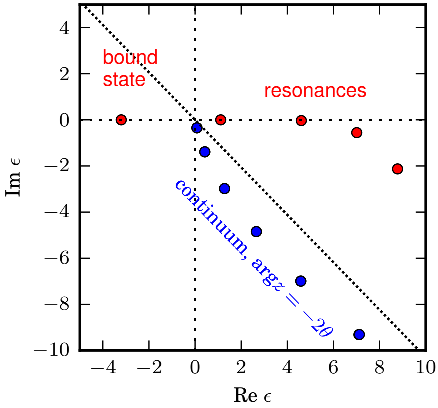




- Bound-state energies unaffected
- Continuous spectrum rotates
- Resonances unaffected once "uncovered"







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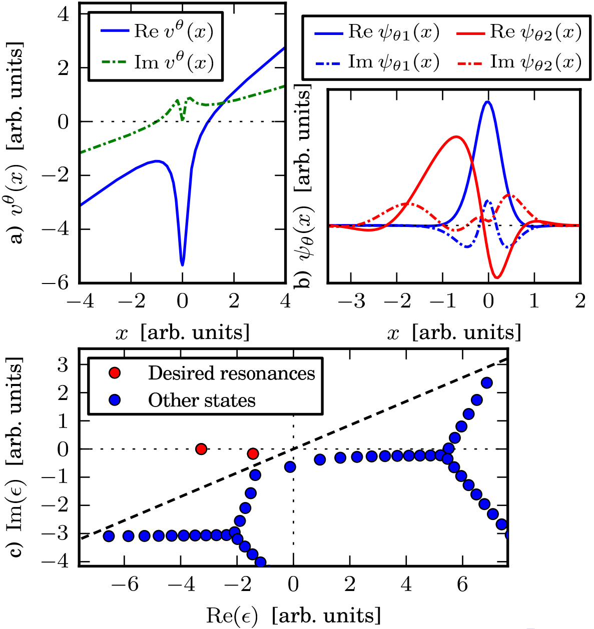
In electric field

- Upper left: Potential
- Upper right: Wavefunctions
- Below: Spectrum



Complex-scaling in DFT

- DFT is based on an energy functional expressible as matrix elements of occupied states
- We “complex-scale” DFT by complex-scaling all matrix elements in the functional:

$$
\begin{aligned}
E_{\mathrm{res}} - i\frac{\Gamma}{2} = {} & \mathrm{e}^{-i2\theta} \sum_n \int \psi_n^\theta(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 \right) \psi_n^\theta(\mathbf{r}) \,\mathrm{d}\mathbf{r} \\
& + \mathrm{e}^{-i\theta} \frac{1}{2} \iint \frac{n^\theta(\mathbf{r}) n^\theta(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} \,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \\
& + E_{\mathrm{xc}}^\theta[n^\theta] + \int v_{\mathrm{ext}}^\theta(\mathbf{r}) n^\theta(\mathbf{r}) \,\mathrm{d}\mathbf{r}
\end{aligned}
$$

- Then we take the derivative to obtain complex-scaled Kohn–Sham equations for stationary point of functional

Some definitions

- States $\psi_n^\theta(\mathbf{r}) = \mathrm{e}^{i3\theta/2}\psi_n(\mathbf{r}\mathrm{e}^{i\theta})$
- Density $n^\theta(\mathbf{r}) = \sum_n f_n[\psi_n^\theta(\mathbf{r})]^2$ (no conjugation!)
- Operators $\hat{O}^\theta(\mathbf{r}) = \hat{O}(\mathbf{r}\mathrm{e}^{i\theta})$, e.g., $\frac{\mathrm{d}^2}{\mathrm{d}x^2} \to e^{-i2\theta}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$

Self-consistency loop

- Solve non-Hermitian KS equations for $\psi_n^\theta(\mathbf{r}), \epsilon_n$
- Figure out occupations f_n depending on energies ϵ_n
- Calculate density
- Solve Poisson equation, calculate XC potential, add external potential
- Repeat until self-consistent

Exchange and correlation

- The only tricky term in the energy functional is $E^{\theta}_{\text{xc}}[n^{\theta}]$ which we must, for one thing, actually define.
- Analytic continuation is unique → only one correct definition of E^{θ}_{xc}
- Change integration contour for some ordinary real density $n(\mathbf{r})$:

$$E_{\text{xc}}[n] = \int n(\mathbf{r})\epsilon(n(\mathbf{r}))\,\mathrm{d}\mathbf{r} = \int n(\mathbf{r}\mathrm{e}^{i\theta})\epsilon(n(\mathbf{r}\mathrm{e}^{i\theta}))\,\mathrm{d}\mathbf{r}\,\mathrm{e}^{i3\theta}$$

- Define potential as $v^{\theta}_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n_{\theta}]}{\delta n_{\theta}(\mathbf{r})}$.
- For LDA, exchange potential becomes

$$v^{\theta}_{\text{x}}(\mathbf{r}) = -\left(\frac{3}{\pi}\right)^{1/3}\mathrm{e}^{-i\theta}[n^{\theta}(\mathbf{r})]^{1/3} = v_{\text{x}}(\mathbf{r}\mathrm{e}^{i\theta})$$

“Stitching” potentials

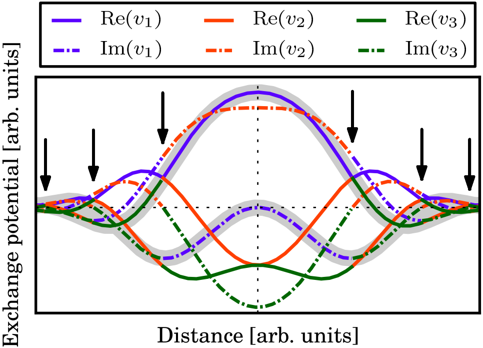
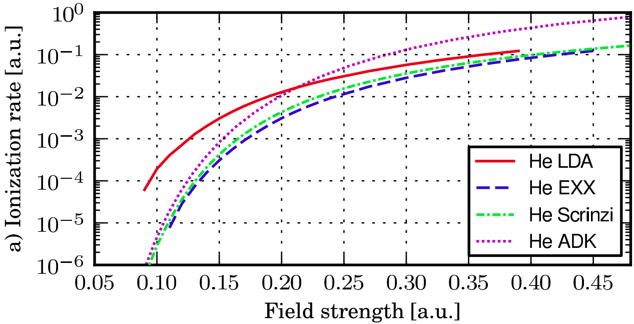


Figure: Stitching of LDA exchange potential. Continuously connecting the branches of $v_x^\theta(\mathbf{r}) \sim \mathrm{e}^{-i\theta}[n^\theta(\mathbf{r})]^{1/3}$

Pseudopotentials

- Atoms are represented by the HGH pseudopotentials
- Pseudopotentials parametrized from Gaussians and polynomials
- Can be analytically continued explicitly
- Disadvantage: Gaussians displaced from 0 oscillate upon scaling

Ionization of Helium atom in static electric field

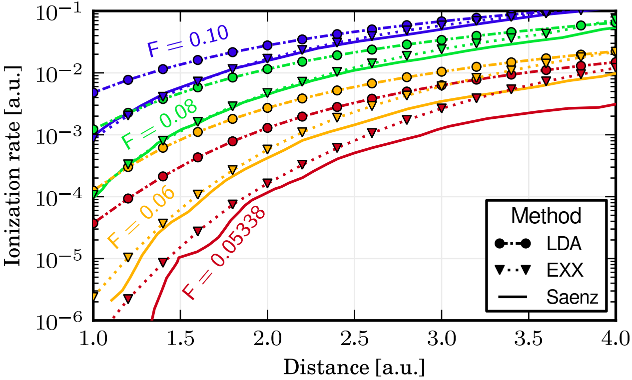


- Ionization rates compared to accurate reference (Scrinzi)
- LDA: overestimates ionization rates for small fields
- EXX: quite accurate
- ADK: perturbative approximation, works for small fields only

Exchange and correlation: Discussion

- ADK depends only on ionization potential
- Error in LDA attributable to overestimate of IP/HOMO
- LDA overestimates IP because of wrong asymptotic decay
- XC functionals that improve upon asymptotic decay may be the key: LB94, ...
- EXX has correct Coulomb-like asymptotic form and agrees well

H_2 dissociative ionization



- Ionization of H_2 at different atomic separations
- Electric field axially aligned
- Accurate reference calculations by Saenz

Features/misfeatures of DFRT implementation

- Implemented in Octopus (not very user friendly/documented)
- Non-Hermitian eigensolver (ARPACK) slowly solves KS equations
- Atoms represented by explicitly complex-scaled HGH pseudopotentials
- Linear density mixing (for now)
- Occupation order of Kohn–Sham states chosen by heuristic
- We have implemented LDA and two-particle EXX

Publications

- Ask Hjorth Larsen, Umberto de Giovannini, Daniel Lee Whitenack, Adam Wasserman, Angel Rubio
  Stark Ionization of Atoms and Molecules within Density Functional Resonance Theory. J. Phys. Chem. Lett., **2013**, 4 (16), pp 2734–2738
- Ask Hjorth Larsen, Umberto De Giovannini, Angel Rubio.
  Dynamical Processes in Open Quantum Systems from a TDDFT Perspective: Resonances and Electron Photoemission
  Density-Functional Methods for Excited States, volume 368 of Topics in Current Chemistry, pages 219–271. Springer International Publishing, 2015

Conclusions

Features of DFRT

- Resonances with efficiency of DFT (almost; same computational complexity at least)
- Almost formally justified

"Disadvantages"

- Small imaginary energies ($\sim 10^{-5}$) difficult to converge
- Gaussian-shaped pseudopotentials oscillate when displaced
- Hartree potential and other density-dependent quantities are not formally entirely justified