

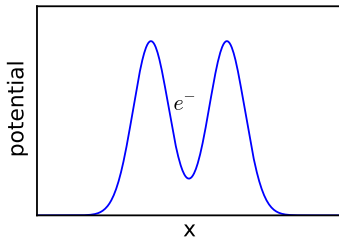
Metastable states from density functional theory using the complex-scaling method

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Resonances and metastable systems



- ▶ Above: Electron locally trapped, will tunnel to escape
- ▶ We want to calculate the properties of such systems
- ▶ See: Ask Hjorth Larsen, Umberto de Giovannini, Daniel Lee Whitenack, Adam Wasserman, Angel Rubio.

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(spoiler alert)

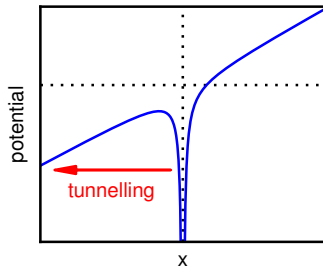
Examples of resonances

Negatively charged molecules

- ▶ Electrons may be bound by exchange/correlation, but be eternally repelled once they escape beyond a certain radius
- ▶ Examples: N_2^- , Be^- , Anything^{sufficiently many-}_{many}, ...

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 \rightarrow DFRT,
“density functional resonance theory”

The complex-scaling method

- ▶ Initial work by Aguilar, Balslev, Combes (1970s) on operators under the “dilation” $\hat{H}(\mathbf{r}) \rightarrow \hat{H}^\theta(\mathbf{r}) \equiv \hat{H}(\mathbf{r}e^{i\theta})$
- ▶ Original equation:

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

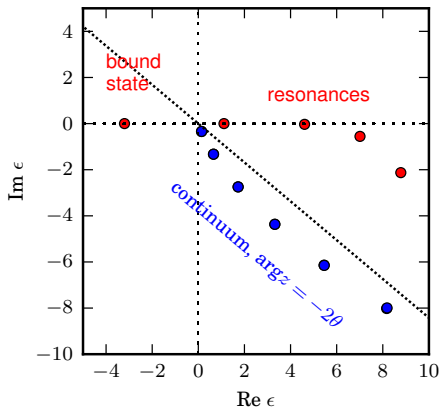
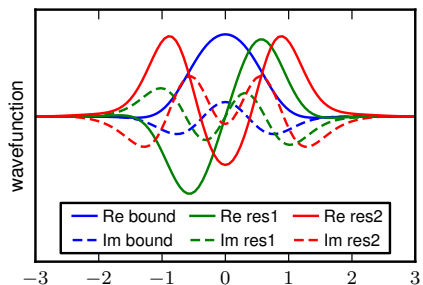
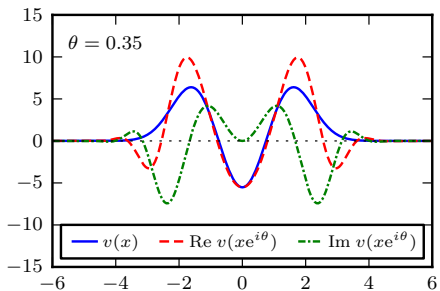
- ▶ Complex-scaled by some fixed angle θ :

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

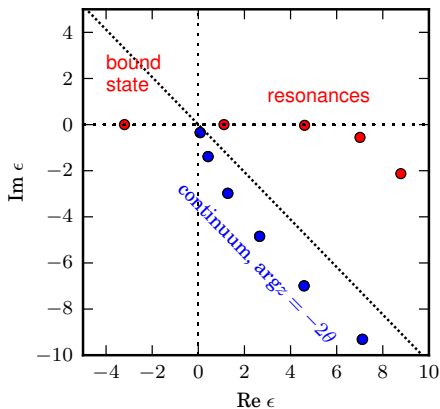
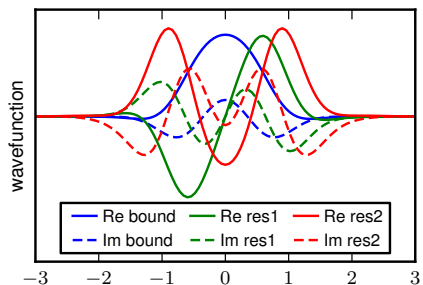
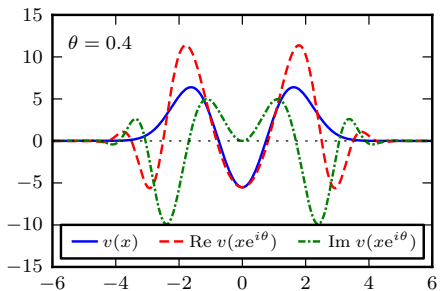
- ▶ Transformation differently affects eigenvalues of discrete versus continuous spectrum.

The complex-scaling method

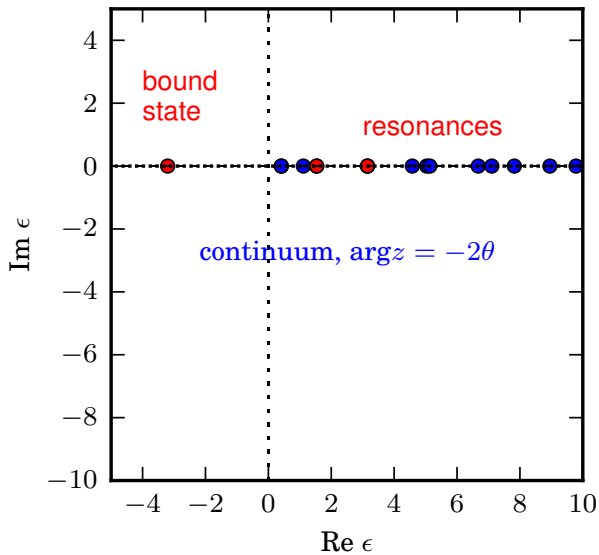
- ▶ The complex Hamiltonian $\hat{H}^\theta(\mathbf{r})$ is **non-Hermitian**
- ▶ A “Resonant” eigenstate with energy $\epsilon_R + i\epsilon_I$ is characterized by uniform decay under time propagation
- ▶ Decay rate is $\Gamma = -2\epsilon_I$
- ▶ Let us diagonalize some complex-scaled Hamiltonians and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

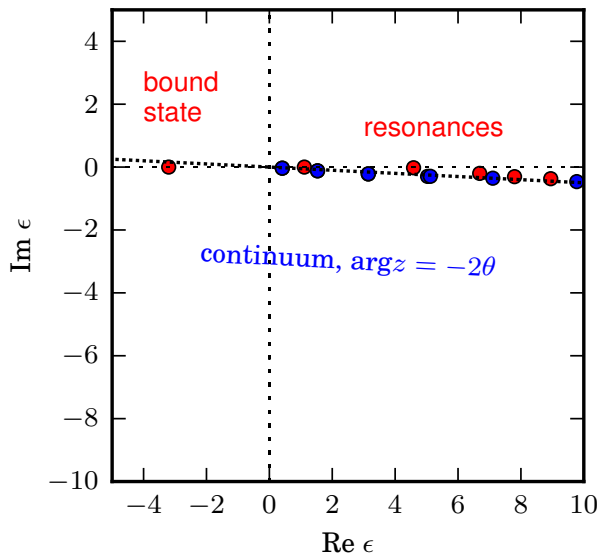


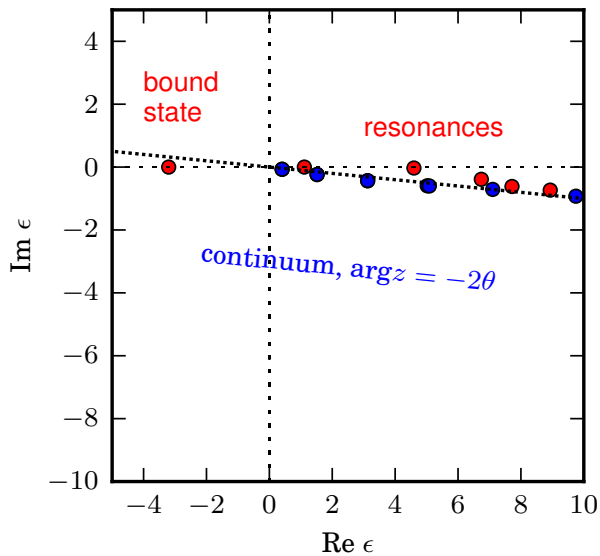
- ▶ Bound-state energies **unaffected**
- ▶ Continuous spectrum **rotates**
- ▶ Resonances unaffected once **“uncovered”**

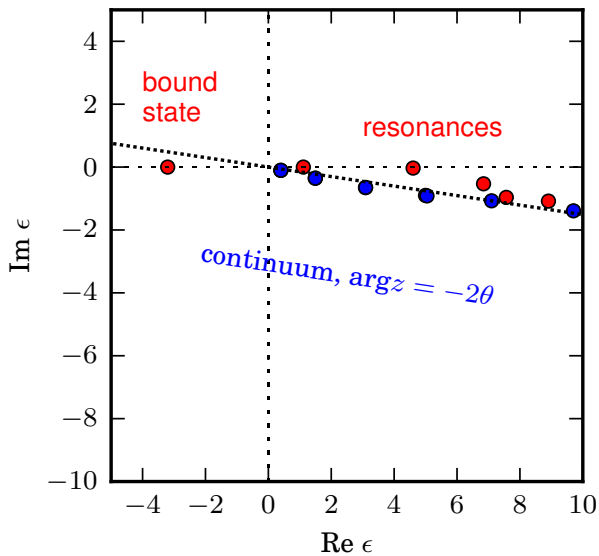


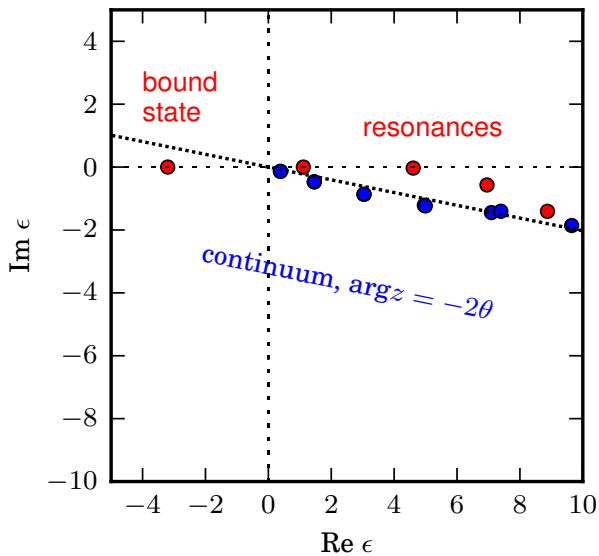
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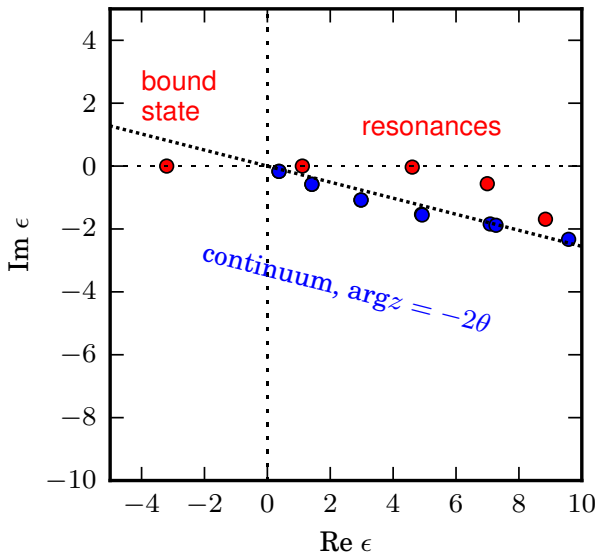


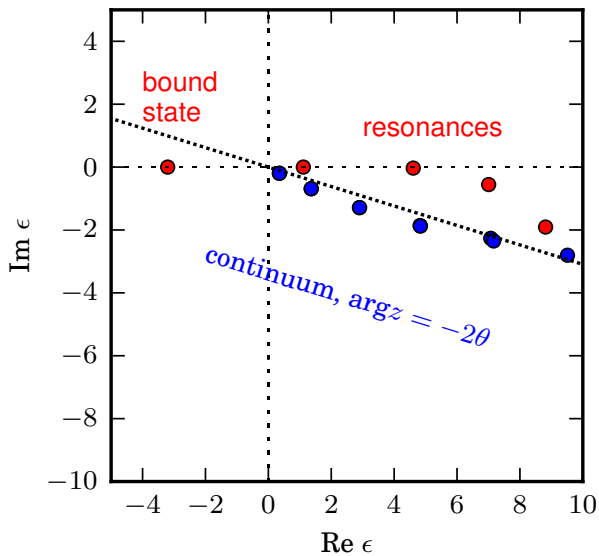


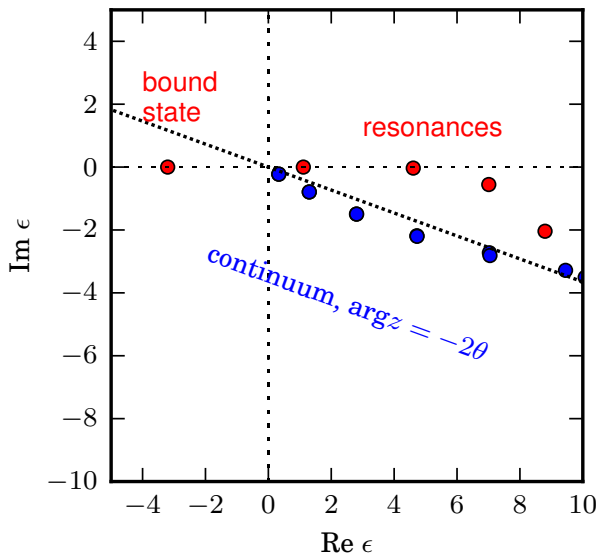


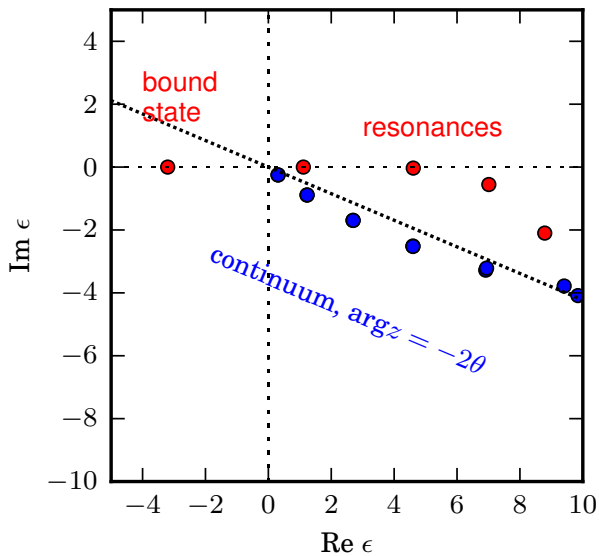


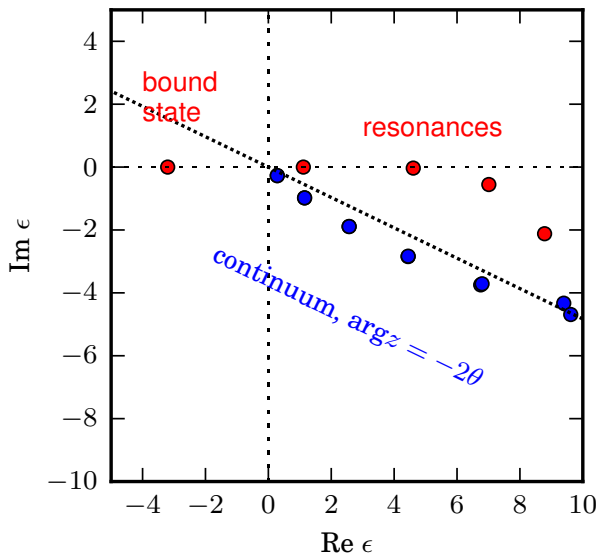


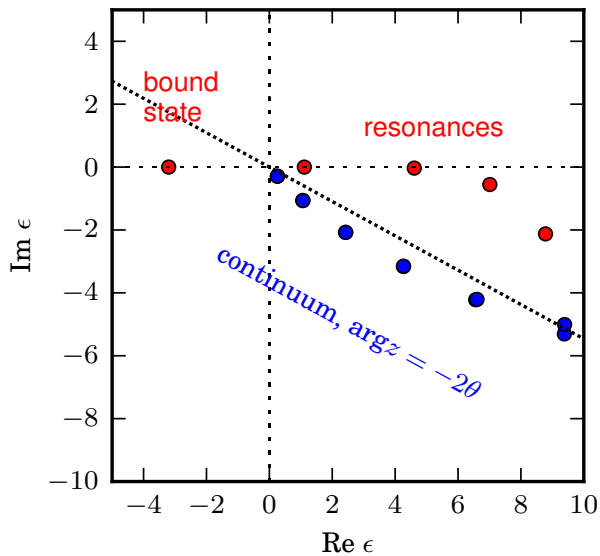


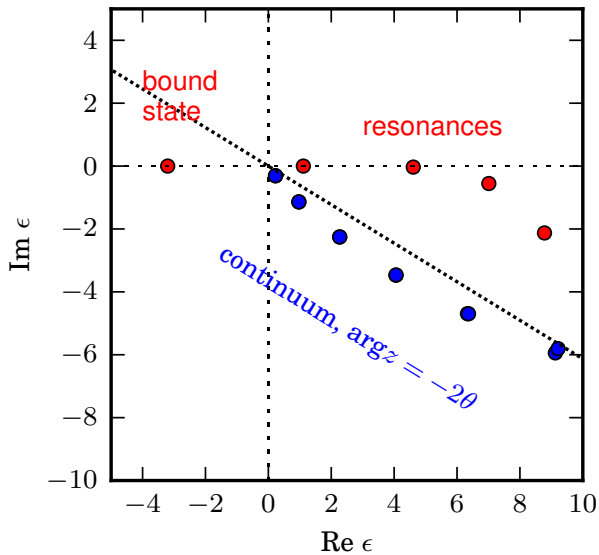


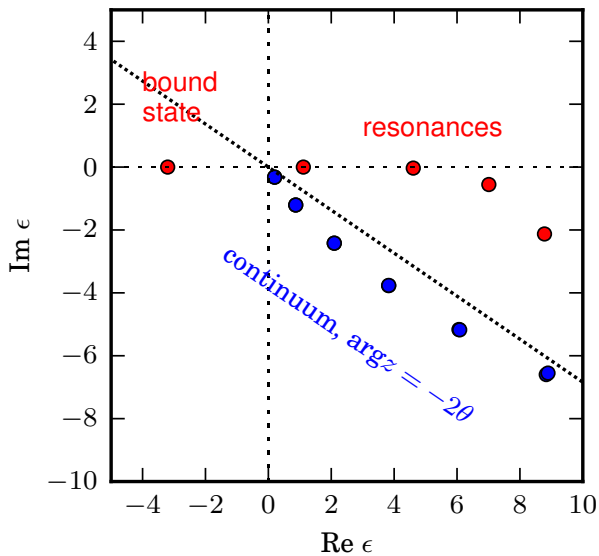






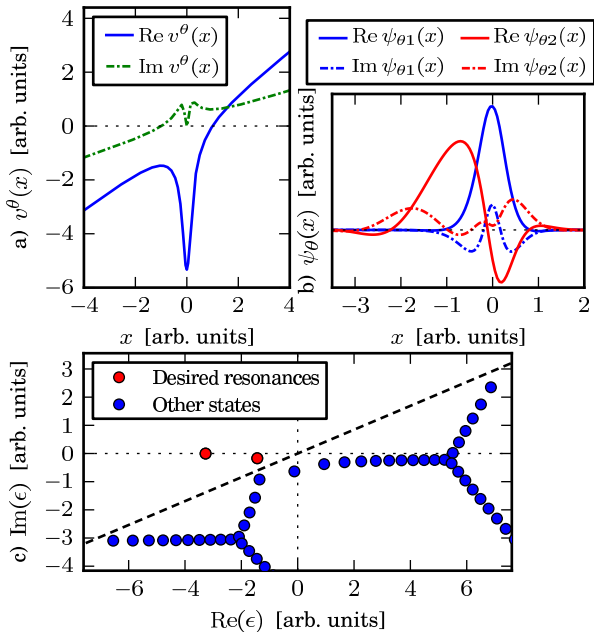




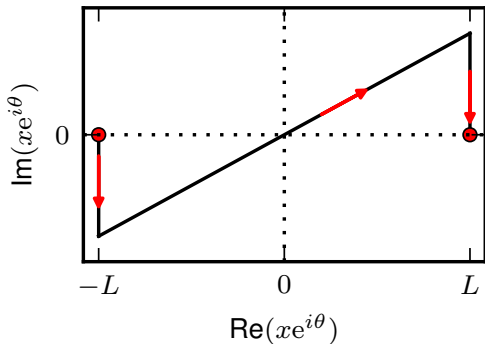


In electric field

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



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**

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:

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

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

Some definitions

- ▶ States $\psi_n^\theta(\mathbf{r}) = e^{i3\theta/2}\psi_n(\mathbf{r}e^{i\theta})$
- ▶ Density $n^\theta(\mathbf{r}) = \sum_n f_n[\psi_n^\theta(\mathbf{r})]^2$
- ▶ Operators $\hat{O}^\theta(\mathbf{r}) = \hat{O}(\mathbf{r}e^{i\theta})$, e.g. $\frac{d^2}{dx^2} \rightarrow e^{-i2\theta} \frac{d}{dx}$

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 $E_{\text{xc}}^\theta[n^\theta]$ which we must, for one thing, actually define.
- ▶ Analytic continuation is unique \rightarrow only one correct definition of E_{xc}^θ
- ▶ Change integration contour for some ordinary real density $n(\mathbf{r})$:

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

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

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

“Stitching” potentials

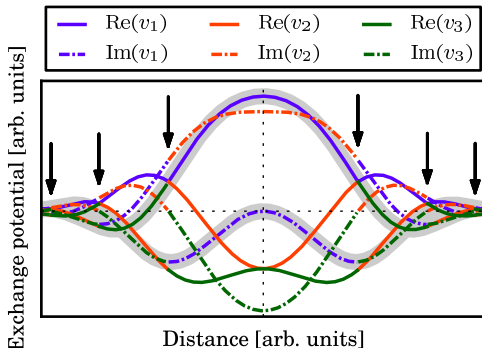
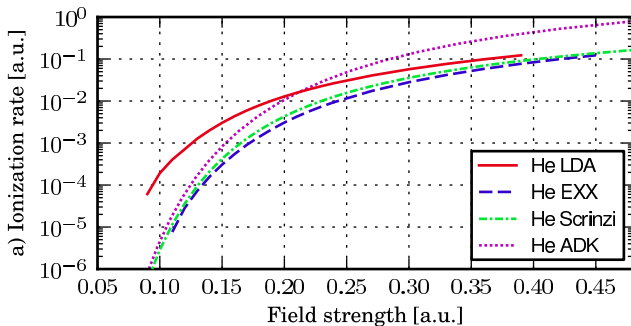


Figure: Stitching of LDA exchange potential. Continuously connecting the branches of $v_x^\theta(\mathbf{r}) \sim e^{-i\theta} [n^\theta(\mathbf{r})]^{1/3}$

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

The Helium atom

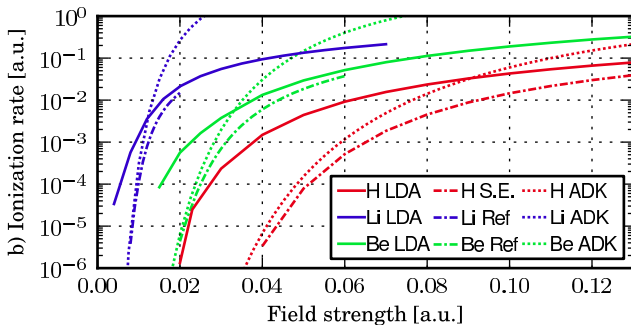


- ▶ Ionization rates compared to accurate reference (Scrinzi)
- ▶ LDA: overestimates ionization rates for small fields
- ▶ EXX: quite accurate
- ▶ ADK: perturbative approximation, works for small fields only

Exchange and correlation: Discussion

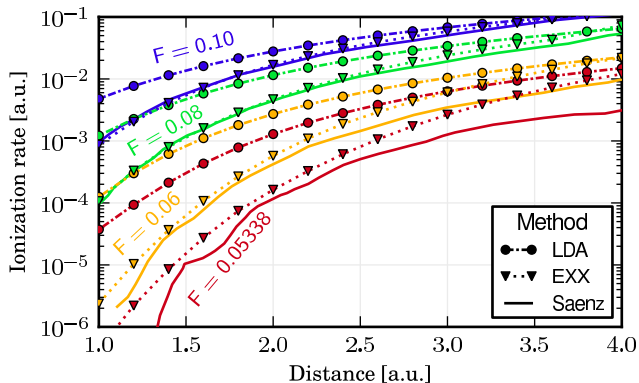
- ▶ ADK depends only on ionization potential
- ▶ Error in LDA attributable to overestimate of IP/HOMO
- ▶ LDA overestimates IP because of wrong asymptotic decay
- ▶ XC functionals that improve upon asymptotic decay may be the key: LB94, ...
- ▶ EXX has correct Coulomb-like asymptotic form and agrees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

Ionization of more atoms



- ▶ Same trends as for He

H₂ dissociative ionization



- ▶ Ionization of H₂ 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/documentated)
- ▶ 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

Conclusions

Features of DFRT

- ▶ Formally justified unlike some other methods
- ▶ D, F, R, T adjacent on keyboard

“Disadvantages”

- ▶ Small imaginary energies ($\sim 10^{-5}$) difficult to converge
- ▶ Gaussian-shaped pseudopotentials oscillate when displaced

Outlook

- ▶ Generalization to “exterior complex scaling”
- ▶ Must figure out better which states to occupy
- ▶ Better XC approximations