

Resonances in Octopus using Density Functional Resonance Theory

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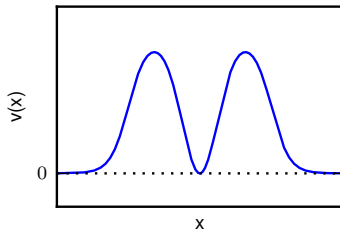
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Resonances

- ▶ Consider a negatively charged molecule such that the removal of an electron would lower the energy, e.g. $\text{N}_2^- \rightarrow \text{N}_2 + e^-$
- ▶ Depending on the shape of the potential, the electron may be trapped on the molecule for a while, then eventually escape
- ▶ Such a state, called a **resonance**, can be described as an eigenstate of a non-Hermitian “Hamiltonian” corresponding to outgoing boundary conditions
- ▶ We would like to describe such states in DFT. In Octopus to be specific

Example potential which will have some nice resonances



A few more words on resonances

- ▶ Resonances can be understood from Hermitian QM as certain linear combinations of states in the continuum
- ▶ From a non-Hermitian Hamiltonian one can describe a resonance in terms of a complex energy

$$E = \mathcal{E} - \frac{i}{2}\Gamma,$$

where Γ is the “width” and $\mathcal{L} = \Gamma^{-1}$ the lifetime with a peak at energy \mathcal{E}

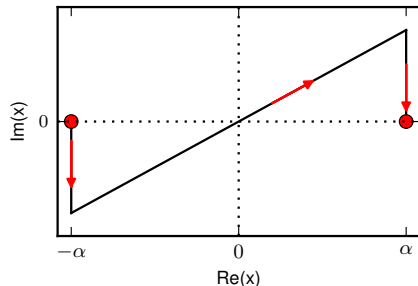
Resonances and DFT

- ▶ Suppose we put N_2 into a system and add one electron, then calculate everything with DFT
- ▶ DFT then finds the ground state by moving the electron as far away as possible. That wasn't really what we wanted
- ▶ A method exists whereby one can effectively impose outgoing boundary conditions by means of a complex position variable:
the complex-scaling method

The complex-scaling method

- ▶ Consider an integral of e.g. a matrix element

$$\langle \phi | \hat{O} | \psi \rangle = \int \phi^*(\mathbf{r}) \hat{O}(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r}$$



- ▶ If the integrand is nice and analytic, we can choose a different integration contour in the complex plane (pictured).
- ▶ If the states are localized enough and α is large, the vertical segments of the integration contour (pictured) do not contribute:

$$\langle \phi | \hat{O} | \psi \rangle = \lim_{\alpha \rightarrow \infty} \int_{-\alpha e^{i\theta}}^{\alpha e^{i\theta}} \phi^*(\mathbf{r}) \hat{O}(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r}$$

The complex-scaling method

- ▶ Now substitute $\mathbf{r} \rightarrow \mathbf{r}e^{i\theta}$ and rewrite:

$$\begin{aligned}\langle \phi | \hat{O} | \psi \rangle &= \int \phi^*(\mathbf{r}e^{i\theta}) \hat{O}(\mathbf{r}e^{i\theta}) \psi(\mathbf{r}e^{i\theta}) d\mathbf{r} e^{iN\theta} \\ &= \int \bar{\phi}_\theta(\mathbf{r}) \hat{O}^\theta(\mathbf{r}) \psi_\theta(\mathbf{r}) d\mathbf{r},\end{aligned}$$

where N is the dimension (so mostly around 3), and

$$\bar{\phi}_\theta(\mathbf{r}) = e^{iN\theta/2} \phi^*(\mathbf{r}e^{i\theta}),$$

$$\psi_\theta(\mathbf{r}) = e^{iN\theta/2} \psi(\mathbf{r}e^{i\theta}),$$

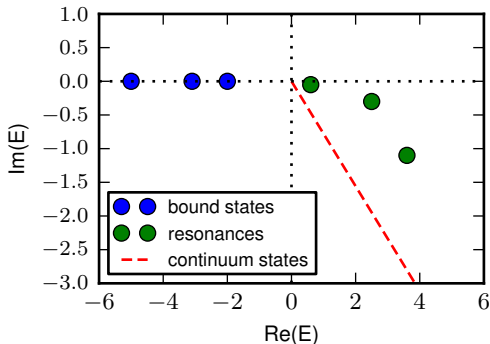
$$\hat{O}^\theta(\mathbf{r}) = \hat{O}(\mathbf{r}e^{i\theta}).$$

- ▶ A calculation in terms in these quantities will yield the same results as long as the states are bounded

The complex-scaling method

- ▶ Long story short, the transformation $\mathbf{r} \rightarrow \mathbf{r}e^{i\theta}$ makes the Hamiltonian non-Hermitian
- ▶ Resonances appear as **square-integrable functions** with complex energy for θ large enough
- ▶ Bound states and resonances will be independent of θ while continuum states “rotate” with θ

“Hand-drawn” example



- ▶ (Fictional) eigenvalues plotted in the complex plane using complex-scaling method
- ▶ The continuum states are rotated by -2θ from the real axis
- ▶ Larger values of θ may “reveal” more resonances

Derivation of complex-scaled quantities

- Density:

$$\begin{aligned} n_{\theta}(\mathbf{r}) &= \sum_n f_n \bar{\psi}_{\theta n}(\mathbf{r}) \psi_{\theta n}(\mathbf{r}) \\ &= e^{iN\theta} n(\mathbf{r}e^{i\theta}) \end{aligned}$$

- Coulomb energy:

$$\begin{aligned} E_{\text{Ha}}[\rho] &= \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r} d\mathbf{r}' \\ &= \frac{1}{2} \iint \frac{\rho(\mathbf{r}e^{i\theta})\rho(\mathbf{r}'e^{i\theta})}{\|\mathbf{r} - \mathbf{r}'\|e^{i\theta}} d\mathbf{r} d\mathbf{r}' e^{i2N\theta} \\ &= \frac{1}{2} e^{-i\theta} \iint \frac{\rho_{\theta}(\mathbf{r})\rho_{\theta}(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r} d\mathbf{r}' \\ &= e^{-i\theta} E_{\text{Ha}}[\rho_{\theta}] \end{aligned}$$

Complex-scaled Kohn–Sham equations

- ▶ This way one can scale the whole energy functional
- ▶ Instead of minimizing energy, one technically searches for a stationary point

$$\left[-\frac{e^{-i2\theta}}{2} \nabla^2 + \frac{e^{-i\theta}}{2} \int \frac{\rho_\theta(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r}' + v_{\text{xc}}^\theta(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}e^{i\theta}) \right] \psi_{\theta n}(\mathbf{r}) = \epsilon_n \psi_{\theta n}(\mathbf{r}),$$

- ▶ Now we are ready to run actual calculations

Steps in a DFRT calculation

Initialization

- ▶ Complex-scale pseudopotentials and external potentials
- ▶ Complex-scale atomic core charges

SCF cycle

- ▶ Calculate $n_{\theta}(\mathbf{r})$ from complex wavefunctions
- ▶ Complex Hartree potential can be obtained by solving real/imaginary parts separately, as Poisson equation is linear
- ▶ Exchange–correlation functionals must be evaluated from the complex density somehow
- ▶ Solve KS equations for non-Hermitian Hamiltonian; in a static calculation it can generally be taken to be symmetric though.
- ▶ States must be filled to “minimize energy”

Local density approximation

- ▶ In LDA, the exchange potential is given by

$$v_X(\mathbf{r}) = C_x n^{\frac{1}{3}}(\mathbf{r})$$

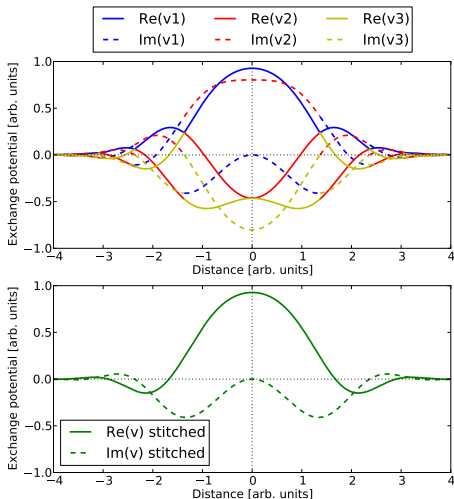
or

$$v_X(\mathbf{r}e^{i\theta}) = C_x e^{-iN\theta/3} n_{\theta}^{\frac{1}{3}}(\mathbf{r})$$

- ▶ But the complex cube root is multiple-valued with **three branches**

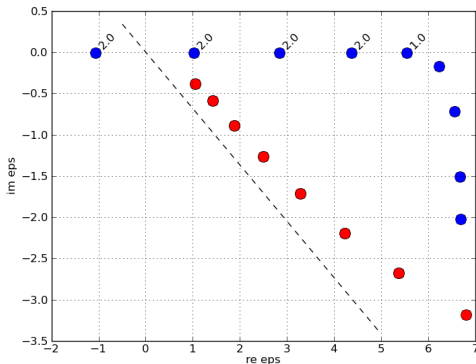
“Stitching” the LDA

- ▶ The correct complex LDA potential must reduce continuously to a real function as $\theta \rightarrow 0$ and must be real in 0
- ▶ Thus we can choose the correct branch in 0, then “stitch” the entire potential by looping over all points
- ▶ For correlation, one must also stitch $\sqrt{r_s} = n^{-1/6}$ and the logarithm function



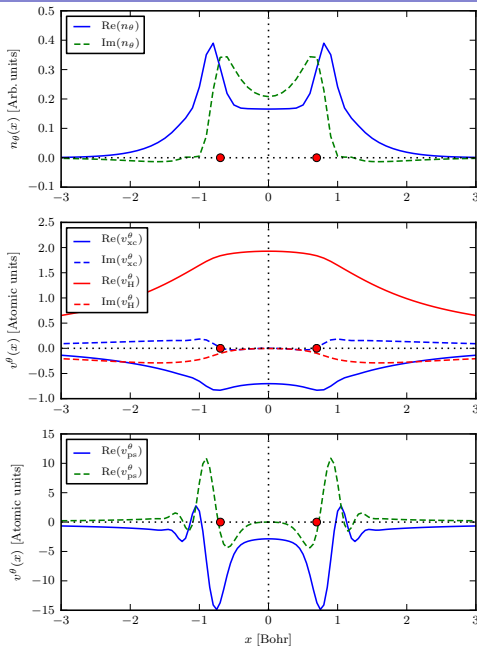
1D model potential with DFT and LDA

- ▶ Potential well enclosed between two tunnelable barriers, $\theta = 0.3$
- ▶ Bound state (negative real axis), resonances (blue, 4th quadrant), other continuum states (arg $\epsilon \approx 2\theta$).



Pseudopotentials

- ▶ Hartwigsen–Goedecker–Hutter pseudopotentials consist of projectors, local short-range potential and compensation charges
- ▶ Pseudopotentials defined from polynomials and Gaussians and can be complex-scaled directly
- ▶ We still lack support for non-local projectors, but can do calculations with purely local ones (H and Be)



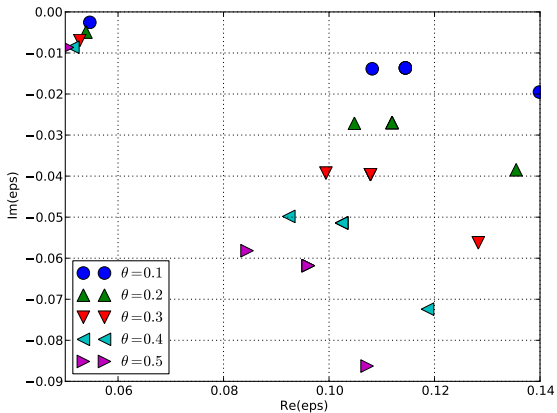


Figure: Eigenvalues for H^- for different values of θ

Numerical issues

- ▶ Very large cell is required to avoid small imaginary parts in results
- ▶ Fine grid spacing required as well
- ▶ Several states may be required to “recognize” resonances from ordinary continuum states

Eigensolver

- ▶ It turns out to be rather expensive to solve non-Hermitian equations
- ▶ So far we use the ARPACK solver for this: Unfathomably slow, sometimes hangs, horrible scaling, FORTRAN77, ...
- ▶ Does anyone know some efficient non-Hermitian eigensolvers?
- ▶ We consider truncating imaginary parts and use a Hermitian solver to obtain a basis with which to expand the complex-scaled problem, then solve only within this basis

Coding issues

- ▶ Code presently exists in external GIT archive
- ▶ Must pass θ as an (optional) variable to many many functions
- ▶ Must add support for (optional) imaginary part of density
- ▶ Must add `if`-statements every time we do something special

Conclusion

- ▶ In principle everything almost works
- ▶ In practice we cannot yet converge 3D systems as they are too expensive and ARPACK won't run on them