

Density Functional Resonance Theory of Unbound Electronic Systems

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Outline

1. Problem / Motivation
2. Resonance wavefunctions / densities
3. Density Functional Resonance Theory (DFRT)
4. Orbital Energies and Lifetimes / Derivative Discontinuities
5. Conclusions / Future Work

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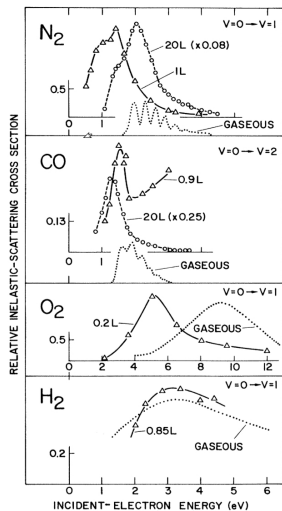
Problem / Motivation

- ▶ Add an electron to a system that has “negative electron affinity” or an affinity of zero.
- ▶ This system will decay, but it could be long-lived.
- ▶ If we want properties (e.g. energy and lifetime) of the anion, we can not apply DFT in a straightforward way.

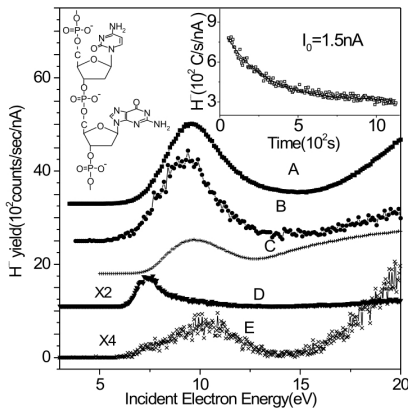


- ▶ DFT brings us back to the neutral ground state so we have no new initial state for TDDFT.

Problem / Motivation



Rev. Mod. Phys. **64**, 383 (1992)



Phys. Rev. Lett. **90**, 208102

Problem / Motivation

Tools for finding metastable states:

1. Stabilization methods (Taylor)
2. Finite basis sets or potential walls (can't get lifetimes)
3. Many-body scattering

They present “*Special* challenges to theory” (Jack Simons):

1. Divergent wavefunctions (densities)
2. Bound-free correlations

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Resonance Wavefunctions / Densities

- ▶ A resonance wavefunction is divergent:

$$\Psi(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}} + f(\theta, \phi) \frac{ikr}{r^2}$$

a solution of the TISE with outgoing boundary conditions.

- ▶ However, consider a similarity transformation \hat{S} such that $\hat{S}\Psi_{res}$ is square integrable, or

$$\hat{S}\Psi_{res}(\mathbf{r}) \rightarrow 0 \quad \text{as} \quad r \rightarrow \infty$$

Then, $\hat{S}\Psi_{res}$ is a normalizable eigenfunction of,

$$(\hat{S}\hat{H}\hat{S}^{-1})\hat{S}\Psi_{res} = (\mathcal{E}_n - (i/2)\Gamma_n)\hat{S}\Psi_{res}$$

Resonance Wavefunctions / Densities

- ▶ One such transformation is the *complex-scaling* transformation: $\mathbf{r} \rightarrow \mathbf{r}e^{i\theta}$
- ▶ The complex-scaled Hamiltonian, \hat{H}_θ , can be diagonalized with bound-state techniques to find the $E_n = \mathcal{E}_n - (i/2)\Gamma_n$.
- ▶ Since $\hat{S}\Psi_{res}(\mathbf{r}) \rightarrow 0$ as $r \rightarrow \infty$,

$$n_\theta(\vec{r}) = \langle \psi_\theta^L | \hat{n}(\vec{r}) | \psi_\theta^R \rangle$$

is a “complex density.”

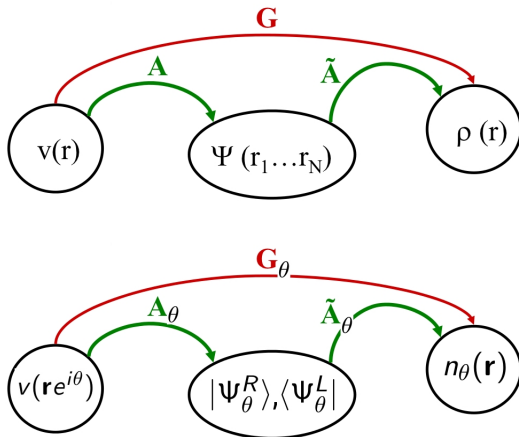
- ▶ Is information about a resonance (\mathcal{E} and Γ) contained in n_θ ?

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Density Functional Resonance Theory

The answer is YES for the *Lowest Energy Resonance* (LER) of an unbound electronic system.



Phys. Rev. Lett. **98**, 093003 (2007)

Density Functional Resonance Theory

DFT

$$\hat{H}, v(\mathbf{r})$$

$$n(\mathbf{r}) = \langle \psi | \hat{n}(\vec{r}) | \psi \rangle$$

$$E_{\text{GS}}[n]$$

$$v_s[n](\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2$$

DFRT

$$\hat{H}_\theta, v(\mathbf{r}e^{i\theta})$$

$$n_\theta(\vec{r}) = \langle \psi_\theta^L | \hat{n}(\vec{r}) | \psi_\theta^R \rangle$$

$$E_\theta^{\text{LER}}[n_\theta] = \mathcal{E}[n_\theta] - \frac{i}{2} \mathcal{L}^{-1}[n_\theta]$$

$$v_s^\theta[n_\theta](\mathbf{r}) = v(\mathbf{r}e^{i\theta}) + v_{\text{HXC}}^\theta[n_\theta](\mathbf{r})$$

$$n_\theta(\mathbf{r}) = \sum_i^N \phi_i^{\theta,L}(\mathbf{r}) \phi_i^{\theta,R}(\mathbf{r})$$

Phys. Rev. Lett. **107**, 163002 (2011)

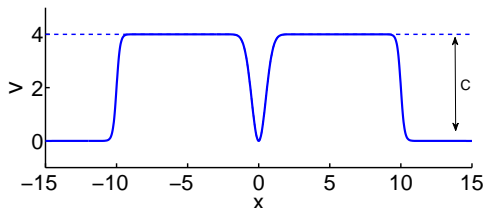
J. Phys. Chem. Lett. **1**, 407 (2010)

Density Functional Resonance Theory

- ▶ 2 soft Coulomb interacting electrons in:

$$v(x) = a \left(\frac{1}{1+e^{-2c(x+d)}} - \frac{1}{1+e^{-2c(x-d)}} - e^{-\frac{x^2}{b}} \right)$$

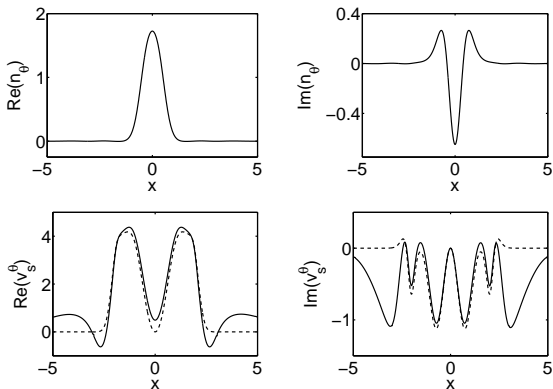
a , b , c , d - constants, λ - interaction strength.



- ▶ The complex-scaled system is solved exactly with finite differences.
- ▶ Also, the complex Kohn-Sham equations self-consistently with a functional exact up to exchange (excluding correlation).

Density Functional Resonance Theory

The complex density, scaled external potential (dotted line), and complex Kohn-Sham potential (solid line).



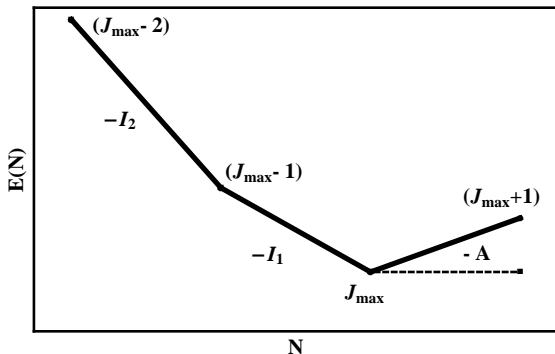
- ▶ A close-coupling scattering calculation (bound state approx) gives an error of 22% in the resonance energy, comparable to our DFRT exchange-only results.

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Derivative Discontinuities

- ▶ The exact XC potential of an open system jumps discontinuously as the particle number crosses an integer.
- ▶ But what happens at the specific integer value that is the maximum number of bound electrons (J_{max})?



DFRT for Fractional Particle Number

- ▶ We write the complex ensemble energy and density as:

$$E^\theta(N) = [1 - (N - J)]E_J^\theta + (N - J)E_{J+1}^\theta$$

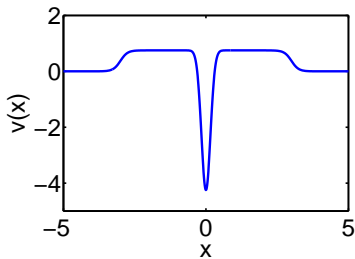
$$n_\theta^N(\mathbf{r}) = [1 - (N - J)]n_\theta^J(\mathbf{r}) + (N - J)n_\theta^{J+1}(\mathbf{r})$$

for a fractional particle number N ($J < N < J + 1$).

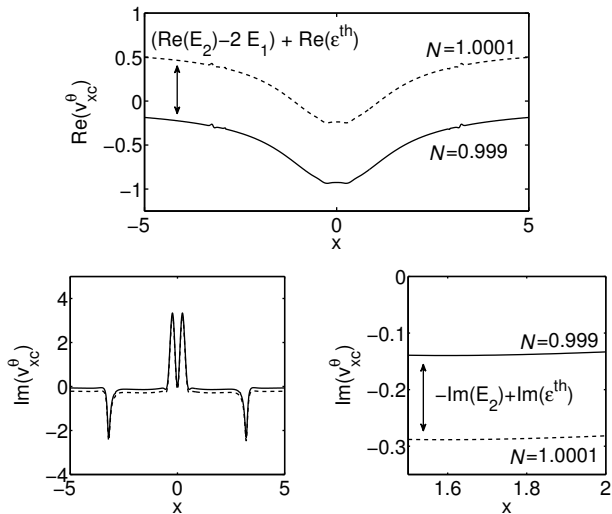
- ▶ We also need to know about the orbital energies and lifetimes of the DFRT Kohn-Sham system (discussed on my poster).

Derivative Discontinuities

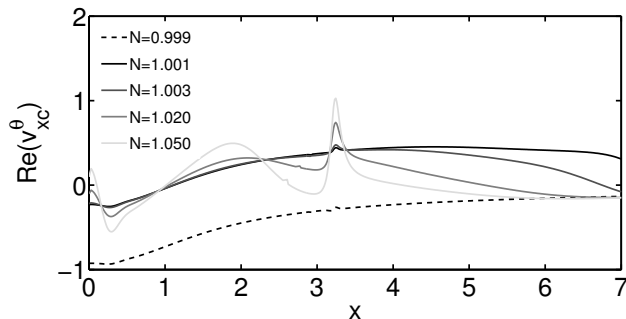
- ▶ Consider our model potential, $v(x)$, with parameters that permit only a 1 electron bound state and a 2 electron resonance.
- ▶ v_{XC}^θ is evaluated on an ensemble density that integrates to a fractional number (N) on either side of $J_{max} = 1$.



Derivative Discontinuities



Derivative Discontinuities



- ▶ At integers below J_{max} only the real part of v_{XC}^{θ} experiences a jump because the chemical potential experiences a purely real jump.
- ▶ At J_{max} both the real and imaginary parts of v_{XC}^{θ} jump discontinuously.

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Future Work

- ▶ An implementation of DFRT for real systems is under construction. (See David Strubbe for the Octopus DFRT tutorial at Benasque 2014)
- ▶ Can the Runge-Gross theorem be extended to complex densities? (Ask me at March Meeting)
 - ▶ photo-induced resonances
 - ▶ high energy resonances
 - ▶ photo absorption of metastable systems
 - ▶ etc...
- ▶ What else can we learn about metastable systems from n_θ (Reactivity)?

Conclusions

- ▶ DFRT (an analog of KS-DFT) can give the in-principle exact resonance energy and lifetime for the LER of a system.
- ▶ DFRT could help us learn more about problems in approximate DFT
- ▶ Acknowledgements:
 - ▶ Martin Mosquera (Purdue) and Yu Zhang (UC Irvine)
 - ▶ Donors of the American Chemical Society Petroleum Research Fund for support of this research under grant No.PRF# 49599-DNI6.
- ▶ DLW, Y. Zhang and A. Wasserman, Submitted 2011, arXiv:1111.1934
- ▶ DLW and A. Wasserman, Phys. Rev. Lett. 2011 **107**, 163002
- ▶ DLW and A. Wasserman, J. of Phys. Chem. Lett. 2010 **1**, 407-411

Density Functional Resonance Theory (DFRT)

- ▶ **Goal:** establish an analog of Kohn Sham DFT that provides the in-principle exact LER density along with its energy and lifetime.
- ▶ To find $n_\theta(\mathbf{r})$, we *complex-scale*,

$$\hat{H}_v = \hat{T} + \hat{V}_{ee} + \int d\mathbf{r} \hat{n}(\mathbf{r}) v(\mathbf{r})$$

by multiplying all electron coordinates by $e^{i\theta}$, diagonalize \hat{H}_v^θ , and calculate $n_\theta(\mathbf{r}) = \langle \Psi_\theta^L | \hat{n}(\mathbf{r}) | \Psi_\theta^R \rangle$, where $|\Psi_\theta^R\rangle$ and $\langle \Psi_\theta^L|$ are right and left eigenstates corresponding to the LER.

- ▶ The LER's lifetime \mathcal{L} is given by $(-2\text{Im}(E_\theta))^{-1}$,

$$E_\theta[n_\theta] = \mathcal{E}[n_\theta] - \frac{i}{2} \mathcal{L}^{-1}[n_\theta]$$

Density Functional Resonance Theory (DFRT)

- ▶ The “Kohn-Sham” potential, $v_s^\theta(\mathbf{r})$, is defined such that its N occupied complex orbitals $\{\phi_i^\theta(\mathbf{r})\}$ yield the interacting LER-density via

$$n_\theta(\mathbf{r}) = \sum_{i=1}^N \langle \phi_i^{\theta,L} | \hat{n}(\mathbf{r}) | \phi_i^{\theta,R} \rangle$$

- ▶ The complex Kohn-Sham equations are:

$$\begin{pmatrix} \hat{h}_1 - \varepsilon_i & -\hat{h}_2 - 2\tau_i^{-1} \\ \hat{h}_2 + 2\tau_i^{-1} & \hat{h}_1 - \varepsilon_i \end{pmatrix} \begin{pmatrix} \text{Re}(\phi_i^\theta) \\ \text{Im}(\phi_i^\theta) \end{pmatrix} = 0 \quad ,$$

where $\hat{h}_1 = -\frac{1}{2} \cos(2\theta) \nabla^2 + \text{Re}(v_s^\theta(\mathbf{r}))$, and $\hat{h}_2 = \frac{1}{2} \sin(2\theta) \nabla^2 + \text{Im}(v_s^\theta(\mathbf{r}))$.

- ▶ The set of $\{\varepsilon_i\}$ and $\{\tau_i\}$ provide the orbital resonance energies and lifetimes of the Kohn-Sham particles.

Density Functional Resonance Theory (DFRT)

- ▶ We write $E_\theta[n_\theta]$ as:

$$E_\theta[n_\theta] = T_s^\theta[n_\theta] + \int d\mathbf{r} n_\theta(\mathbf{r})v(\mathbf{r}e^{i\theta}) + E_H^\theta[n_\theta] + E_{XC}^\theta[n_\theta]$$

and require: $T_s^\theta[n_\theta] = e^{-2i\theta} T_s[n_\theta]$ and $E_H^\theta[n_\theta] = e^{-i\theta} E_H[n_\theta]$.

- ▶ The complex variational principle along with the assumption that the orbitals used to construct the density can be expanded in an orthonormal basis leads to:

$$\delta E_\theta[n_\theta]/\delta n_\theta - \mu \int d\mathbf{r} n_\theta(\mathbf{r}) = 0 \quad .$$

- ▶ Performing the variation in $E_\theta[n_\theta]$ and comparing with the Kohn-Sham equations,

$$v_s^\theta(\mathbf{r}) = v(\mathbf{r}e^{i\theta}) + e^{-i\theta} v_H[n_\theta](\mathbf{r}) + v_{XC}^\theta[n_\theta](\mathbf{r}) \quad ,$$

where $v_{XC}^\theta[n_\theta](\mathbf{r}) = \delta E_{XC}^\theta[n_\theta]/\delta n_\theta(\mathbf{r})|_{\text{LER}}$.

DFRT for Fractional Particle Number

- ▶ Define an ensemble of pure states of the non-Hermitian Hamiltonian:

$$\hat{\Gamma}_\theta = \sum_i |\Psi_{\theta,i}^R\rangle p_i \langle \Psi_{\theta,i}^L|$$

where the sum of the probabilities p_i is defined to be 1.

- ▶ The constrained search universal functional is:

$$F_{\text{LL}}^\theta[n_\theta] = \min_{\hat{\Gamma}_\theta \rightarrow n_\theta} \begin{pmatrix} \text{Re} \\ -2\text{Im} \end{pmatrix} \text{Tr} \left[\hat{\Gamma}_\theta (e^{-2i\theta} \hat{T} + \hat{V}_{ee}^\theta) \right]$$

- ▶ And the ensemble energy is:

$$E^\theta[n_\theta] = \min_{n_\theta} \begin{pmatrix} \text{Re} \\ -2\text{Im} \end{pmatrix} (F_{\text{LL}}^\theta[n_\theta] + \int d\mathbf{r} n_\theta(\mathbf{r}) v(\mathbf{r}e^{i\theta}))$$

Orbital Energies and Lifetimes

System:	Decay Channel:	$\epsilon_{\text{H}}^{\theta}$
Bound J -electron	No decay	$-I$
Metastable $(J + 1)$ -electron	J electron bound state	$(-A - \frac{\Gamma}{2}i) + \epsilon^{th}$
Metastable $(J + 1)$ -electron	Multiple	Multiple contributions

$\epsilon_{\text{H}}^{\theta}$, KS-DFRT HOMO energy

I , Positive ionization potential of a J -electron system

ϵ^{th} , KS "threshold energy" defined below

A , Negative electron affinity of a J -electron system

Γ , $(J + 1)$ -electron resonance width (inverse lifetime)

Submitted 2011, arXiv:1111.1934