Steps in the Exact Kohn-Sham Potential of Ensemble Density Functional Theory for Excited States and Their Relation to the Derivative Discontinuity

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Ensemble Density Functional Theory

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Electron density:

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n(r) = \delta |\phi_{N+1}(r)|^2 + (1 - \delta) |\phi_N(r)|^2 + \sum_{i=1}^{N-1} |\phi_i(r)|^2
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The accuracy of the density relies on the approximation to the exchange-correlation part of $v_s$.

The iDEA code
Model simple 1D systems consisting of a few electrons

Choose any external potential we like
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1. Calculate the exact ground-state and first excited-state electron density

2. The electron density is a linear combination of these two densities:

\[ n(r) = (1 - \delta) \cdot n_0(r) + \delta \cdot n_1(r) \]

3. Next reverse-engineer the exact Kohn-Sham potential
Derivative discontinuity of an atom

\[ N = 3 \]
Derivative discontinuity of an atom

\[ \Delta = I - A + \varepsilon^{ho} - \varepsilon^{lu} \]

\[ N = 3 + \delta \]

\[ 0 < \delta << 1 \]
Charge transfer excitation in a 1D molecule
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\[ v_{\text{ext}} \quad n_1(x) \]
Charge transfer excitation in a 1D molecule

\[ n(x) = (1 - \delta)n_0(x) + \delta n_1(x) \]

\[ 0 < \delta \ll 1 \]
Ground-state 1D molecule
\[ S = I_R - I_L + \eta_R^{ho} - \eta_L^{ho} \]
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Ionisation energy
$S = I_R - I_L + \eta^h_R - \eta^h_L$

Kohn-Sham molecular energies

Bonded case: $\eta^h_R = \eta^h_L$

$\Rightarrow S = I_R - I_L$

Charge transfer excitation in a 1D molecule
Charge transfer excitation in a 1D molecule

\[ \Delta_{L \rightarrow R} = I_L - A_R + \eta_{L}^{ho} - \eta_{R}^{lu} \]

\[ \Delta_R = I_R - A_R + \varepsilon_{R}^{ho} - \varepsilon_{R}^{lu} \]

Derivative discontinuity of Atom R:

\[ \delta \]
Charge transfer excitation in a 1D molecule

\[ \Delta_{CT}^{L \rightarrow R} = I_L - A_R + \eta_{LU}^L - \eta_{LU}^R \]

Derivative discontinuity of Atom R:

\[ \Delta_R = I_R - A_R + \varepsilon_{ho}^R - \varepsilon_{lu}^R \]

What's this?
Charge-transfer derivative discontinuity

\[ \Delta_{L \rightarrow R}^{\text{CT}} = I_L - A_R + \eta_L^{\text{ho}} - \eta_R^{\text{lu}} \]
Charge-transfer derivative discontinuity

\[ \Delta_{L \to R}^{\text{CT}} = I_L - A_R + \eta_L^{\text{ho}} - \eta_R^{\text{lu}} \]

Derivative discontinuity of Atom R:

\[ \Delta_R = I_R - A_R + \varepsilon_R^{\text{ho}} - \varepsilon_R^{\text{lu}} = I_R - A_R + \eta_R^{\text{ho}} - \eta_R^{\text{lu}} \]
Charge-transfer derivative discontinuity

$$\Delta_{L \rightarrow R}^{CT} = I_L - A_R + \eta_{L}^{ho} - \eta_{R}^{lu}$$

Derivative discontinuity of Atom R:

$$\Delta_{R} = I_{R} - A_{R} + \varepsilon_{R}^{ho} - \varepsilon_{R}^{lu} = I_{R} - A_{R} + \eta_{R}^{ho} - \eta_{R}^{lu}$$

$$S = S_1 + S_2 = \Delta_{R} - \Delta_{L \rightarrow R}^{CT} = I_{R} - I_{L} + \eta_{R}^{ho} - \eta_{L}^{ho}$$
\[ S = S_1 + S_2 = \Delta_R - \Delta_{CT}^{L \rightarrow R} = I_R - I_L + \eta_R^{ho} - \eta_L^{ho} \]
Conclusions

1. Ensemble density functional theory can be used to model charge transfer

2. Upon charge transfer two plateaus form around the atoms of a diatomic molecule – one corresponds to the derivative discontinuity of the acceptor and the other corresponds to the ‘charge-transfer derivative discontinuity’

3. The steps which correspond to the two derivative discontinuities add together to make the interatomic step which determines the distribution of charge in the molecule
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Thanks for listening!

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