

RDMFT: a solution to the dissociation and charge transfer problems?

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Outline

- 1 Motivation
- 2 Introduction to RDMFT
- 3 Dissociation of molecules
- 4 Excitations in RDMFT
- 5 Conclusions

Motivation

- Dissociation of **molecules**, even **H₂**, difficult to describe in **DFT**
- Calculations with **reduced density matrix functional theory** (RDMFT) have produced very good results for several **simple functionals**
- **Charge transfer** excitations at too low energies in DFT
- No **1/R** dependence of excitation energy

RDMFT versus DFT

- Difference lies in the **fundamental** variable

$$\begin{aligned}\gamma(\mathbf{r}, \mathbf{r}') &= N \int d^3 r_2 \dots d^3 r_N \Psi^*(\mathbf{r}', \mathbf{r}_2 \dots \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2 \dots \mathbf{r}_N) \\ n(\mathbf{r}) &= \gamma(\mathbf{r}, \mathbf{r})\end{aligned}$$

- **Occupation numbers** and **natural orbitals**

$$\int d^3 r' \gamma(\mathbf{r}, \mathbf{r}') \varphi_j(\mathbf{r}') = n_j \varphi_j(\mathbf{r})$$

- N -representability

$$\sum_{j=1}^{\infty} n_j = N \quad 0 \leq n_j \leq 1$$

Introduction to RDMFT

- **Gilbert's theorem**¹

$$\Psi(\mathbf{r}_1 \dots \mathbf{r}_N) \leftrightarrow \gamma(\mathbf{r}, \mathbf{r}')$$

- Total energy is a **functional** of $\gamma(\mathbf{r}, \mathbf{r}')$
- **Kinetic** energy is known explicitly

$$E_{\text{kin}} = \iint d^3r d^3r' \delta(\mathbf{r} - \mathbf{r}') \left(-\frac{\nabla^2}{2} \right) \gamma(\mathbf{r}, \mathbf{r}')$$

- **Orbital functionals**²

$$E_{xc} = \sum_{j,k=1}^{\infty} f(n_j, n_k) \iint d^3r d^3r' \frac{\varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_k(\mathbf{r}') \varphi_k^*(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$

¹PRB **12** 2111 (1975)

²PRL **81**, 866 (1998), JCP **122**, 204102 (2005)

Introduction to RDMFT

- **No** KS system due to idempotency
- **Direct minimization** of the total energy with respect to n_j and φ_j
- No simple access to an **energy spectrum** as in DFT
- Physical **properties** of natural orbitals still largely unknown
- Defined as purely **mathematical** objects
- Many times **similar** to Hartree-Fock orbitals in practical calculations

Strategy

- Using an **approximate** functional pollutes the calculation
- Introduce 2 electron 1-dimensional **model systems**

$$H = -\frac{d^2}{dx_1^2} - \frac{d^2}{dx_2^2} + v_0(x_1) + v_0(x_2) + v_{\text{int}}(x_1, x_2)$$

- 2 electrons in 1D are **identical** to 1 electron in 2D
- Treated **numerically exactly** by any code that can handle 1 electron in 2D

$$\begin{aligned}\gamma(x, x') &= 2 \int dx_2 \Psi^*(x', x_2) \Psi(x, x_2) \\ n(x) &= \gamma(x, x)\end{aligned}$$

Strategy

- Obtain natural orbitals and occupation numbers from **diagonalization**
- Obtain **exact** Kohn-Sham orbital and potential

$$\varphi_1(\mathbf{x}) = \sqrt{\frac{n(\mathbf{x})}{2}}, \quad v_s(\mathbf{x}) = \frac{1}{2} \frac{\nabla^2 \sqrt{n(\mathbf{x})}}{\sqrt{n(\mathbf{x})}} + \epsilon_1$$

- OCTOPUS code³



³<http://www.tddft.org/programs/octopus>

Dissociation

- Two interacting electrons
- 1-dimensional system
- Two $1/\cosh^2$ -potentials, short-range interaction

$$H = -\frac{d^2}{2dx_1^2} - \frac{d^2}{2dx_2^2} + v_0(x_1) + v_0(x_2) + \frac{0.5}{\cosh^2(x_1 - x_2)}$$

$$v_0(x) = -\frac{v_1}{\cosh^2(x + d/2)} - \frac{v_2}{\cosh^2(x - d/2)}$$

DFT Results

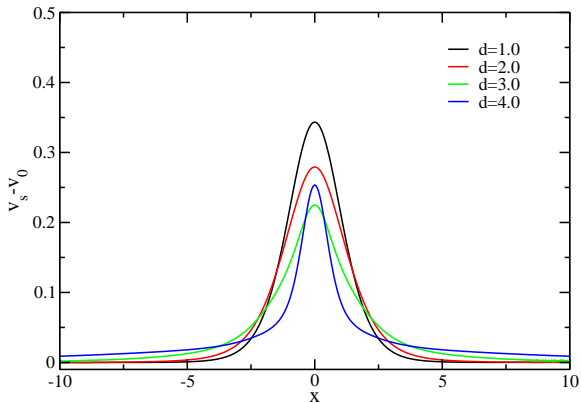


Fig. 1: KS potential of two symmetric wells, $v_1 = v_2 = 0.9^4$

⁴JCP **131**, 224105 (2009)

DFT Results

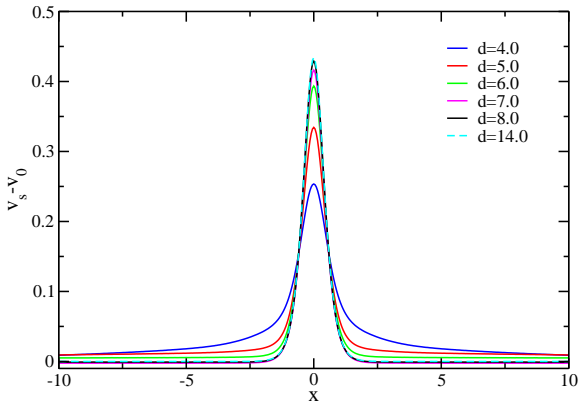


Fig. 1: KS potential of two symmetric wells, $v_1 = v_2 = 0.9^4$

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Theoretical analysis

- Density is given as the sum of the densities of **two separate wells** with one electron in each well
- Region around $x = 0$, i.e. far away from the wells

$$n(x) \propto e^{-\kappa d} \cosh(2\kappa x)$$

Theoretical analysis

- Density is given as the sum of the densities of **two separate wells** with one electron in each well
- Region around $x = 0$, i.e. far away from the wells

$$n(x) \propto e^{-\kappa d} \cosh(2\kappa x)$$

- Effective potential around $x = 0$

$$v_s(x) = \frac{\kappa^2}{2 \cosh^2(2\kappa x)}$$

- **Universal** result for symmetric systems

DFT Results

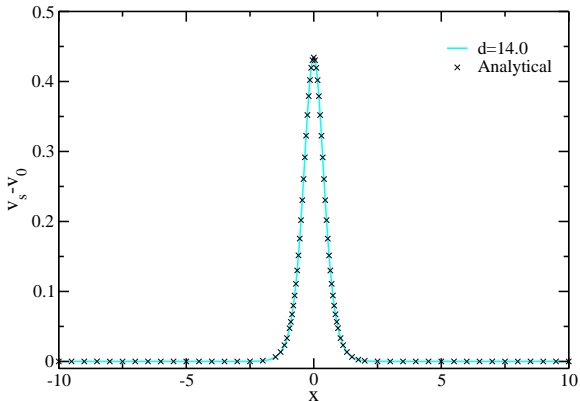


Fig. 1: Dissociation of two symmetric wells, $v_1 = v_2 = 0.9^4$

⁴JCP **131**, 224105 (2009)

What about existing functionals?

- **LDA** does not produce a peak in the KS potential
- GGA by Becke and correction by Perdew⁵ show a peak, but **wrong** height⁶ at $d \rightarrow \infty$
- Specifics of the **peak structure** apparently important
- **Impact** on observables can be small due to negligible density

⁵PRA **38**, 3098 (1988), PRB **33**, 8822 (1986)

⁶IJQC **52**, 711 (1994)

RDMFT Results

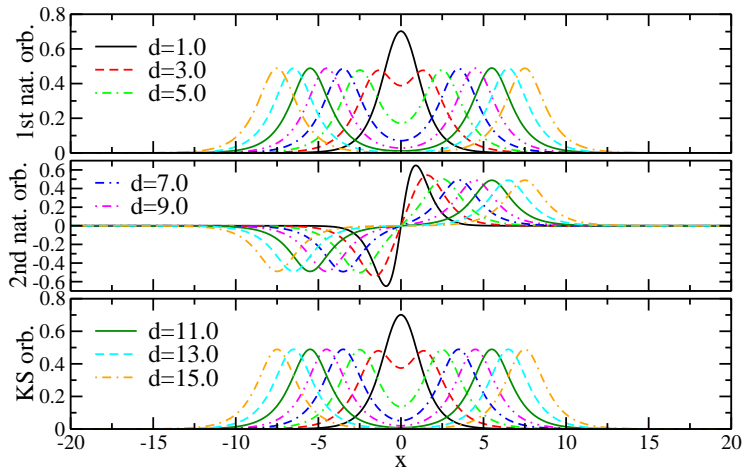


Fig 2: KS orbital and first two natural orbitals, $v_1 = v_2 = 0.9$

RDMFT Results

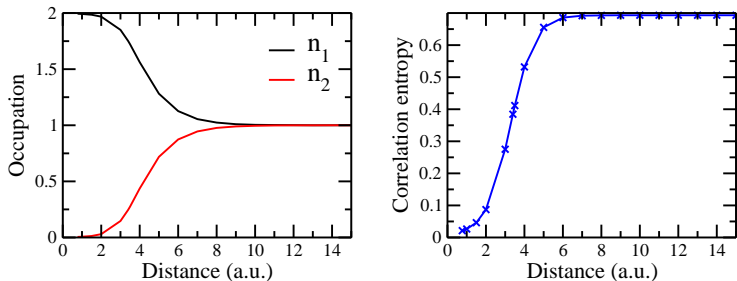


Fig 3: First two occupation numbers and correlation entropy

- Correlation entropy

$$s = -\frac{1}{N} \sum_{j=1}^{\infty} \frac{n_j}{2} \ln \frac{n_j}{2}$$

Excitations

- $1/\cosh^2$ -potential, **short-range** interaction

$$H = -\frac{d^2}{2dx_1^2} - \frac{d^2}{2dx_2^2} + v_0(x_1) + v_0(x_2) + \frac{b}{\cosh^2(x_1 - x_2)}$$

$$v_0(x) = -\frac{v}{\cosh^2 x}$$

- Single particle eigenfunctions known **analytically**
- **Finite** number of bound states
- $v = 0.9$ corresponds to **one bound state** in non-interacting case
- $v = 2.0$ contains **two bound states**

Results for $v=0.9$

- Non-interacting system has exactly **one** bound state

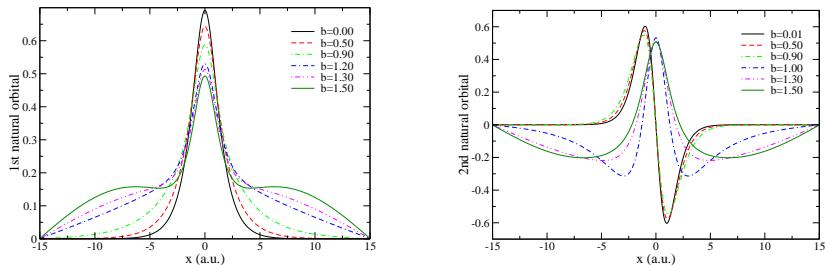


Fig. 4: First and second natural orbital of the ground state⁷

⁷PRA **81**, 022504 (2010)

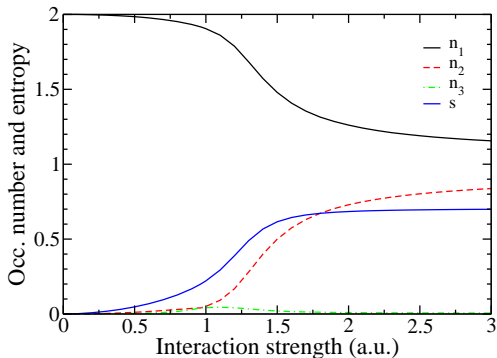
Results for $v=0.9$ 

Fig. 5: First three occupation numbers and entropy of the ground state⁷

⁷Phys. Rev. A **81**, 022504 (2010)

Results for $v=0.9$

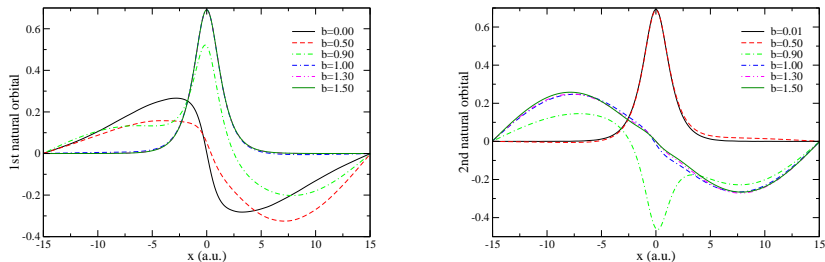


Fig. 6: First and second natural orbital of the 1st excited state⁷

⁷Phys. Rev. A **81**, 022504 (2010)

Results for $v=2.0$

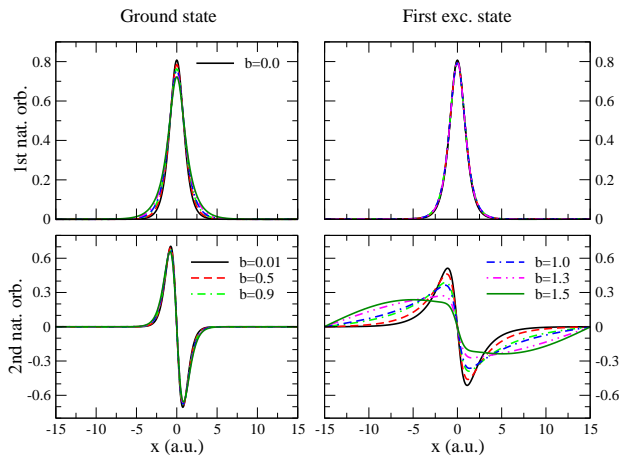


Fig. 7: 1st and 2nd natural orbital, ground and 1st excited state⁷

⁷Phys. Rev. A **81**, 022504 (2010)

Charge Transfer Excitations

- **Difficult** to describe with local functionals in DFT
- Simplest system HeH^+ at large distances
- Model system

$$H = -\frac{d^2}{2dx_1^2} - \frac{d^2}{2dx_2^2} + v_0(x_1) + v_0(x_2) + \frac{1.0}{\cosh^2(x_1 - x_2)}$$

$$v_0(x) = -\frac{1.0}{\cosh^2(x + d/2)} - \frac{2.0}{\cosh^2(x - d/2)}$$

Occupation numbers

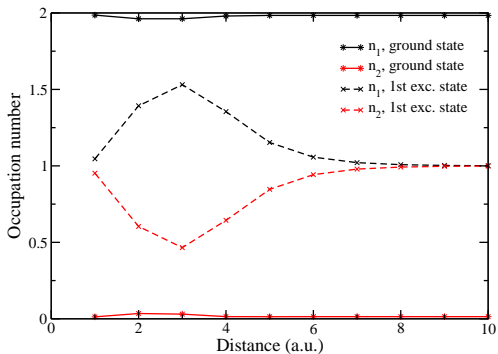


Fig. 8: 1st and 2nd occupation number, ground and 1st excited state

Natural orbitals

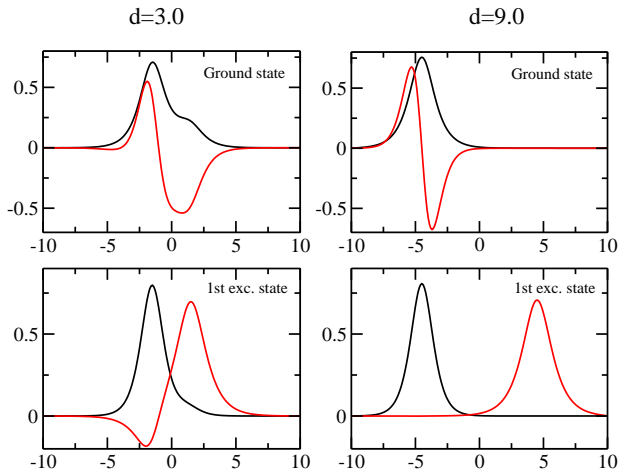


Fig. 9: 1st and 2nd natural orbital, ground and 1st excited state

Conclusions

- First natural and KS orbitals look **similar** at all distances
- Natural orbital only **half occupied** at large distances
- Additional freedom due to **fractional occupation** numbers allows for description of correlation
- **Degenerate** natural orbitals at $d \rightarrow \infty$, linear combinations localize one orbital at each site
- **Approximate** functionals show same trends in the occupation numbers

Conclusions

- Describe excitations as **simple change** in occupation numbers
- Good description if states have **similar localization**
- **ionization** and **charge transfer** need additional change in orbitals
- Problem of assigning **excitation energies** remains
- Linear response requires proper **extension** to time-dependent theory

Thanks to ...



Ilya Tokatly



Matthieu Verstraete



Angel Rubio

References:

N.H., I.V. Tokatly, A. Rubio, J. Chem. Phys. **131**, 224105 (2009)

N.H., I.V. Tokatly, A. Rubio, Phys. Rev. A **81**, 022504 (2010)