

Is there a physical meaning of the natural orbitals? Analysis of exactly solvable models

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Outline

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- 2 Model System
- 3 Results
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Motivation

- One-body **reduced density matrix**

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

- **Natural orbitals** and **occupation numbers**

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

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_{j=1}^{\infty} n_j \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r})$$

- **N -representability** conditions

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

Motivation

- One body density matrix is used as **basic variable** in reduced density matrix functional theory
- Total energy is a **functional** of $\gamma(\mathbf{r}, \mathbf{r}')$
- Correlation energy needs to be **approximated**
- Approximations are often **orbital functionals**
- Interacting systems have **fractional** occupation numbers

Open Questions

- Physical **properties** of natural orbitals still largely unknown
- Defined as purely **mathematical** objects
- Many times **similar** to Hartree-Fock orbitals in practical calculations
- How can we describe **electronic excitations** with the natural orbitals?
- ...

Model system

- Using an **approximate** functional pollutes the calculation
- **Two** interacting electrons in a **1-dimensional** system
- $1/\cosh^2$ -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

Model system

- 2 electrons in 1D are **identical** to 1 electron in 2D

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

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

$$\gamma(x, x') = 2 \int dy \Psi^*(x', y) \Psi(x, y)$$

- Obtain natural orbitals and occupation numbers from **diagonalization**

- OCTOPUS code¹



¹<http://www.tddft.org/programs/octopus>, development version only

Results for $v=0.9$

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

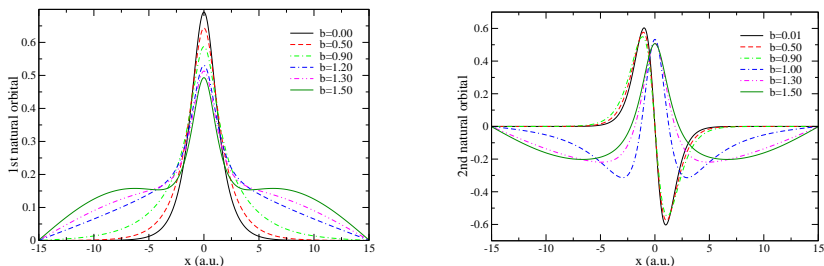
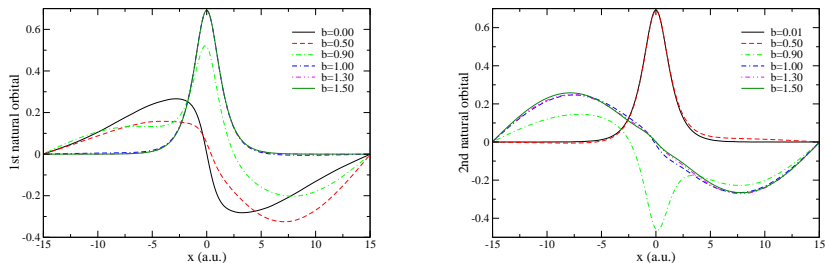
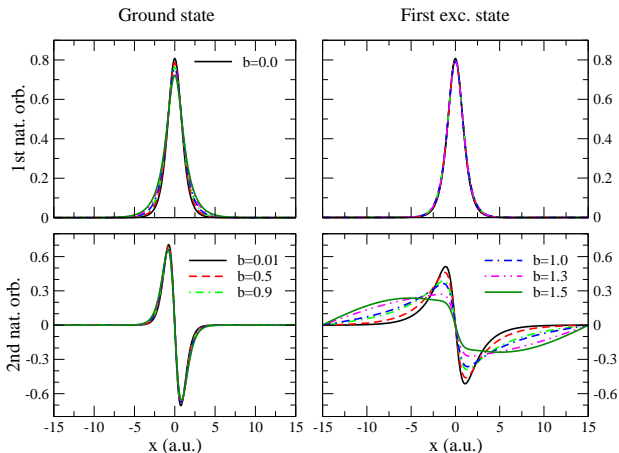


Fig. 1: First and second natural orbital of the ground state²

²Phys. Rev. A **81**, 022504 (2010)

Results for $v=0.9$ Fig. 2: First and second natural orbital of the 1st excited state²²Phys. Rev. A **81**, 022504 (2010)

Results for $v=2.0$ Fig. 3: 1st and 2nd natural orbital, ground and 1st excited state²²Phys. Rev. A **81**, 022504 (2010)

Conclusions and Outlook

- Natural orbitals change with interaction strength in a **physically sensible** way
- Excitations can only be described by a change in occupation numbers if the states are of **similar character**
- **lonization** is **not** well described by a change in occupation numbers alone

Conclusions and Outlook

- Natural orbitals change with interaction strength in a **physically sensible** way
- Excitations can only be described by a change in occupation numbers if the states are of **similar character**
- **Ionization** is **not** well described by a change in occupation numbers alone
- Add **more** particles
- Increase number of **dimensions**
- **Evolution** of the natural orbitals and occupation numbers in time
- Investigate **adiabatic** vs. **non-adiabatic** behavior