

Physical meaning of natural orbitals and natural occupation numbers

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Outline

- 1 Introduction
- 2 General properties
 - Non-interacting electrons
 - Interacting electrons
 - Correlation entropy
- 3 A toy model
 - Natural orbitals and occupation numbers
 - Description of excitations
- 4 Conclusions and Outlook

Reduced density-matrix functional theory

One-body reduced density matrix

$$\begin{aligned}\gamma_{gs}(\mathbf{r}, \mathbf{r}') &= N \int d^3r_2 \dots d^3r_N \Psi_{gs}^*(\mathbf{r}' \dots \mathbf{r}_N) \Psi_{gs}(\mathbf{r} \dots \mathbf{r}_N) \\ &= \sum_{j=1}^{\infty} n_j \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r})\end{aligned}$$

Ground-state energy

$$E[\gamma] = E_{\text{kin}}[\gamma] + E_{\text{ext}}[\gamma] + E_H[\gamma] + E_{\text{xc}}[\gamma] = E[\{n_j\}, \{\varphi_j(\mathbf{r})\}]$$

Reduced density-matrix functional theory

- Minimize total energy with respect to occupation numbers and natural orbitals
- N -representability conditions

$$0 \leq n_j \leq 1, \quad \sum_{j=1}^{\infty} n_j = N, \quad \int d^3r \varphi_j^*(\mathbf{r}) \varphi_k(\mathbf{r}) = \delta_{jk}$$

- Ensemble N -representability

$$\sum_j w_j |\Psi_j\rangle \langle \Psi_j|$$

instead of a pure state $|\Psi\rangle$ (see talks tomorrow)

Reduced density-matrix functional theory

Problem

The exact $E_{xc}[\gamma]$ is unknown

- From energy minimization one obtains **approximate** natural orbitals and occupation numbers
 - For **exact** natural orbitals and occupation numbers one needs to calculate $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$
- Introduce a one-dimensional model system

Non-interacting electrons

Slater determinant

$$\Psi(\mathbf{r}_1 \dots \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \dots & \varphi_1(\mathbf{r}_N) \\ \vdots & & \vdots \\ \varphi_N(\mathbf{r}_1) & \dots & \varphi_N(\mathbf{r}_N) \end{vmatrix}$$

Density matrix

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

- Natural orbitals are **single-particle** orbitals
- Occupation numbers are either **zero or one**

Non-interacting electrons

Single-particle orbitals satisfy

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) \right] \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j(\mathbf{r})$$

Lowest energy states are occupied

$$\begin{aligned} \epsilon_1 \leq \epsilon_2 \leq \dots \quad \Rightarrow \quad n_j = 1 \quad \text{for} \quad 1 \leq j \leq N \\ n_j = 0 \quad \text{for} \quad j > N \end{aligned}$$

The same holds for **Hartree-Fock** theory
(except that v_{ext} is replaced by the HF potential)

Interacting electrons

Many-body wave function

$$\Psi(\mathbf{r}_1 \dots \mathbf{r}_N) = \sum_j c_j \Phi_j(\mathbf{r}_1 \dots \mathbf{r}_N)$$

with Slater determinants $\Phi_j(\mathbf{r}_1 \dots \mathbf{r}_N)$ and $\sum_j |c_j|^2 = 1$.

Density matrix

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

No single-particle equation associated to the natural orbitals

Interacting electrons

- Use M natural orbitals to set up the Slater determinants
Minimizes

$$\int d^3r_1 \cdots d^3r_N |\Psi(\mathbf{r}_1 \cdots \mathbf{r}_N) - \Psi_M(\mathbf{r}_1 \cdots \mathbf{r}_N)|^2$$

compared to any other set of M orbitals.

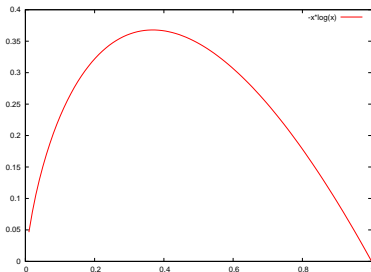
- Relation between coefficients and occupation numbers

$$n_j = \sum_{k, \varphi_j \in \Phi_k} |c_k|^2$$

- If $n_j = 1(0)$ the corresponding natural orbital appears in all (none) of the Slater determinants.

Correlation entropy

Measure for correlation $s = - \sum_{j=1}^{\infty} n_j \log n_j$



For non-interacting electrons $s = 0$.

Small toy model

One-dimensional system with two electrons

$$v_{\text{ext}}(x) = -\frac{v}{\cosh^2(x)}$$

For non-interacting electrons

$$\epsilon_j = -\frac{1}{8} \underbrace{\left[\sqrt{1 + 8v} - 1 - 2(j - 1) \right]}_{>0}^2$$

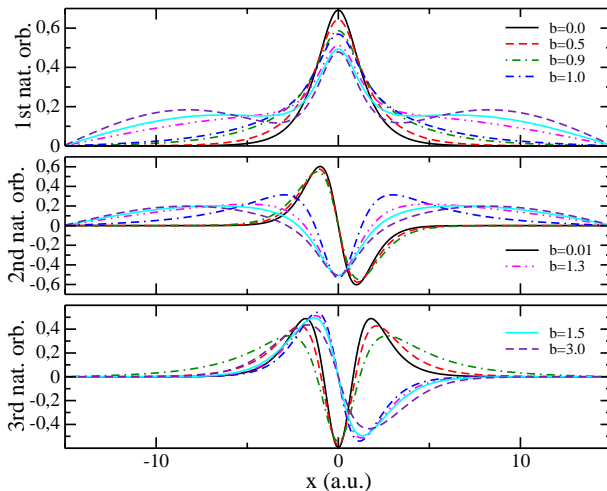
For $v = 0.9$: only one bound state

For $v = 2.0$: two bound states

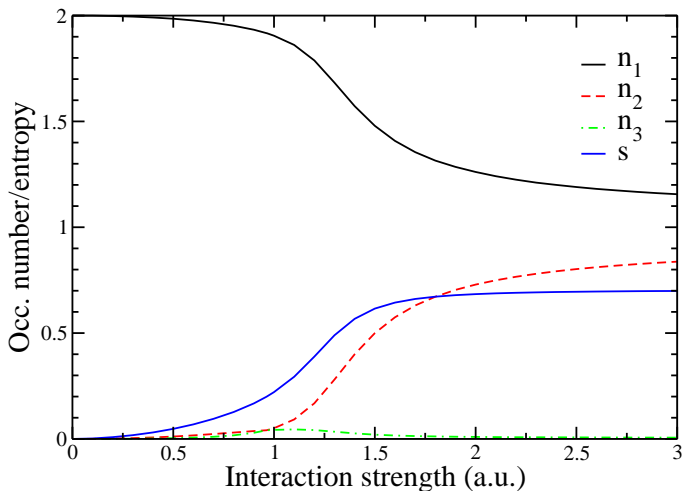
Interaction

$$v_{\text{int}}(x_1, x_2) = \frac{b}{\cosh^2(x_1 - x_2)}$$

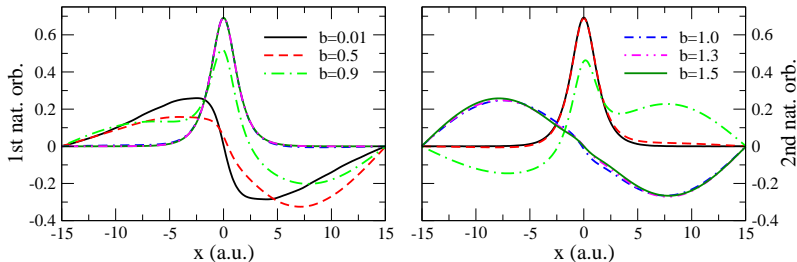
Natural orbitals



Occupation numbers



Excited state

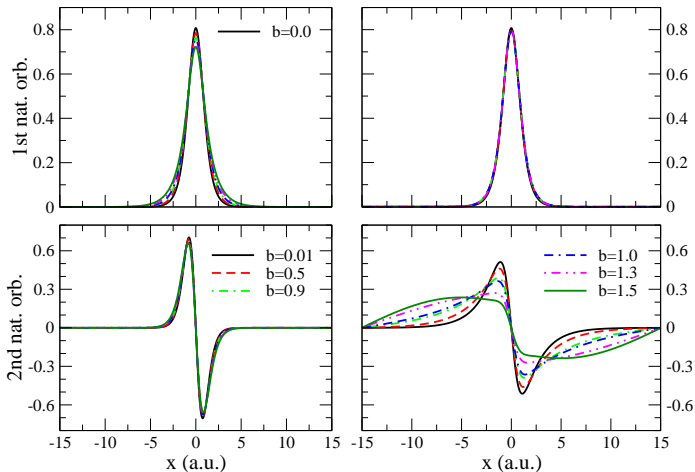


One natural orbital always **unbound**.

Excitations

- For $b < 1.0$ the natural orbitals of the ground state are localized.
- Excited state *always* has one *unbound* natural orbital.
- First excited state of this system is *ionized*.
- *Excitations* cannot be described by just changing the occupation of the ground-state natural orbitals.
- This is however what we always do for non-interacting electrons, even for ionization.

More bound states, $\nu = 2.0$



Excitations

- For $b < 1.0$ the first two natural orbitals of the ground state and the excited state are **localized**.
- **Excitation** can be approximately described by just **changing the occupations** of the ground-state natural orbitals.

Excitations

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Can excitations be described from ground-state natural orbitals?

It depends, sometimes **yes**, sometimes **no**.

Molecular dissociation

Two potential wells at distance d

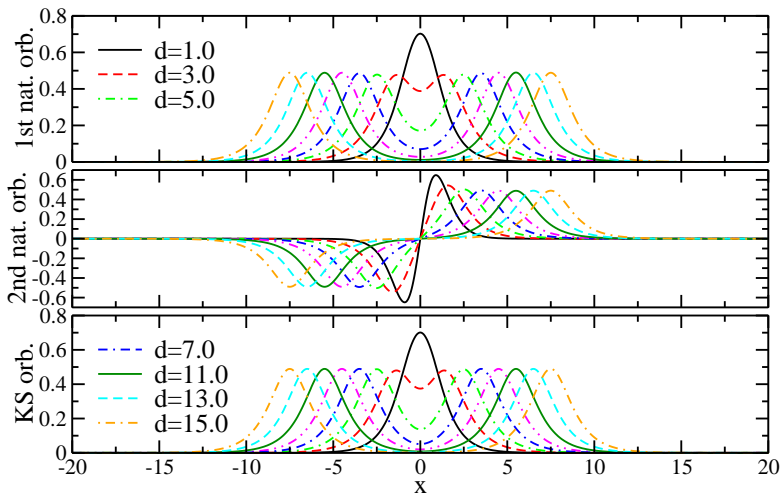
$$v_{ext}(x) = -\frac{v}{\cosh^2(x - d/2)} - \frac{v}{\cosh^2(x + d/2)}$$

Interaction

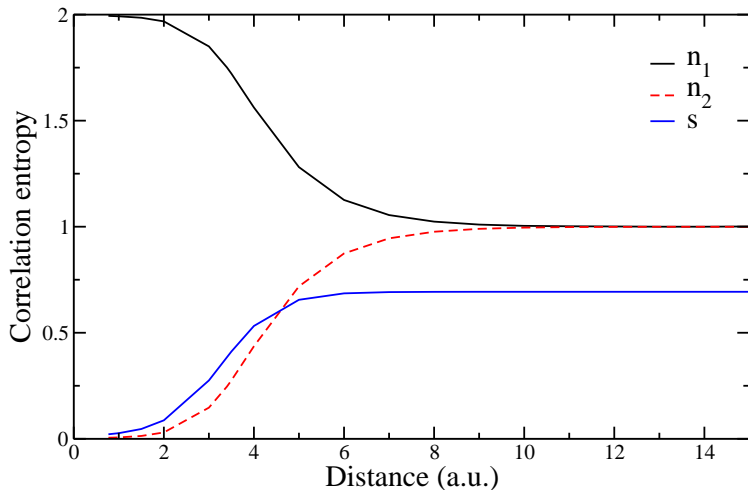
$$v_{int}(x_1, x_2) = \frac{1}{\cosh^2(x_1 - x_2)}$$

Interaction **decays exponentially** with distance.

Molecular dissociation



Molecular dissociation



Conclusions

- **Natural orbitals** change dramatically from non-interacting to interacting particles.
- Excitations can be described by a **change in the occupation numbers** if the two states are similar in their localization.
- Occupation numbers provide a measure for **correlation**.
- $n_j = 0$ and $n_j = 1$ give more information on wave function.

Work done together with...

I.V. Tokatly *UPV/EHU, San Sebastián (Spain)*

A. Rubio *UPV/EHU, San Sebastián (Spain), MPI, Hamburg (Germany)*

References:

Phys. Rev. A **81**, 022504 (2010)

