Physical meaning of natural orbitals and natural occupation numbers
Outline

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   - Interacting electrons
   - Correlation entropy
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Reduced density-matrix functional theory

One-body reduced density matrix

\[ \gamma_{gs}(r, r') = N \int d^3r_2...d^3r_N \psi^*_{gs}(r'...r_N) \psi_{gs}(r...r_N) \]
\[ = \sum_{j=1}^{\infty} n_j \varphi^*_j(r') \varphi_j(r) \]

Ground-state energy

\[ E[\gamma] = E_{\text{kin}}[\gamma] + E_{\text{ext}}[\gamma] + E_H[\gamma] + E_{xc}[\gamma] = E[\{n_j\}, \{\varphi_j(r)\}] \]
Reduced density-matrix functional theory

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

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

- 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 $\Psi(r_1, \ldots, r_N)$

→ Introduce a one-dimensional model system
Non-interacting electrons

Slater determinant

\[ \Psi(r_1, ..., r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(r_1) & \cdots & \varphi_1(r_N) \\ \vdots & \ddots & \vdots \\ \varphi_N(r_1) & \cdots & \varphi_N(r_N) \end{vmatrix} \]

Density matrix

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

- Natural orbitals are single-particle orbitals
- Occupation numbers are either zero or one
Non-interacting electrons

Single-particle orbitals satisfy

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

Lowest energy states are occupied

$$\epsilon_1 \leq \epsilon_2 \leq \ldots \Rightarrow n_j = 1 \quad \text{for} \quad 1 \leq j \leq N$$

$$n_j = 0 \quad \text{for} \quad j > N$$

The same holds for Hartree-Fock theory (except that $v_{\text{ext}}$ is replaced by the HF potential)
Interacting electrons

Many-body wave function

$$\Psi(r_1...r_N) = \sum_j c_j \Phi_j(r_1...r_N)$$

with Slater determinants $\Phi_j(r_1...r_N)$ and $\sum_j |c_j|^2 = 1$.

Density matrix

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

No single-particle equation associated to the natural orbitals
Interacting electrons

- Use \( M \) natural orbitals to set up the Slater determinants
- Minimizes
  \[
  \int d^3 r_1 \cdots d^3 r_N |\psi(r_1 \cdots r_N) - \psi_M(r_1 \cdots r_N)|^2
  \]
  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

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

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

![Graph showing occupation numbers and entropy as a function of interaction strength. The graph includes curves for different occupation numbers and entropy, labeled as $n_1$, $n_2$, $n_3$, and $s$. The x-axis represents interaction strength (a.u.), and the y-axis represents occurrence number/entropy. The graph illustrates the relationship between occupation numbers and interaction strength.]
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, $v = 2.0$
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

- 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.

Can excitations be described from ground-state natural orbitals?

It depends, sometimes yes, sometimes no.
Molecular dissociation

Two potential wells at distance $d$

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

Interaction

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

Interaction decays exponentially with distance.
Molecular dissociation

![Graph showing molecular dissociation with labels for different orbitals and distances.]

- **First natural orbital:**
  - d=1.0
  - d=3.0
  - d=5.0

- **Second natural orbital:**
  - d=1.0
  - d=3.0
  - d=5.0

- **KS orbital:**
  - d=7.0
  - d=11.0
  - d=13.0
  - d=15.0
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: