Time evolution of the natural occupation numbers

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[joint with Miguel A. L. Marques (Halle), Christian Schilling (Oxford), Peter Vrana (Budapest), Nektarios Lathiotakis (Athens)]

Outline

Density operator techniques

The time-dependent Hamiltonian

$$\hat{H}_{1\ldots N}(t) = \sum_{i=1}^{N} \hat{h}_i(t) + \sum_{i<j}^{N} \hat{W}_{ij}.$$

BBGYK-hierarchy

Instead of the full N-particle density operator, it is often convenient to consider simple quantities, namely, the n-body reduced density matrices

$$i\hbar\partial_t \hat{\gamma}_1 = [\hat{h}(t), \hat{\gamma}_1] + 2\mathrm{Tr}_2[\hat{W}_{12}, \hat{\gamma}_2]$$
$$i\hbar\partial_t \hat{\gamma}_2 = [\hat{H}_{12}, \hat{\gamma}_2] + 3\mathrm{Tr}_3[\hat{W}_{13} + \hat{W}_{23}, \hat{\gamma}_3]$$
$$\vdots$$

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In Burgdörfer's talk $\hat{\gamma}_3[\hat{\gamma}_2]$.

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In Burgdörfer's talk $\hat{\gamma}_3[\hat{\gamma}_2]$. In RDMFT $\hat{\gamma}_2[\hat{\gamma}_1]$.

Gilbert theorem (1975)

Gilbert theorem guarantees that the ground-state energy of a fermionic system can be obtained by minimizing some energy functional on $\hat{\gamma}_1$:

$$\mathcal{E}[\hat{\gamma}_1] = \langle \hat{h}, \hat{\gamma}_1 \rangle + \frac{1}{2} \int dx dx' \frac{\gamma_1(x,x)\gamma_1(x',x')}{|r-r'|} + \mathcal{E}_{\mathrm{xc}}[\hat{\gamma}_1].$$

Some advantages of RDMFT:

- The kinetic-energy functional is exact.
- The correlation-energy errors are at least an order of magnitude smaller than B3LYP.
- Superconductivity, temperature-dependent...

Some disadvantages:

- Inefficient compared to DFT.
- While DFT resorts to a large zoo of density functionals, only about a dozen of 1-RDM-functionals have been proposed so far.

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Müller (or Buijse-Baerends) functional:

$$\mathcal{E}_{\mathrm{xc}}[\hat{\gamma}_1] = -\frac{1}{2} \int d\boldsymbol{x} d\boldsymbol{x}' \frac{|\gamma_1 \quad (\boldsymbol{x}, \boldsymbol{x}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

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Time-dependent RDMFT

$$\hat{\gamma}_1(t) = \sum_i n_i(t)|\varphi_i(t)\rangle\langle\varphi_i(t)|.$$

$$i\hbar\partial_t\hat{\gamma}_1(t) = [\hat{h}(t), \hat{\gamma}_1(t)] + 2\mathrm{Tr}_2[\hat{W}_{12}, \hat{\gamma}_2[\hat{\gamma}_1]],$$

The current ground-state reconstructions in RDMFT are very restrictive, for they only contain the so-called two-index (direct and exchange) Coulomb integrals (Requist 2011).
As a result, by and large,

$$\partial_t n_i(t) = 2\mathfrak{Im}\langle\varphi_i|\mathrm{Tr}_2[\hat{W}_{12}, \hat{\gamma}_2[\hat{\gamma}_1]]|\varphi_i\rangle = 0.$$

Quantum marginal problem

From the many-fermion wave function to the n-particle reduced density matrices:

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From the 1-particle reduced density matrix to the wave function:

$$\hat{\gamma}_1 \longrightarrow ?$$

Pure quantum marginal problem

Pauli exclusion principle (Coleman 1963)

This is the is the ensemble N-representability problem. The matrix $\hat{\gamma}_1 = N\mathrm{Tr}_{N-1}\left[\sum_i \alpha_i |\Psi_i\rangle\langle\Psi_i|\right]$ satisfies:

$$0 \leq \hat{\gamma}_1 \leq 1 \quad \text{and} \quad \mathrm{Tr}\,\hat{\gamma}_1 = N.$$

The eigenvalues of $\hat{\gamma}_1$ obey $0 \leq n_i \leq 1$, with $(n_1 \geq n_2 \geq \cdots)$.

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Generalized Pauli exclusion principle (Klyachko 2008)

For pure states there is also a finite set of linear constraints:

$$\mathcal{D}(\vec{n}) = \kappa_0 + \kappa_1 n_1 + \cdots + \kappa_d n_d \geq 0, \qquad \kappa_i \text{ integer.}$$

Generalized Pauli constraints for 3 electrons

$N = 3, d = 6$

$$1 - (n_1 + n_6) \geq 0$$
$$1 - (n_2 + n_5) \geq 0$$
$$1 - (n_3 + n_4) \geq 0$$
$$2 - (n_1 + n_2 + n_4) \geq 0$$

$N = 3, d = 7$

$$2 - (n_1 + n_2 + n_4 + n_7) \geq 0$$
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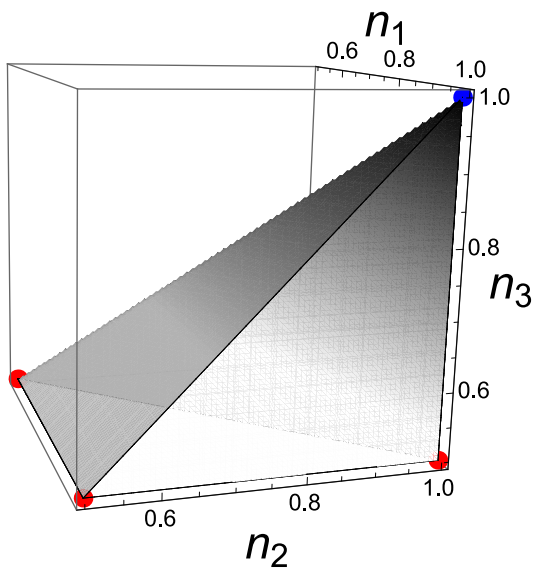
$$1 - (n_1 + n_8) \geq 0$$
$$\vdots$$

Example: Borland-Dennis setting $N = 3, d = 6$

Borland-Dennis setting

Consider a system of three electrons and a six-dimensional one-particle Hilbert space. Apart from the Pauli's inequalities:

$$n_1 \leq 1 \qquad n_2 \leq 1 \qquad n_3 \leq 1$$
$$n_1 + n_2 \leq 2$$



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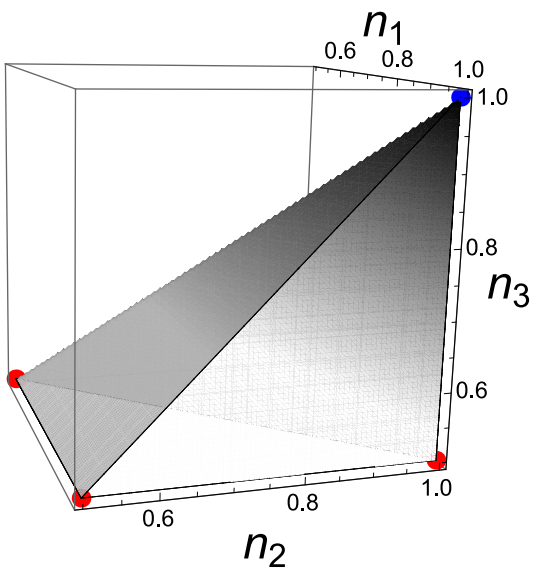

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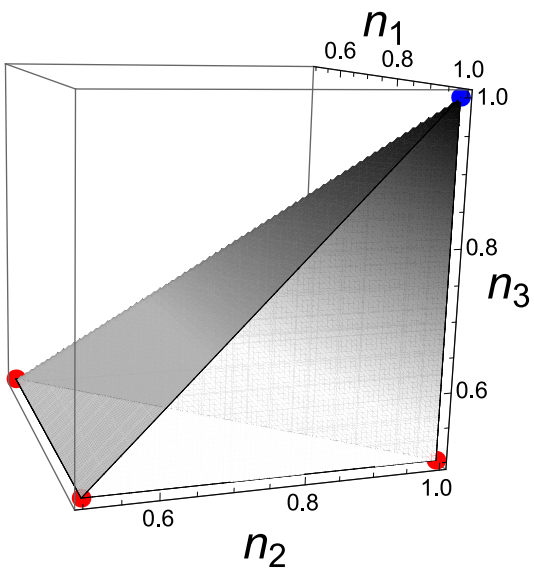

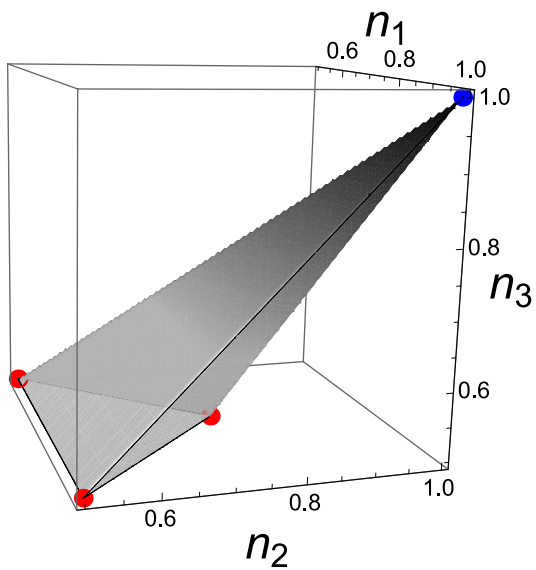

Structural simplification

Pinning

When *pinning* holds $\mathcal{D}(\vec{n}) = \kappa_0 + \kappa_1 n_1 + \cdots + \kappa_d n_d = 0$, any compatible wave function fullfills

$$(\kappa_0 \mathbf{1} + \kappa_1 \hat{n}_1 + \cdots + \kappa_d \hat{n}_d)|\Phi\rangle = 0$$

and remarkably simplifies:

$$|\Phi\rangle = \sum_{\{i_1,\ldots,i_N\}} c_{i_1,\ldots,i_N} |\varphi_{i_1} \cdots \varphi_{i_N}\rangle,$$

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for the configurations satisfying:

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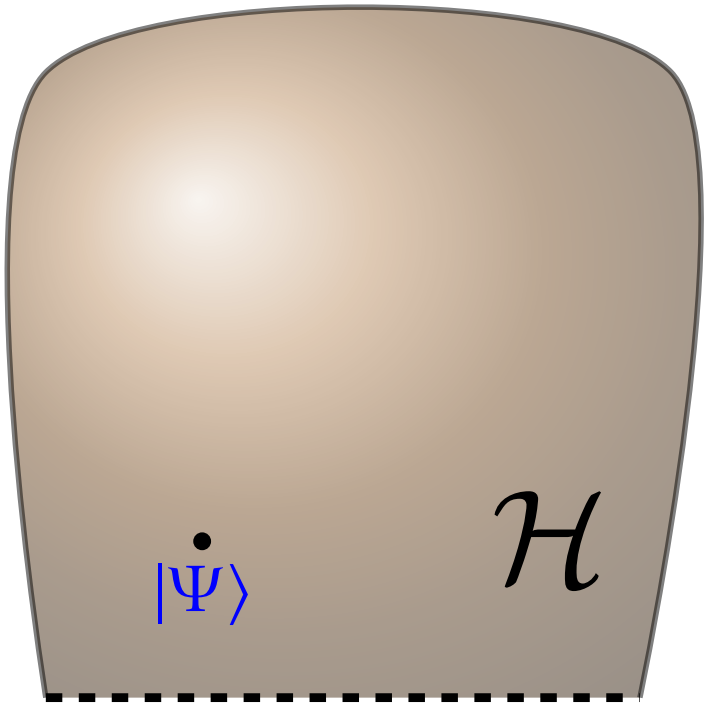
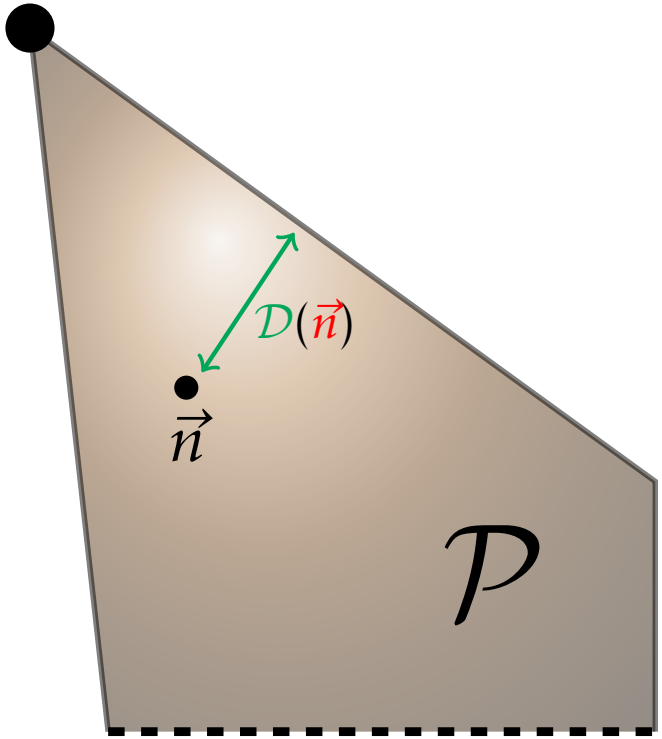


1-particle



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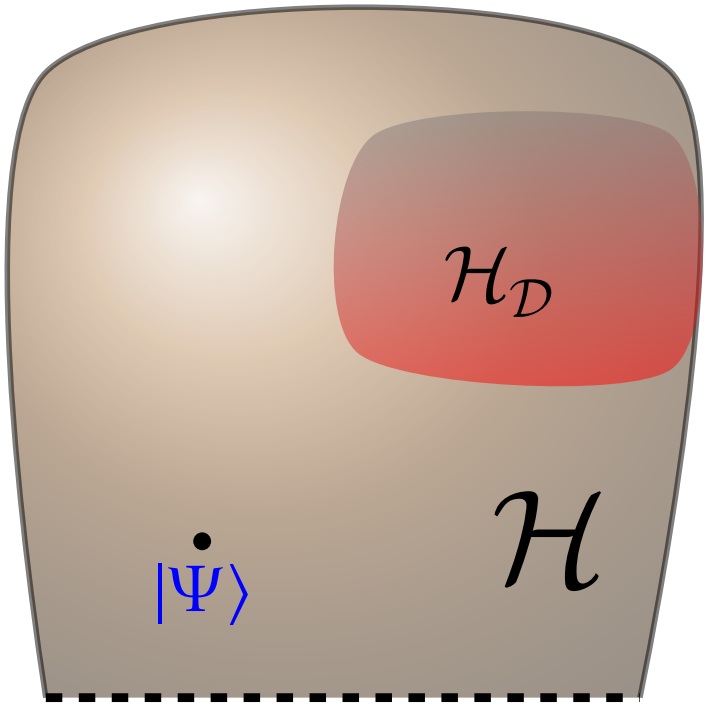

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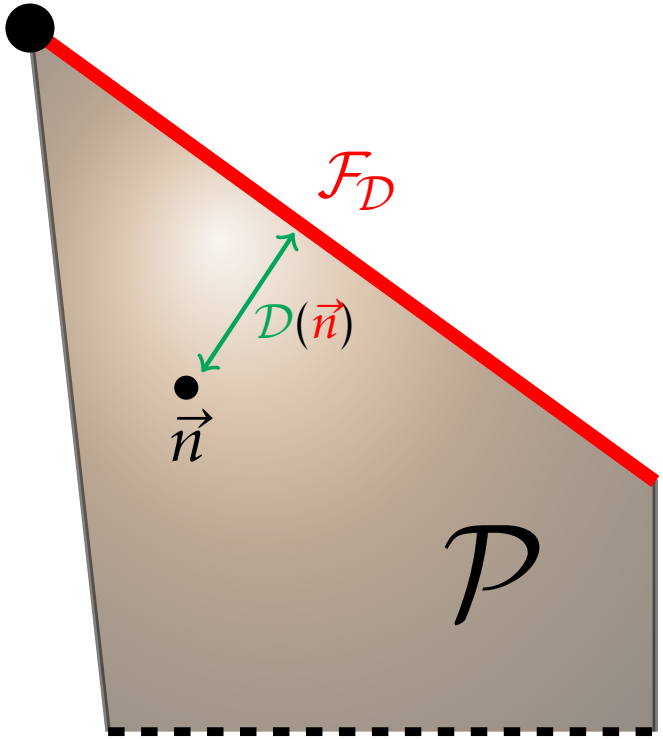

$$1 - \|\hat{P}_{\mathcal{D}}\Psi\|^2 \leq 2\mathcal{D}(\vec{n})$$

PRA **96**, 052312 (2017)

PCCP **19**, 12655 (2017)

First news: pinning is robust!

Assume that $|\Psi_0\rangle$ is the ground state of a Hamiltonian $\hat{H}$, and assume also that

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In Rayleigh-Schrödinger perturbation theory for the ground state of the perturbed Hamiltonian $\hat{H}(\lambda) \equiv \hat{H} + \lambda\hat{V}$ we have

$$\left.\frac{\partial \mathcal{D}(\vec{n}_\lambda)}{\partial \lambda}\right|_{\lambda=0} = 0.$$

Therefore, for pinned systems,

$$\mathcal{D}(\vec{n}_\lambda) \approx \mathcal{D}(\vec{n}_0) = 0.$$

CLBR and Miguel A. L. Marques (to be published).

Second news: quasipinnig!

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C. Schilling, D, Gross and M. Christandl, PRL **110**, 040404 (2013)
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- Hubbard model, Lithium isoelectronic series, molecules...

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- In the context of 2RDM and 1RDM theories

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Up-to-date review: CLBR, Chemical Modelling **14**, 71 (2018).

Time evolution of the natural occupation numbers

For the three-electron system, the rank six approximation is

$$|\Phi_{\mathrm{BD}}[\qquad]\rangle$$

Time evolution of the natural occupation numbers

The Borland-Dennis state is

$$|\Phi_{\mathrm{BD}}[\vec{n},\vec{\varphi},\vec{\xi}]\rangle = \sqrt{n_3}e^{i\xi_3}|\varphi_1\varphi_2\varphi_3\rangle - \sqrt{n_5}e^{i\xi_5}|\varphi_1\varphi_4\varphi_5\rangle + \sqrt{n_6}e^{i\xi_6}|\varphi_2\varphi_4\varphi_6\rangle$$

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Time-evolution of the natural occupation numbers

$$\partial_t n_i = -4\sum_{j\neq i}\sqrt{n_i n_j}\sin(\xi_i-\xi_j) \int \begin{vmatrix} \varphi_i(\boldsymbol{x})\varphi_j(\boldsymbol{x}) & \varphi_i(\boldsymbol{x}')\varphi_{7-i}(\boldsymbol{x}') \\ \varphi_{7-j}(\boldsymbol{x})\varphi_j(\boldsymbol{x}) & \varphi_{7-j}(\boldsymbol{x}')\varphi_{7-i}(\boldsymbol{x}') \end{vmatrix} v(\boldsymbol{x},\boldsymbol{x}')d\boldsymbol{x}d\boldsymbol{x}'.$$

Time evolution of the natural occupation numbers

Time-evolution of the relative phases

From the stationary of the action $\mathcal{A}[\Phi_{\mathrm{BD}}] = \int_0^t \langle \Phi_{\mathrm{BD}}(\tau)| i\partial_\tau - \hat{H}(\tau)|\Phi_{\mathrm{BD}}(\tau)\rangle d\tau$:

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Similar equations for four-electron systems.

Take-home messages

- Pure 1-body reduced density matrix satisfies the generalized Pauli principle.
- (quasi)pinning is physically relevant: fermionic ground states are much simpler than expected!
- (quasi)pinning is robust!
- we have found an equation for the time evolution of the natural occupation numbers for three-electron systems.