Introducing Relativistic Reduced Density Matrix Functional Theory (RE-RDMFT)

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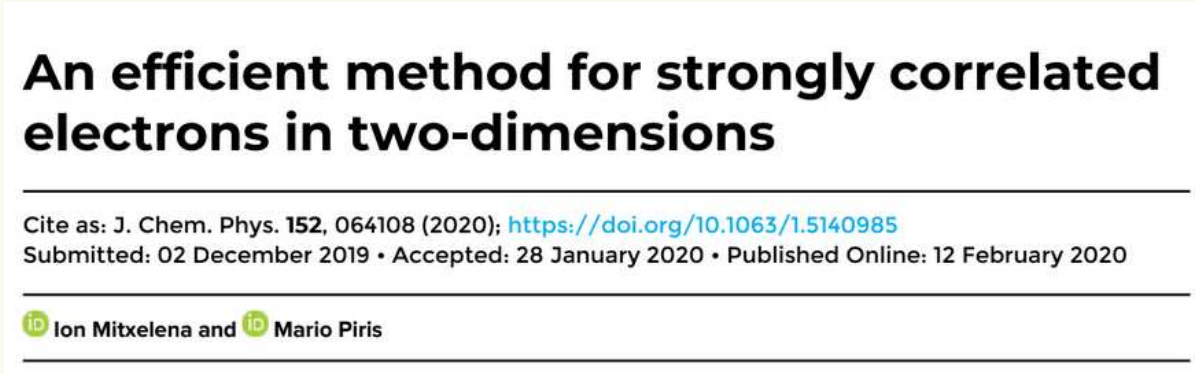
Toulouse, January 11, 2022

Non-relativistic RDMFT (a.k.a. NOFT)

- Why to use RDMFT?



An efficient method for strongly correlated electrons in two-dimensions

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Ion Mitxelena and Mario Piris

- Recent extensions of RDMFT in other fields

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Reduced density matrix functional theory for superconductors

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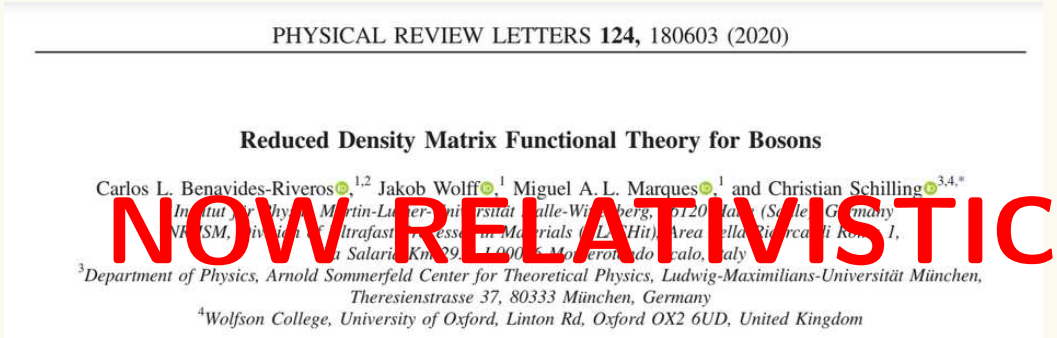

PHYSICAL REVIEW LETTERS **124,** 180603 (2020)

Reduced Density Matrix Functional Theory for Bosons

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NOW RELATIVISTIC!

The Dirac equation for a single particle I

$$\widehat{\mathbf{T}}_D(\mathbf{r})\psi_A(\mathbf{r}) + \int d\mathbf{r}' \mathbf{v}^{\mathrm{nl}}_{\mathrm{ext}}(\mathbf{r}', \mathbf{r})\psi_A(\mathbf{r}') = E_A\psi_A(\mathbf{r})$$

where

$$\widehat{\mathbf{T}}_D(\mathbf{r}) = -\mathrm{i}c(\boldsymbol{\alpha}_{\mathbf{r}} \cdot \boldsymbol{\nabla}_{\mathbf{r}}) + c^2 m\boldsymbol{\beta}$$

$$\begin{aligned}\boldsymbol{\alpha}_{\mathbf{r}} &= (\boldsymbol{\alpha}_x, \boldsymbol{\alpha}_y, \boldsymbol{\alpha}_z) \\ &= \left(\begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma}_x \\ \boldsymbol{\sigma}_x & \mathbf{0}_2 \end{pmatrix}, \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma}_y \\ \boldsymbol{\sigma}_y & \mathbf{0}_2 \end{pmatrix}, \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma}_z \\ \boldsymbol{\sigma}_z & \mathbf{0}_2 \end{pmatrix} \right)\end{aligned}$$

$$\boldsymbol{\beta} = \begin{pmatrix} \mathbb{I}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & -\mathbb{I}_2 \end{pmatrix}$$

$$\mathbf{v}^{\mathrm{nl}}_{\mathrm{ext}}(\mathbf{r}', \mathbf{r}) = \begin{pmatrix} v^{\mathrm{nl}}_{\mathrm{ext},1,1}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},1,2}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},1,3}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},1,4}(\mathbf{r}', \mathbf{r}) \\ v^{\mathrm{nl}}_{\mathrm{ext},2,1}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},2,2}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},2,3}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},2,4}(\mathbf{r}', \mathbf{r}) \\ v^{\mathrm{nl}}_{\mathrm{ext},3,1}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},3,2}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},3,3}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},3,4}(\mathbf{r}', \mathbf{r}) \\ v^{\mathrm{nl}}_{\mathrm{ext},4,1}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},4,2}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},4,3}(\mathbf{r}', \mathbf{r}) & v^{\mathrm{nl}}_{\mathrm{ext},4,4}(\mathbf{r}', \mathbf{r}) \end{pmatrix}$$

with $v^{\mathrm{nl}}_{\mathrm{ext},\mu,\nu}(\mathbf{r}', \mathbf{r}) = \left[v^{\mathrm{nl}}_{\mathrm{ext},\nu,\mu}(\mathbf{r}, \mathbf{r}') \right]^*$

The Dirac equation for a single particle II

$$\psi_A(\mathbf{r}) = \begin{pmatrix} \phi_{A,1}(\mathbf{r}) \\ \phi_{A,2}(\mathbf{r}) \\ \phi_{A,3}(\mathbf{r}) \\ \phi_{A,4}(\mathbf{r}) \end{pmatrix},$$

whose conjugate-transpose form reads

$$\psi_A^\dagger(\mathbf{r}) = \begin{pmatrix} \phi_{A,1}^*(\mathbf{r}) & \phi_{A,2}^*(\mathbf{r}) & \phi_{A,3}^*(\mathbf{r}) & \phi_{A,4}^*(\mathbf{r}) \end{pmatrix}.$$

$\int d\mathbf{r}\psi_A^\dagger(\mathbf{r})\psi_B(\mathbf{r}) = \delta_{AB}$ and $\{\psi_A\} = \{\psi_R\} \cup \{\psi_I\}$ (NS and PS).
Field operators:

$$\widehat{\psi}^\dagger(\mathbf{r}) = \sum_A \widehat{a}_A^\dagger \psi_A(\mathbf{r}) = \sum_I \widehat{b}_I^\dagger \psi_I(\mathbf{r}) + \sum_R \widehat{d}_R \psi_R(\mathbf{r}).$$

$$\widehat{\psi}(\mathbf{r}) = \sum_A \widehat{a}_A \psi_A(\mathbf{r}) = \sum_I \widehat{b}_I \psi_I(\mathbf{r}) + \sum_R \widehat{d}_R^\dagger \psi_R(\mathbf{r}).$$

From now on, we will use blue for NS!

The Dirac equation for many particles (Fock space) I

$$\begin{aligned}\widehat{H}_0^v &= \widehat{T}_D + \widehat{V}_{\rm ext}^{\rm nl} \\ &= \int d\mathbf{r}d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')\mathrm{Tr}\left[\widehat{\mathbf{T}}_D(\mathbf{r})\widehat{\mathbf{n}}_1(\mathbf{r},\mathbf{r}')\right] + \int d\mathbf{r}d\mathbf{r}'\mathrm{Tr}\left[\mathbf{v}_{\rm ext}^{\rm nl}(\mathbf{r}',\mathbf{r})\widehat{\mathbf{n}}_1(\mathbf{r},\mathbf{r}')\right] \\ &= \sum_{\mu,\tau}\int d\mathbf{r}d\mathbf{r}'\left[\delta(\mathbf{r}-\mathbf{r}')\,T_{D,\mu,\tau}(\mathbf{r}) + v_{{\rm ext},\mu,\tau}^{\rm nl}(\mathbf{r}',\mathbf{r})\right]\widehat{n}_{1,\tau,\mu}(\mathbf{r},\mathbf{r}'),\end{aligned}$$

where we have introduced the one-particle density matrix operator

$$\begin{aligned}\widehat{n}_{1,\tau,\mu}(\mathbf{r},\mathbf{r}') &= \mathcal{N}\left[\widehat{\psi}_\mu^\dagger(\mathbf{r}')\widehat{\psi}_\tau(\mathbf{r})\right] \\ &= \sum_{I,J}\widehat{b}_I^\dagger\widehat{b}_J\phi_{I,\mu}^*(\mathbf{r}')\phi_{J,\tau}(\mathbf{r}) + \sum_I\sum_R\widehat{b}_I^\dagger\widehat{d}_R^\dagger\phi_{I,\mu}^*(\mathbf{r}')\phi_{R,\tau}(\mathbf{r}) \\ &+ \sum_S\sum_J\widehat{d}_S\widehat{b}_J\phi_{S,\mu}^*(\mathbf{r}')\phi_{J,\tau}(\mathbf{r}) + \sum_{R,S}\mathcal{N}\left[\widehat{d}_R\widehat{d}_S^\dagger\right]\phi_{R,\mu}^*(\mathbf{r}')\phi_{S,\tau}(\mathbf{r})\end{aligned}$$

with normal ordering ($\mathcal{N}\left[\widehat{\psi}_\mu^\dagger(\mathbf{r}')\widehat{\psi}_\tau(\mathbf{r})\right]$) taken w.r.t. $|0_v\rangle$ ($\langle 0_v|\widehat{H}_0^v|0_v\rangle = 0$).

The Dirac equation for many particles (Fock space) I

$$\begin{aligned}\widehat{H}_0^v &= \widehat{T}_D + \widehat{V}_{\rm ext}^{\rm nl} \\ &= \int d\mathbf{r}d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')\mathrm{Tr}\left[\widehat{\mathbf{T}}_D(\mathbf{r})\widehat{\mathbf{n}}_1(\mathbf{r},\mathbf{r}')\right] + \int d\mathbf{r}d\mathbf{r}'\mathrm{Tr}\left[\mathbf{v}_{\rm ext}^{\rm nl}(\mathbf{r}',\mathbf{r})\widehat{\mathbf{n}}_1(\mathbf{r},\mathbf{r}')\right] \\ &= \sum_{\mu,\tau}\int d\mathbf{r}d\mathbf{r}'\left[\delta(\mathbf{r}-\mathbf{r}')T_{D,\mu,\tau}(\mathbf{r}) + v_{{\rm ext},\mu,\tau}^{\rm nl}(\mathbf{r}',\mathbf{r})\right]\widehat{n}_{1,\tau,\mu}(\mathbf{r},\mathbf{r}'),\end{aligned}$$

where we have introduced the one-particle density matrix operator

$$\begin{aligned}\widehat{n}_{1,\tau,\mu}(\mathbf{r},\mathbf{r}') &= \mathcal{N}\left[\widehat{\psi}_\mu^\dagger(\mathbf{r}')\widehat{\psi}_\tau(\mathbf{r})\right] \\ &= \sum_{I,J}\widehat{b}_I^\dagger\widehat{b}_J\phi_{I,\mu}^*(\mathbf{r}')\phi_{J,\tau}(\mathbf{r}) + \sum_I\sum_R\widehat{b}_I^\dagger\widehat{d}_R^\dagger\phi_{I,\mu}^*(\mathbf{r}')\phi_{R,\tau}(\mathbf{r}) \\ &+ \sum_S\sum_J\widehat{d}_S\widehat{b}_J\phi_{S,\mu}^*(\mathbf{r}')\phi_{J,\tau}(\mathbf{r}) - \sum_{R,S}\widehat{d}_S^\dagger\widehat{d}_R\phi_{R,\mu}^*(\mathbf{r}')\phi_{S,\tau}(\mathbf{r})\end{aligned}$$

with normal ordering ($\mathcal{N}\left[\widehat{\psi}_\mu^\dagger(\mathbf{r}')\widehat{\psi}_\tau(\mathbf{r})\right]$) taken w.r.t. $|0_v\rangle$ ($\langle 0_v|\widehat{H}_0^v|0_v\rangle = 0$).

NS $\rightarrow$ POSITRONIC STATES

The Dirac equation for many particles (Fock space) II

$\left[\widehat{H}_0^v, \widehat{Q}\right] = 0$ in any basis

$$\widehat{Q} = \sum_I \widehat{b}_I^\dagger \widehat{b}_I - \sum_R \widehat{d}_R^\dagger \widehat{d}_R$$

$Q = N_e - N_p$ sectors

$$\mathcal{F} = \bigoplus_{Q=-\infty}^{\infty} \mathcal{H}_Q.$$

Non-diag rep. Hamiltonian to a diag. representation (Bogoliubov transformation)

$$\widetilde{\psi}_A(\mathbf{r}) = \sum_B \psi_B^0(\mathbf{r}) V_{BA}.$$

with $\mathbf{V} = e^{\boldsymbol{\kappa}}$ and $\kappa_{AB} \in \mathbb{C}$.

$$\widehat{\widetilde{a}}_A = e^{\widehat{\kappa}} \widehat{a}_A e^{-\widehat{\kappa}} = \sum_B \widehat{a}_B V_{BA}^*$$

$$\widehat{\widetilde{\psi}}(\mathbf{r}) = \sum_A \widehat{\widetilde{a}}_A \widetilde{\psi}_A(\mathbf{r}) = \sum_I \widehat{\widetilde{b}}_I \widetilde{\psi}_I(\mathbf{r}) + \sum_R \widehat{\widetilde{d}}_R^\dagger \widetilde{\psi}_R(\mathbf{r})$$

We may define $\widehat{\widehat{H}}_0^v$ with normal ordering w.r.t. $|\widetilde{0}_v\rangle$

The Dirac equation for many particles (Vacuum polarization) III

$$\langle 0_v|\widehat{H}_0^v|0_v\rangle = \langle \widetilde{0}_v|\widehat{\widetilde{H}}_0^v|\widetilde{0}_v\rangle = 0$$

but

$$\langle 0_v|\widehat{\widetilde{H}}_0^v|0_v\rangle \neq \langle \widetilde{0}_v|\widehat{H}_0^v|\widetilde{0}_v\rangle \neq 0$$

Vacuum polarization energy:

$$\widetilde{E}_0^0 = \langle \widetilde{0}_v|\widehat{H}_0^v - \widehat{\widetilde{H}}_0^v|\widetilde{0}_v\rangle = \int d\mathbf{r}d\mathbf{r}' \mathrm{Tr}\left[\left(\delta(\mathbf{r}-\mathbf{r}')\widehat{\mathbf{T}}_D(\mathbf{r}) + \mathbf{v}_{\mathrm{ext}}^{\mathrm{nl}}(\mathbf{r}',\mathbf{r})\right)\widetilde{\mathbf{n}}_1^{\mathrm{vp}}(\mathbf{r},\mathbf{r}')\right],$$

where

$$\widetilde{\mathbf{n}}_1^{\mathrm{vp}}(\mathbf{r},\mathbf{r}') = \sum_R \widetilde{\psi}_R(\mathbf{r})\widetilde{\psi}_R^\dagger(\mathbf{r}') - \sum_R \psi_R(\mathbf{r})\psi_R^\dagger(\mathbf{r}')$$

When we define an effective vacuum there is a VP energy whenever we apply spinor rotations! (e.g. in the diag. of the Hamiltonian when the geometry changed)

The Dirac equation for many particles (fermion-fermion interac.) IV

For the fermion-fermion interac. we use the Coulomb and Gaunt terms:

$$\begin{aligned}\widehat{H} &= \widehat{H}_0^v + \widehat{W} \\ &= \widehat{H}_0^v + \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \mathrm{Tr}\left[\mathbf{W}(\mathbf{r}_1,\mathbf{r}_2)\widehat{\mathbf{n}}_2(\mathbf{r}_1,\mathbf{r}_2)\right] \\ &= \widehat{H}_0^v + \frac{1}{2}\sum_{\mu,\nu,\tau,\eta}\int d\mathbf{r}_1 d\mathbf{r}_2 W_{\mu,\nu,\tau,\eta}(\mathbf{r}_1,\mathbf{r}_2)\widehat{n}_{2,\tau,\eta,\mu,\nu}(\mathbf{r}_1,\mathbf{r}_2),\end{aligned}$$

where

$$W_{\mu,\nu,\tau,\eta}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{r_{12}}\left[\delta_{\mu,\tau}\delta_{\nu,\eta} - (\boldsymbol{\alpha}_{\mu,\tau}\cdot\boldsymbol{\alpha}_{\nu,\eta})\right]$$

with the second-order red. density matrix operator

$$\widehat{n}_{2,\tau,\eta,\mu,\nu}(\mathbf{r}_1,\mathbf{r}_2) = \mathcal{N}\left[\widehat{\psi}_\nu^\dagger(\mathbf{r}_2)\widehat{\psi}_\mu^\dagger(\mathbf{r}_1)\widehat{\psi}_\tau(\mathbf{r}_1)\widehat{\psi}_\eta(\mathbf{r}_2)\right].$$

The Dirac equation for many particles its energy and wavefunction V

$$E = \min_{|\Psi\rangle \in \mathcal{H}_Q} \langle \Psi | \widehat{H}_0^v + \widehat{W} | \Psi \rangle.$$

For $Q > 0$

$$|\Psi\rangle = \left(\sum_{I_1,\ldots,I_Q} c_{I_1\ldots I_Q} \widehat{b}_{I_1}^\dagger \cdots \widehat{b}_{I_Q}^\dagger + \sum_{I_1,\ldots,I_Q,I_{Q+1}} \sum_{R_1} c_{I_1\ldots I_Q I_{Q+1} R_1} \widehat{b}_{I_1}^\dagger \cdots \widehat{b}_{I_Q}^\dagger \widehat{b}_{I_{Q+1}}^\dagger \widehat{d}_{R_1}^\dagger \right.$$
$$\left. + \sum_{I_1,\ldots,I_Q,I_{Q+1},I_{Q+2}} \sum_{R_1,R_2} c_{I_1\ldots I_Q I_{Q+1} I_{Q+2} R_1 R_2} \widehat{b}_{I_1}^\dagger \cdots \widehat{b}_{I_Q}^\dagger \widehat{b}_{I_{Q+1}}^\dagger \widehat{b}_{I_{Q+2}}^\dagger \widehat{d}_{R_1}^\dagger \widehat{d}_{R_2}^\dagger + \cdots \right) |0_v\rangle.$$

creation of electron-positron pairs.

For $Q = 0$

$$|0^{\mathrm{CI}}\rangle = \left(c_0 + \sum_{I_1} \sum_{R_1} c_{I_1 R_1} \widehat{b}_{I_1}^\dagger \widehat{d}_{R_1}^\dagger + \sum_{I_1,I_2} \sum_{R_1,R_2} c_{I_1 I_2 R_1 R_2} \widehat{b}_{I_1}^\dagger \widehat{b}_{I_2}^\dagger \widehat{d}_{R_1}^\dagger \widehat{d}_{R_2}^\dagger + \cdots \right) |0_v\rangle,$$

NEW VACUUM $\mathcal{N}[\ldots]$ w.r.t. $|0^{\mathrm{CI}}\rangle$

The Dirac equation for many particles the 1-RDM and nat. orb. VI

$$
\begin{aligned}
n_{1,\nu,\mu}(\mathbf{r},\mathbf{r}') =& \langle\Psi|\widehat{n}_{1,\nu,\mu}(\mathbf{r},\mathbf{r}')|\Psi\rangle \\
=& \sum_{I,J} {}^1D_I^J \phi^*_{I,\mu}(\mathbf{r}')\phi_{J,\nu}(\mathbf{r}) + \sum_I \sum_R {}^1D_I^R \phi^*_{I,\mu}(\mathbf{r}')\phi_{R,\nu}(\mathbf{r}) \\
&+ \sum_R \sum_I {}^1D_R^I \phi^*_{R,\mu}(\mathbf{r}')\phi_{I,\nu}(\mathbf{r}) + \sum_{R,S} {}^1D_S^R \phi^*_{R,\mu}(\mathbf{r}')\phi_{S,\nu}(\mathbf{r}),
\end{aligned}
$$

Then,

$$
\begin{aligned}
\mathbf{n}_1(\mathbf{r},\mathbf{r}') =& \sum_{I,J} {}^1D_I^J \psi_J(\mathbf{r})\psi_I^\dagger(\mathbf{r}') + \sum_I \sum_R {}^1D_I^R \psi_R(\mathbf{r})\psi_I^\dagger(\mathbf{r}') \\
&+ \sum_R \sum_I {}^1D_R^I \psi_I(\mathbf{r})\psi_R^\dagger(\mathbf{r}') + \sum_{R,S} {}^1D_S^R \psi_S(\mathbf{r})\psi_R^\dagger(\mathbf{r}').
\end{aligned}
$$

Since ${}^1\mathbf{D}$ is Hermitian we can diag. it to produce the natural orbital representation

$$
\mathbf{n}_1(\mathbf{r},\mathbf{r}') = \sum_A n_A \chi_A(\mathbf{r})\chi_A^\dagger(\mathbf{r}') \qquad 0 \leq n_A \leq 1
$$

Relativistic reduced density matrix functional theory I

Within the constraint search formalism

$$W\left[\mathbf{n}_1\right] = \min_{|\Psi\rangle \in \mathcal{H}_Q(\mathbf{n}_1)} \langle \Psi | \widehat{W} | \Psi \rangle = \langle \Psi\left[\mathbf{n}_1\right] | \widehat{W} | \Psi\left[\mathbf{n}_1\right] \rangle,$$

where $\mathcal{H}_Q(\mathbf{n}_1)$ is the set of states $|\Psi\rangle \in \mathcal{H}_Q$ that yield a constrained 1-RDM ($\mathbf{n}_1$), and $|\Psi\left[\mathbf{n}_1\right]\rangle$ designates the state that minimizes the interaction energy (W).

Relativistic RDMFT

$$E_Q = \min_{\mathbf{n}_1 \in \mathcal{D}_Q} \left[W\left[\mathbf{n}_1\right] + \int d\mathbf{r} d\mathbf{r}' \mathrm{Tr} \left[\left(\delta(\mathbf{r}-\mathbf{r}') \widehat{\mathbf{T}}_D(\mathbf{r}) + \mathbf{v}_{\mathrm{ext}}^{\mathrm{nl}}(\mathbf{r}', \mathbf{r}) \right) \mathbf{n}_1(\mathbf{r}, \mathbf{r}') \right] \right].$$

N-representable 1-RDMs ($\mathbf{n}_1 \in \mathcal{D}_Q$).
For 1-RDM in nat. orb. $\rightarrow$ Re-NOFT $E_Q = E_Q\left[\boldsymbol{\chi}, \mathbf{n}\right]$

A particular case (Relativistic DFT)

$$E_Q = \min_{n \in \mathcal{D}_Q^n} \left[W^n\left[n\right] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) \right].$$

$$W^n\left[n\right] = \min_{|\Psi\rangle \in \mathcal{H}_Q(n)} \langle \Psi | \widehat{T}_D + \widehat{W} | \Psi \rangle = \langle \Psi\left[n\right] | \widehat{T}_D + \widehat{W} | \Psi\left[n\right] \rangle$$

No-pair relativistic reduced density matrix functional theory I

Creation of electron-positron pairs requires too much energy and maybe we can neglect this effect.
The wavefunction will only have its electronic states filled

$$|\Psi_+\rangle = e^{\widehat{\kappa}} \sum_{I_1,\ldots,I_N} c_{I_1\ldots I_N} \widehat{b}_{I_1}^\dagger \cdots \widehat{b}_{I_N}^\dagger |0_v\rangle$$
$$= \sum_{I_1,\ldots,I_N} c_{I_1\ldots I_N} \widehat{\widetilde{b}}_{I_1}^\dagger \cdots \widehat{\widetilde{b}}_{I_N}^\dagger |\widetilde{0}_v\rangle.$$

where the np 1RDM reads as

$$\mathbf{n}_1^+(\mathbf{r},\mathbf{r}') = \sum_{I,J} {}^1\widetilde{D}_I^J \widetilde{\psi}_J(\mathbf{r}) \widetilde{\psi}_I^\dagger(\mathbf{r}').$$

We need spinor rotations...

We will have vacuum polarization effects!!😒

No-pair relativistic reduced density matrix functional theory II

$$\widehat{H} - \widehat{\widetilde{H}} = \widehat{\widetilde{V}}^{\mathrm{vp}} + \widetilde{E}_0,$$

where

$$\begin{aligned}
\widehat{\widetilde{V}}^{\mathrm{vp}} &= \widehat{\widetilde{V}}_H^{\mathrm{vp}} + \widehat{\widetilde{V}}_x^{\mathrm{vp}} \\
&= \sum_{\mu,\tau} \int d\mathbf{r}_1 \left[\sum_{\nu,\eta} \int d\mathbf{r}_2 W_{\mu,\nu,\tau,\eta}(\mathbf{r}_1,\mathbf{r}_2) \widetilde{n}^{\mathrm{vp}}_{1,\eta,\nu}(\mathbf{r}_2,\mathbf{r}_2) \right] \widehat{\widetilde{n}}^{+}_{1,\tau,\mu}(\mathbf{r}_1,\mathbf{r}_1) \\
&\quad - \sum_{\mu,\nu,\tau,\eta} \int\int d\mathbf{r}_1 d\mathbf{r}_2 W_{\mu,\nu,\tau,\eta}(\mathbf{r}_1,\mathbf{r}_2) \widetilde{n}^{\mathrm{vp}}_{1,\eta,\mu}(\mathbf{r}_2,\mathbf{r}_1) \widehat{\widetilde{n}}^{+}_{1,\tau,\nu}(\mathbf{r}_1,\mathbf{r}_2), \\
\widetilde{E}_0 &= \widetilde{E}_0^0 + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \mathrm{Tr}\left[\mathbf{W}(\mathbf{r}_1,\mathbf{r}_2) \widetilde{\mathbf{n}}^{\mathrm{vp}}_2(\mathbf{r}_1,\mathbf{r}_2) \right],
\end{aligned}$$

with

$$\widetilde{n}^{\mathrm{vp}}_{2,\tau,\eta,\mu,\nu}(\mathbf{r}_1,\mathbf{r}_2) = \widetilde{n}^{\mathrm{vp}}_{1,\eta,\nu}(\mathbf{r}_2,\mathbf{r}_2)\widetilde{n}^{\mathrm{vp}}_{1,\tau,\mu}(\mathbf{r}_1,\mathbf{r}_1) - \widetilde{n}^{\mathrm{vp}}_{1,\tau,\nu}(\mathbf{r}_1,\mathbf{r}_2)\widetilde{n}^{\mathrm{vp}}_{1,\eta,\mu}(\mathbf{r}_2,\mathbf{r}_1)$$

that is the Single-Determinant approximation for the 2RDM=2RDM[1RDM].

No-pair relativistic reduced density matrix functional theory III

$$E^{npvp}\left[\mathbf{n}_1^+, \mathbf{n}_1^{\mathrm{vp}}\right] = \int d\mathbf{r} d\mathbf{r}' \mathrm{Tr}\left[\left(\delta(\mathbf{r}-\mathbf{r}')\widehat{\mathbf{T}}_D(\mathbf{r}) + \mathbf{v}_{\mathrm{ext}}^{\mathrm{nl}}(\mathbf{r}',\mathbf{r})\right)\left(\mathbf{n}_1^+(\mathbf{r},\mathbf{r}') + \mathbf{n}_1^{\mathrm{vp}}(\mathbf{r},\mathbf{r}')\right)\right]$$

$$+ \sum_{\mu,\tau}\int d\mathbf{r}_1 \left[\sum_{\nu,\eta}\int d\mathbf{r}_2 W_{\mu,\nu,\tau,\eta}(\mathbf{r}_1,\mathbf{r}_2)\widetilde{n}_{1,\eta,\nu}^{\mathrm{vp}}(\mathbf{r}_2,\mathbf{r}_2)\right]\widetilde{n}_{1,\tau,\mu}^{+}(\mathbf{r}_1,\mathbf{r}_1)$$

$$- \sum_{\mu,\nu,\tau,\eta}\int\int d\mathbf{r}_1 d\mathbf{r}_2 W_{\mu,\nu,\tau,\eta}(\mathbf{r}_1,\mathbf{r}_2)\widetilde{n}_{1,\eta,\mu}^{\mathrm{vp}}(\mathbf{r}_2,\mathbf{r}_1)\widetilde{n}_{1,\tau,\nu}^{+}(\mathbf{r}_1,\mathbf{r}_2)$$

$$+ \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \mathrm{Tr}\left[\mathbf{W}(\mathbf{r}_1,\mathbf{r}_2)\widetilde{\mathbf{n}}_2^{\mathrm{vp}}(\mathbf{r}_1,\mathbf{r}_2)\right] + \widetilde{W}\left[\mathbf{n}_1^+\right]$$

$$\widetilde{W}\left[\mathbf{n}_1^+\right]???$$

$E^{np} = E^{npvp}\left[\mathbf{n}_1^+, 0\right]$ (np-ReRDMFT)

The usual no-pair approximation using a floating vacuum.

No-pair relativistic reduced density matrix functional theory IV

$$\widetilde{W}\left[\mathbf{n}_1^+\right]???$$

$$\widetilde{W}\left[\mathbf{n}_2^+\right] = \sum_{I,J,K,L} {}^2D_{IJ}^{KL} \int d\mathbf{r}_1 d\mathbf{r}_2 \mathrm{Tr}\left[\mathbf{W}(\mathbf{r_1},\mathbf{r}_2)(\widetilde{\chi}_L(\mathbf{r}_1)\otimes\widetilde{\chi}_K(\mathbf{r}_2))(\widetilde{\chi}_I^\dagger(\mathbf{r}_2)\otimes\widetilde{\chi}_J^\dagger(\mathbf{r}_1))\right]$$

thus in np-ReNOFT (np-ReRDMFT)

$$ {}^2D_{IJ}^{KL} = {}^2D_{IJ}^{KL}(n_I, n_J, n_K, n_L).$$

Imposing

$$\mathrm{Tr}\left[{}^2\mathbf{D}\right] = \sum_{I,J} {}^2D_{IJ}^{IJ} = \frac{N_e(N_e-1)}{2}$$

N-representability conditions (${}^2\mathbf{D} \leftrightarrow \Psi_+$)

$$P_{IJ}^{KL} = \frac{1}{2}\langle\Psi_+|\widehat{\widetilde{b}}_I^\dagger \widehat{\widetilde{b}}_I^\dagger \widehat{\widetilde{b}}_L \widehat{\widetilde{b}}_K|\Psi_+\rangle \;, Q_{IJ}^{KL} = \frac{1}{2}\langle\Psi_+|\widehat{\widetilde{b}}_I \widehat{\widetilde{b}}_J \widehat{\widetilde{b}}_L^\dagger \widehat{\widetilde{b}}_K^\dagger|\Psi_+\rangle \;, G_{IJ}^{KL} = \frac{1}{2}\langle\Psi_+|\widehat{\widetilde{b}}_I^\dagger \widehat{\widetilde{b}}_J \widehat{\widetilde{b}}_L^\dagger \widehat{\widetilde{b}}_K|\Psi_+\rangle$$

And reduce to their non-relativistic counterparts in the non-rel. limit.

np-ReRDMFT Kramers restricted I

Let

$$h_{IJ} = \int d\mathbf{r} d\mathbf{r}' \widetilde{\chi}_I^\dagger(\mathbf{r}') \left(\delta(\mathbf{r}-\mathbf{r}') \widehat{\mathbf{T}}_D(\mathbf{r}) + \mathbf{v}_{\mathrm{ext}}^{\mathrm{nl}}(\mathbf{r},\mathbf{r}') \right) \widetilde{\chi}_J(\mathbf{r}),$$

$$\langle IJ|KL\rangle = \int d\mathbf{r} d\mathbf{r}' \frac{(\widetilde{\chi}_I^\dagger(\mathbf{r}) \otimes \widetilde{\chi}_J^\dagger(\mathbf{r}'))(\widetilde{\chi}_K(\mathbf{r}) \otimes \widetilde{\chi}_L(\mathbf{r}'))}{|\mathbf{r}'-\mathbf{r}|},$$

$$\langle IJ|\boldsymbol{\alpha}_r \cdot \boldsymbol{\alpha}_{r'}|KL\rangle = \int d\mathbf{r} d\mathbf{r}' \frac{(\widetilde{\chi}_I^\dagger(\mathbf{r}) \otimes \widetilde{\chi}_J^\dagger(\mathbf{r}'))\,[\boldsymbol{\alpha}_\mathbf{r} \cdot \boldsymbol{\alpha}_{\mathbf{r}'}]\,(\widetilde{\chi}_K(\mathbf{r}) \otimes \widetilde{\chi}_L(\mathbf{r}'))}{|\mathbf{r}'-\mathbf{r}|}.$$

In non-rel. NOFT a restricted formalism is employed $\rightarrow$ Kramers pairs $(i, \bar{i})$
A pair of NOs forms a Kramer's pair $(i, \bar{i})$ if they transform as $\widehat{\mathcal{K}}\widetilde{\boldsymbol{\chi}}_i = \widetilde{\boldsymbol{\chi}}_{\bar{i}}$ and $\widehat{\mathcal{K}}\widetilde{\boldsymbol{\chi}}_{\bar{i}} = -\widetilde{\boldsymbol{\chi}}_i$

$$\widehat{\mathcal{K}} = -\mathrm{i} \begin{pmatrix} \boldsymbol{\sigma}_y & \mathbf{0}_2 \\ \mathbf{0}_2 & \boldsymbol{\sigma}_y \end{pmatrix} \widehat{\mathcal{K}}_0$$

np-ReRDMFT Kramers restricted II

Retaining the electron repulsion integrals with only up to two different indices

$$
\begin{aligned}
E_N^{\mathrm{np}} \approx & \sum_i h_{ii}\,(n_i + n_{\bar{i}}) + \sum_{i,j} \left({}^2D_{ij}^{ij} + {}^2D_{\bar{i}\bar{j}}^{\bar{i}\bar{j}} + {}^2D_{i\bar{j}}^{i\bar{j}} + {}^2D_{\bar{i}j}^{\bar{i}j} \right) J_{ij} \\
& - \sum_{i,j} \left({}^2D_{ij}^{ij} - {}^2D_{\bar{i}\bar{j}}^{\bar{i}\bar{j}} - {}^2D_{i\bar{j}}^{i\bar{j}} + {}^2D_{\bar{i}j}^{\bar{i}j} \right) J_{ij}^G + \sum_{i,j} \left[\left({}^2D_{ij}^{ji} + {}^2D_{\bar{j}\bar{i}}^{\bar{j}\bar{i}} \right) \left(K_{ij} - K_{ij}^G \right) \right] \\
& + \frac{1}{2} \sum_{i,j} \left[\left({}^2D_{\bar{i}j}^{j\bar{i}} + {}^2D_{j\bar{i}}^{i\bar{j}} + {}^2D_{\bar{j}i}^{\bar{i}j} + {}^2D_{i\bar{j}}^{\bar{j}i} \right) \left(L_{ij} - L_{ij}^G \right) \right] + \sum_{i \neq j} \left[\left({}^2D_{i\bar{i}}^{j\bar{j}} + {}^2D_{j\bar{j}}^{\bar{i}i} \right) \left(K_{ij} + K_{ij}^G \right) \right] \\
& - \frac{1}{2} \sum_{i \neq j} \left[\left({}^2D_{j\bar{j}}^{i\bar{i}} + {}^2D_{\bar{i}i}^{j\bar{j}} + {}^2D_{j\bar{j}}^{\bar{i}i} + {}^2D_{\bar{i}i}^{\bar{j}j} \right) \left(L_{ij} + L_{ij}^G \right) \right]
\end{aligned}
$$

where $J_{ij} = \langle ij|ij\rangle$, $J_{ij}^G = \langle ij|\boldsymbol{\alpha}_{\mathbf{r}} \cdot \boldsymbol{\alpha}_{\mathbf{r}'}|ij\rangle$, $K_{ij} = \langle ij|ji\rangle$, $K_{ij}^G = \langle ij|\boldsymbol{\alpha}_{\mathbf{r}} \cdot \boldsymbol{\alpha}_{\mathbf{r}'}|ji\rangle$, $L_{ij} = \langle \bar{i}j|j\bar{i}\rangle$ (notice that $L_{ii} = 0$), and $L_{ij}^G = \langle \bar{i}j|\boldsymbol{\alpha}_{\mathbf{r}} \cdot \boldsymbol{\alpha}_{\mathbf{r}'}|j\bar{i}\rangle$.

WE ONLY NEED TO APPROX. 'FEW' 2-RDM ELEMENTS.

'A np-ReRDMFT Kramers restricted approx.'
The Dirac-Hartree-Fock energy ('spin-compensated')

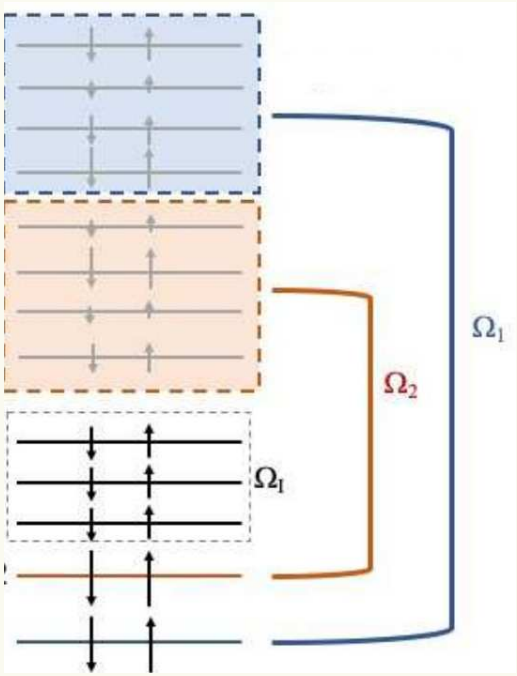
$$n_i = n_{\bar{i}}$$

$${}_{\mathrm{SD}}{}^{2}D_{IJ}^{KL} = \frac{n_I n_J}{2}(\delta_{IK}\delta_{JL} - \delta_{IL}\delta_{JK}).$$

$$\begin{aligned} E^{\mathrm{np,DHF}} &= 2\sum_i h_{ii} n_i + \sum_{i,j} n_i n_j \left[2J_{ij} - \left(K_{ij} - K_{ij}^{G}\right) - \left(L_{ij} - L_{ij}^{G}\right)\right] \\ &= 2\sum_{i}^{N_e/2} h_{ii} + \sum_{i,j}^{N_e/2} \left[2J_{ij} - \left(K_{ij} - K_{ij}^{G}\right) - \left(L_{ij} - L_{ij}^{G}\right)\right]. \end{aligned}$$

First relativistic functionals (rel-PNOF5/7/7s) I

- Let's suppose that we have 26 PS (4-component) forming 13 Kramers pairs
- Having 6e- (3 pairs of electrons).
- Introduce 3 Ω subspaces by coupling the 13 (un)barred PS.
- For each subspace $\sum_{i\in\Omega} n_i = \sum_{\bar{i}\in\Omega} n_{\bar{i}} = 1$



Account for electronic inter- and intra-subspace interactions

First relativistic functionals (rel-PNOF5/7/7s) II

$$E^{\text{rel-PNOF}x} = \sum_{a=1}^{N_e/2} E_a + \sum_{b\neq a}^{N_e/2} E_{ba}.$$

1. The first sum accounts for all intra-subspace contributions and reads as

$$E_a = \sum_{i\in\Omega_a} n_i(2h_{ii} + J_{ii} + J_{ii}^G + L_{ii}^G) + \sum_{\substack{i,j\in\Omega_a \\ i\neq j}} \Pi_{i,j}^{\text{intra}}(K_{ij} + K_{ij}^G + L_{ij} + L_{ij}^G),$$

where

$$\Pi_{i,j}^{\text{intra}} = \begin{cases} -\sqrt{n_i n_j}, & i \text{ or } j \leq N_e/2 \\ +\sqrt{n_i n_j}, & i,j > N_e/2, \end{cases}$$

2. The second sum accounts for inter-subspace contributions (E_{ba}) that can be defined as

$$E_{ba} = \sum_{i\in\Omega_b}\sum_{j\in\Omega_a} n_i n_j \left[2J_{ij} - (K_{ij} - K_{ij}^G) - (L_{ij} - L_{ij}^G)\right] + \Pi_{i,j}^{\text{inter}}(K_{ij} + K_{ij}^G + L_{ij} + L_{ij}^G),$$

where $\Pi_{p,q}^{\text{inter}} = 0$ in rel-PNOF5, $\Pi_{p,q}^{\text{inter}} = -\sqrt{n_p h_p n_q h_q}$ in rel-PNOF7, and $\Pi_{p,q}^{\text{inter}} = -4n_p h_p n_q h_q$ in rel-PNOF7s.

First relativistic functionals (rel-PNOF5/7/7s) III

Properties:

- 2e- system $\rightarrow$ Relativistic Fixed-Phases functional (in non-rel. case has proven to be almost exact).

$$\Psi_+^{2e-}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}\sum_i \sqrt{n_i}e^{-2i\zeta_i}\left[\widetilde{\chi}_i(\mathbf{r}_1)\otimes\widetilde{\chi}_{\bar{i}}(\mathbf{r}_2)-\widetilde{\chi}_i(\mathbf{r}_2)\otimes\widetilde{\chi}_{\bar{i}}(\mathbf{r}_1)\right]$$

$$\begin{aligned}\langle\Psi_+^{2e-}|\widehat{\widetilde{W}}|\Psi_+^{2e-}\rangle=\sum_{i,j}\frac{\sqrt{n_i n_j}}{2}e^{2i(\zeta_j-\zeta_i)}\int d\mathbf{r}_1 d\mathbf{r}_2 \mathrm{Tr}\left[\frac{1}{r_{12}}\left(\mathbb{I}_{16\times16}-\boldsymbol{\alpha}_{\mathbf{r}_1}\cdot\boldsymbol{\alpha}_{\mathbf{r}_2}\right)\right.\\ \times\Big((\widetilde{\chi}_i(\mathbf{r}_1)\otimes\widetilde{\chi}_{\bar{i}}(\mathbf{r}_2)(\widetilde{\chi}_j^\dagger(\mathbf{r}_1)\otimes\widetilde{\chi}_{\bar{j}}^\dagger(\mathbf{r}_2))-(\widetilde{\chi}_i(\mathbf{r}_1)\otimes\widetilde{\chi}_{\bar{i}}(\mathbf{r}_2))(\widetilde{\chi}_j^\dagger(\mathbf{r}_2)\otimes\widetilde{\chi}_{\bar{j}}^\dagger(\mathbf{r}_1))\\ -(\widetilde{\chi}_i(\mathbf{r}_2)\otimes\widetilde{\chi}_{\bar{i}}(\mathbf{r}_1))(\widetilde{\chi}_j^\dagger(\mathbf{r}_1)\otimes\widetilde{\chi}_{\bar{j}}^\dagger(\mathbf{r}_2))+(\widetilde{\chi}_i(\mathbf{r}_2)\otimes\widetilde{\chi}_{\bar{i}}(\mathbf{r}_1))(\widetilde{\chi}_j^\dagger(\mathbf{r}_2)\otimes\widetilde{\chi}_{\bar{j}}^\dagger(\mathbf{r}_1))\Big)\Big]\end{aligned}$$

- rel-PNOF5 $\leftrightarrow$ $\Psi^{\text{rel-APSG}}$. It is fully N-representable!

Conclusions and future perspective

Conclusions:

- Introduced ReRDMFT using the constraint search formalism including electron-positron creation and annihilation processes.
- Presented npvp-ReRDMFT filling only PS and considering vp effects.
- Introduced np-ReRDMFT filling only PS neglecting vp effects (floating vacuum).
- Impossing Kramers symmetry (and some conditions) we have built ${}^2D_{IJ}^{KL} = {}^2D_{IJ}^{KL}(n_I, n_J, n_K, n_L) \rightarrow$ **rel-PNOF5/7/7s**

Future perspective:

- Implement np-ReRDMFT functionals in DIRAC code for X2C and 4–component calculations.

Thanks for your attention!

- Prof. Dr. L. Visscher

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(ReReDMFT H2020-891647)

Introducing Relativistic Reduced Density Matrix Functional Theory (RE-RDMFT)

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