Introduction into fermionic correlation and applications in quantum chemistry

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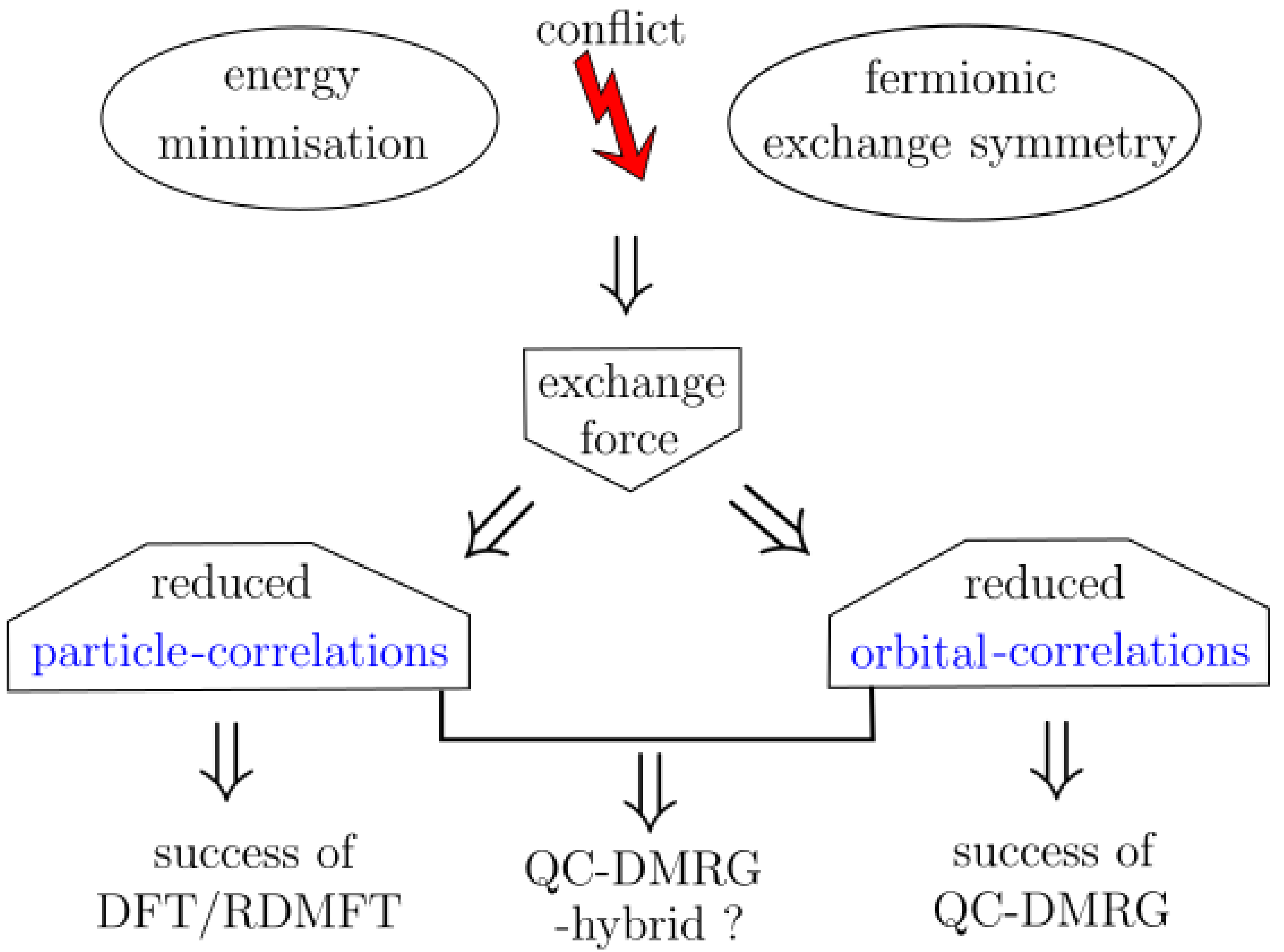
University of Oxford

Budapest, 28 September 2018

in collaboration with O.Legeza, S.Szalay and Z.Zimboras (Budapest)

EPSRC
Engineering and Physical Sciences Research Council

research vision:



Outline

(I) Fermionic (quantum) correlation

(II) Application/Illustration in concrete systems

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<u>recap:</u> distinguishable subsystems A, B

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  density operator ρ ? : $\omega_\rho(\cdot) \equiv \mathrm{Tr}_{\mathcal{H}}[(\cdot)\rho]$

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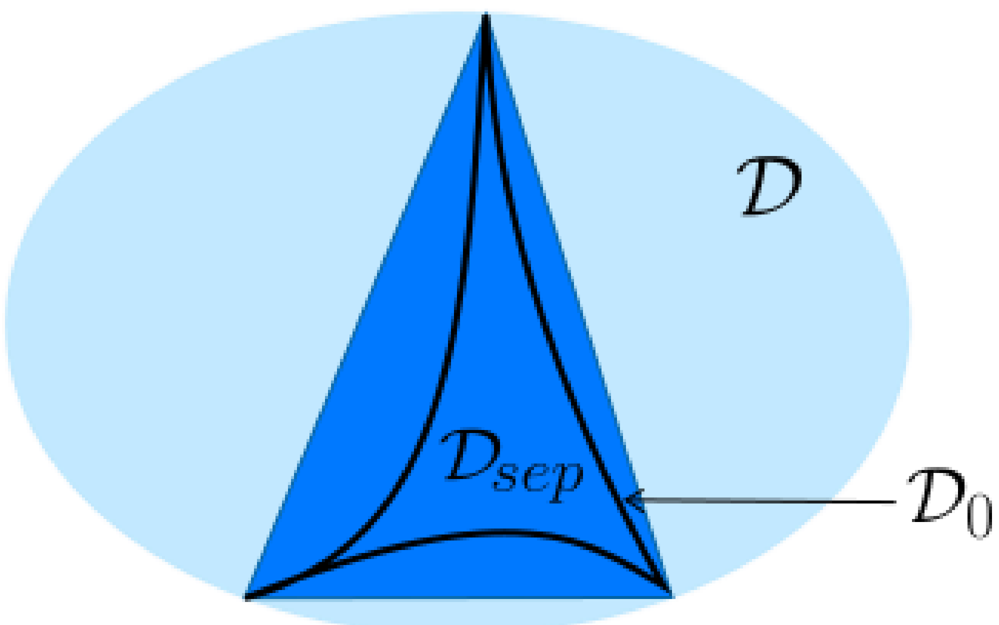

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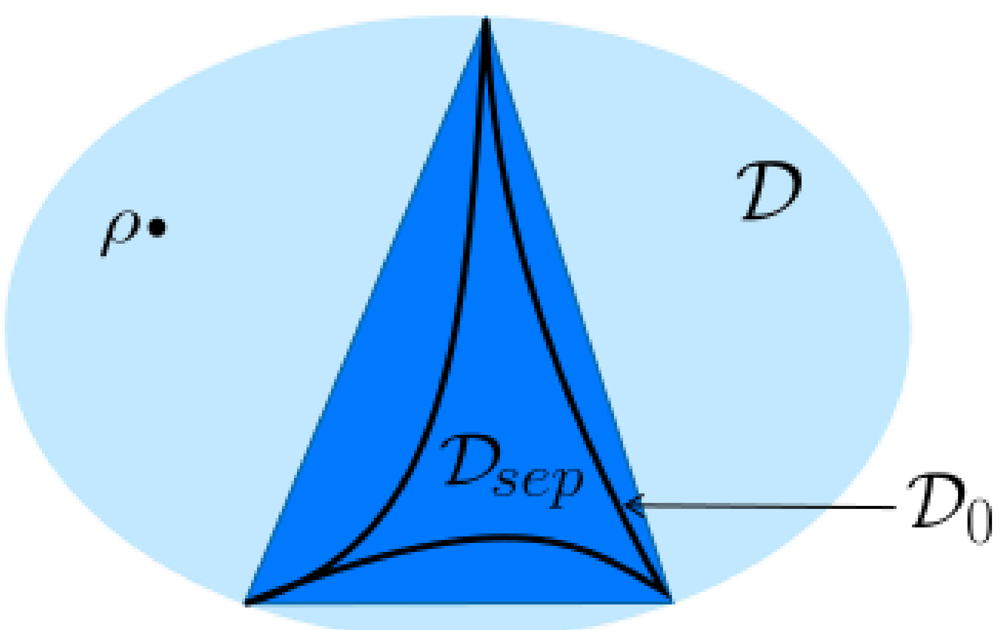

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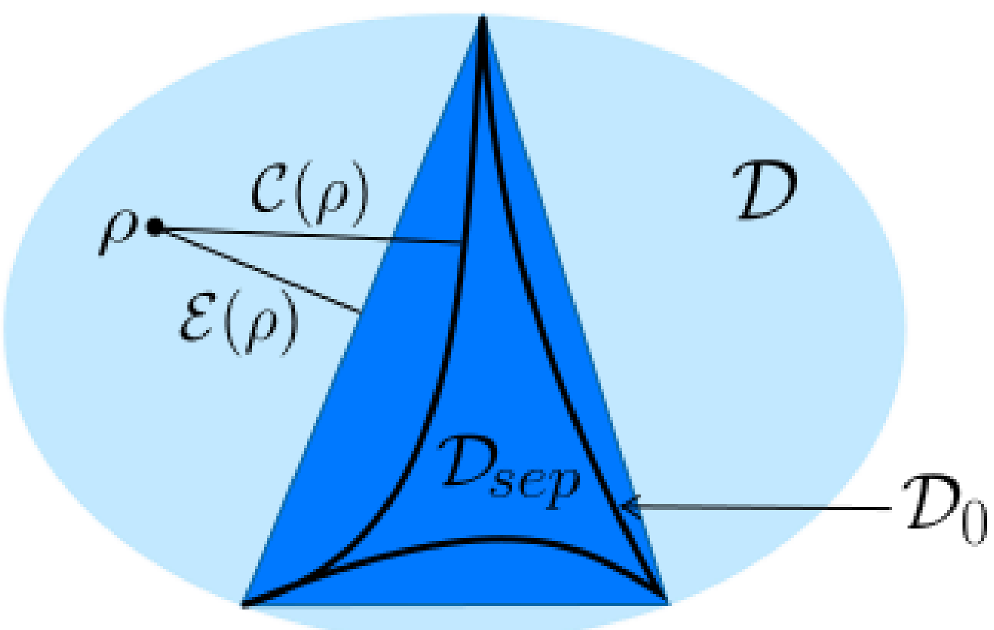

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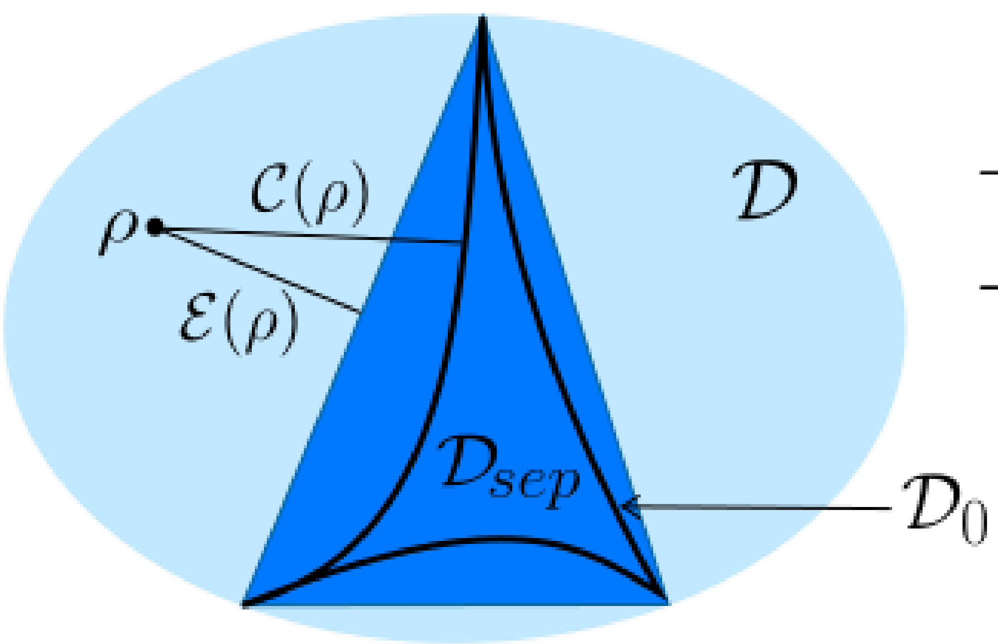

$\rightarrow$ correlation measure $\mathcal{C}$

$\rightarrow$ entanglement measure $\mathcal{E}$

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$\rightarrow$ notion of correlation and entanglement caveat:

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$\rightarrow \mathcal{A}$ smaller ($\rightarrow \mathcal{D}_0$ larger)

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note:

(unnecessary) embedding of $\mathcal{H}$ and $\mathcal{A}$, respectively, can be quite misleading

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LiF at $r = 13.7\mathring{A}$, 25 basis functions (orbitals)

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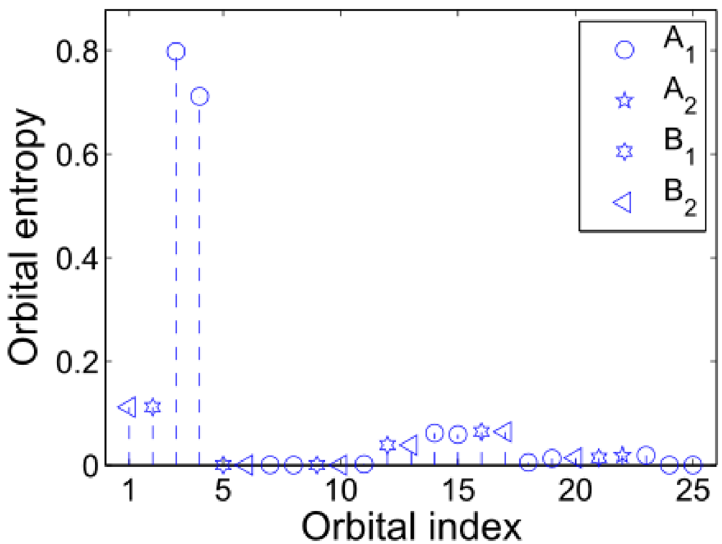

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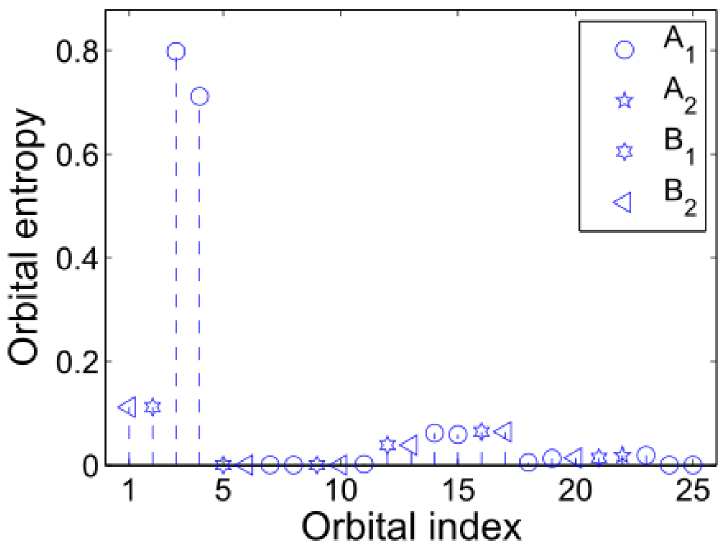

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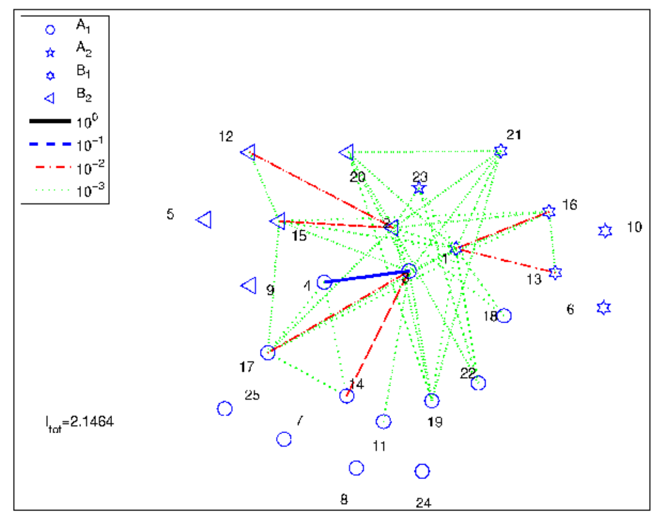

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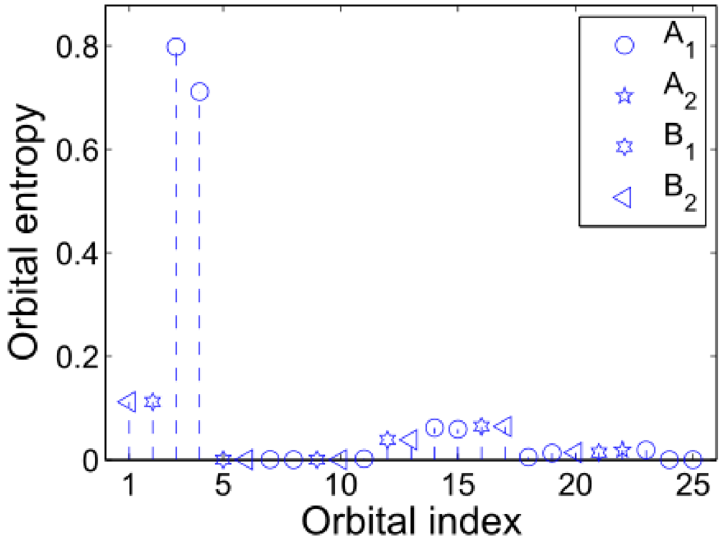

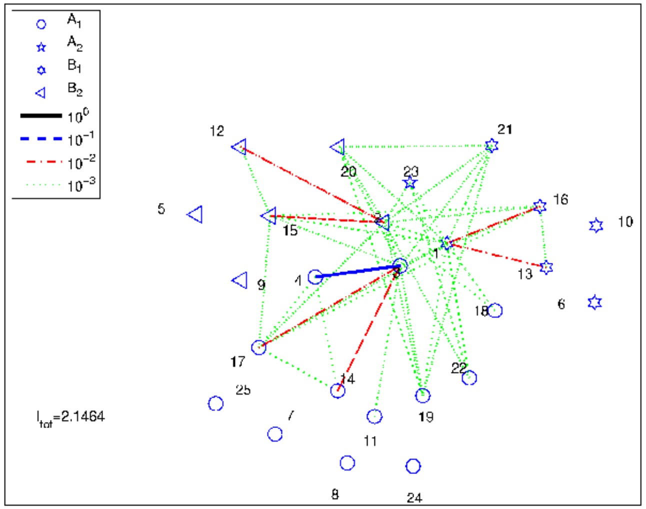

[K. Boguslawski et al., J. Phys. Chem. Lett. 3, 21, 3129 (2012)]

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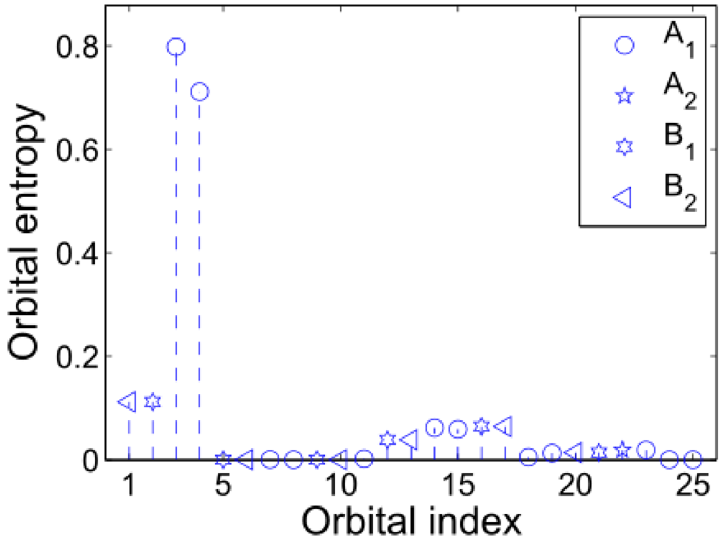
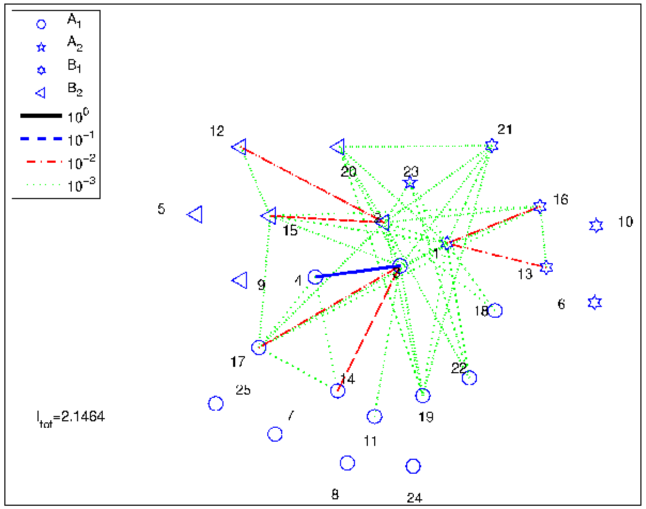


$I(\rho_{ij} || \rho_i \otimes \rho_j)$



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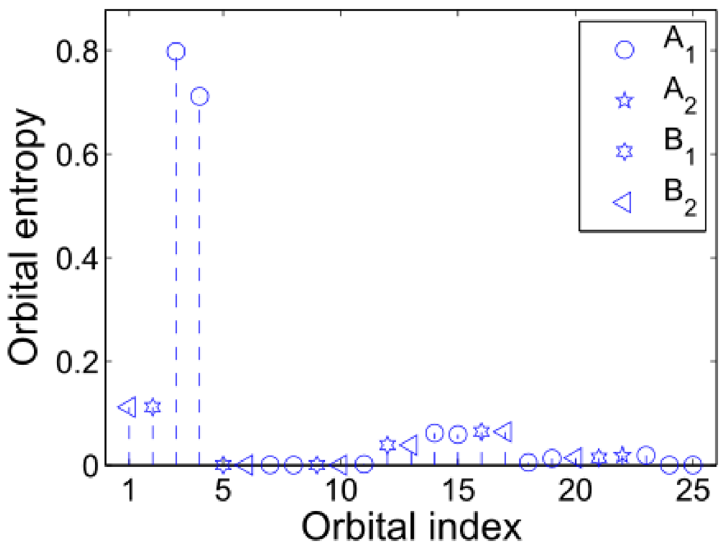
+ many further papers by O. Legeza, M. Reiher,...

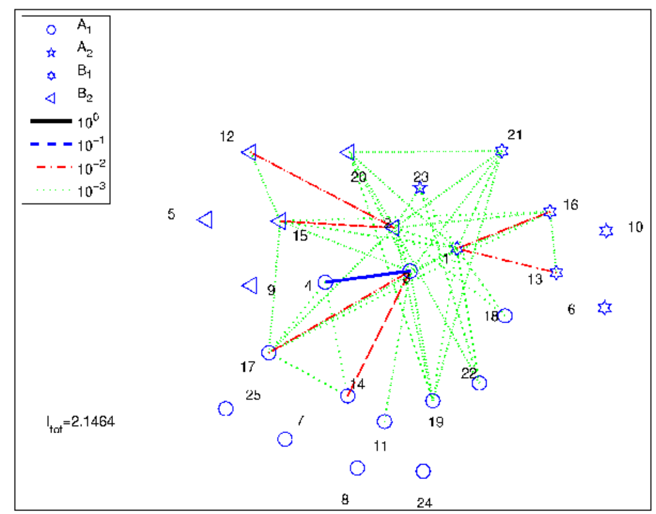
(ii) Mode/orbital correlations in a molecule

LiF at $r = 13.7\mathring{A}$, 25 basis functions (orbitals)

pick two orbitals $\varphi_i, \varphi_j \rightarrow \rho_i, \rho_j, \rho_{ij}$

$S(\rho_i)$ $I(\rho_{ij} || \rho_i \otimes \rho_j)$





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+ generalization to multipartite correlation by S. Szalay

(iii) Correlation paradox of the dissociation limit

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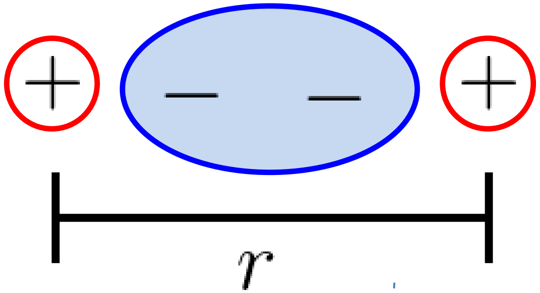
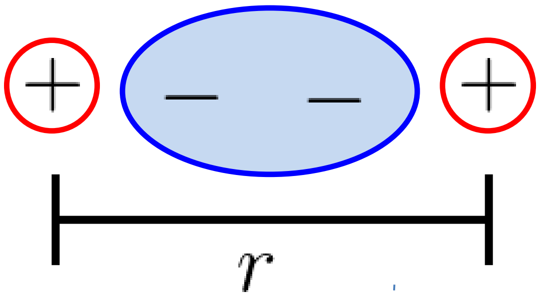
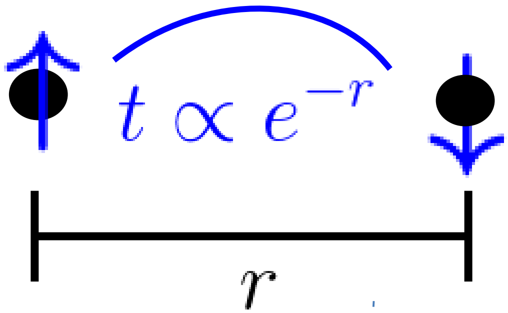
hydrogen molecule



(iii) Correlation paradox of the dissociation limit

hydrogen molecule $\rightarrow$ Hubbard dimer





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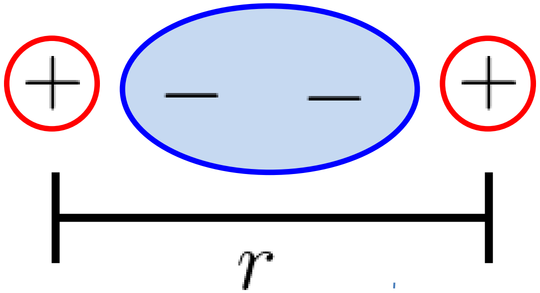
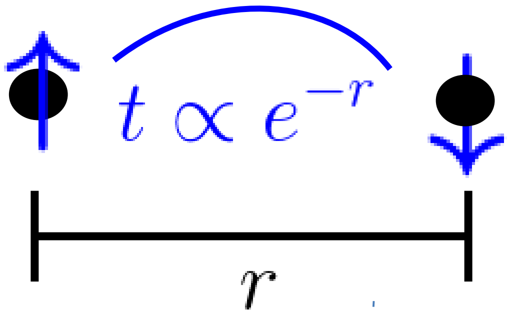
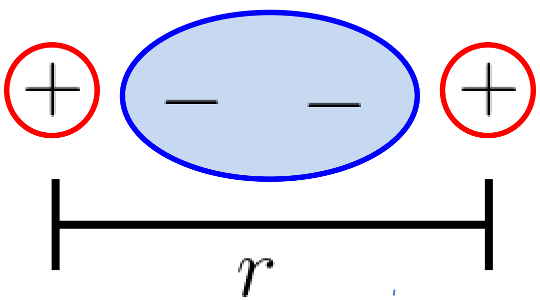


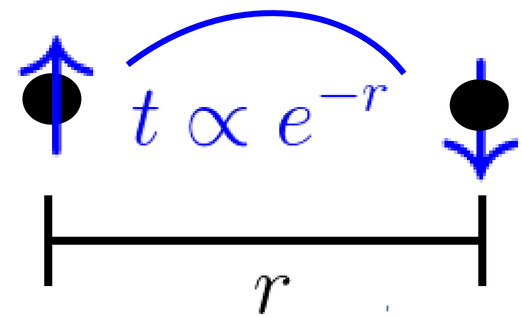


$$\hat{H} = -t \sum_{\sigma} f^{\dagger}_{L\sigma} f_{R\sigma} + h.c. + U \sum_{j=L,R} \hat{n}_{j\uparrow} \hat{n}_{j\downarrow}$$

(iii) Correlation paradox of the dissociation limit

hydrogen molecule → Hubbard dimer





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→ ground state $|\Psi_0(r)\rangle$

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$$|\Psi_0(r)\rangle \approx \frac{1}{\sqrt{2}}\Big[|L\uparrow, R\downarrow\rangle - |L\downarrow, R\uparrow\rangle\Big]\,, \quad \text{for } r \text{ large}$$

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solution of the paradox:

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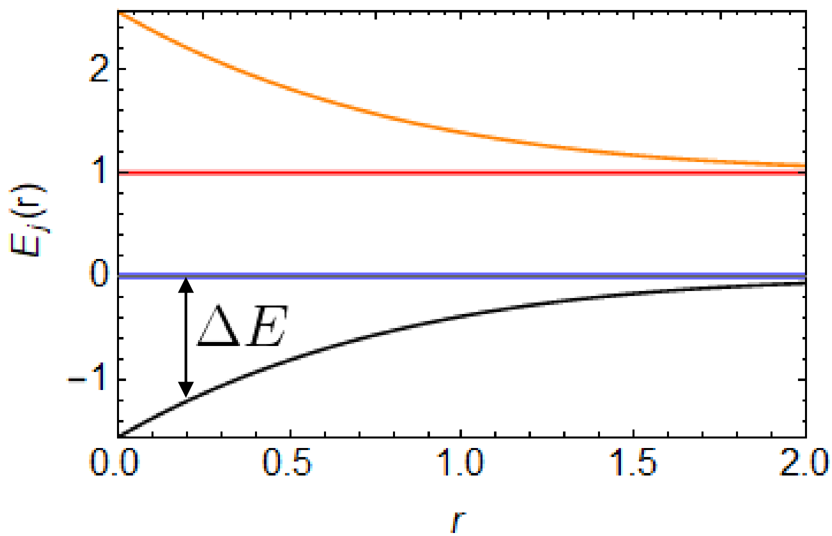
tiny noise destroys entanglement



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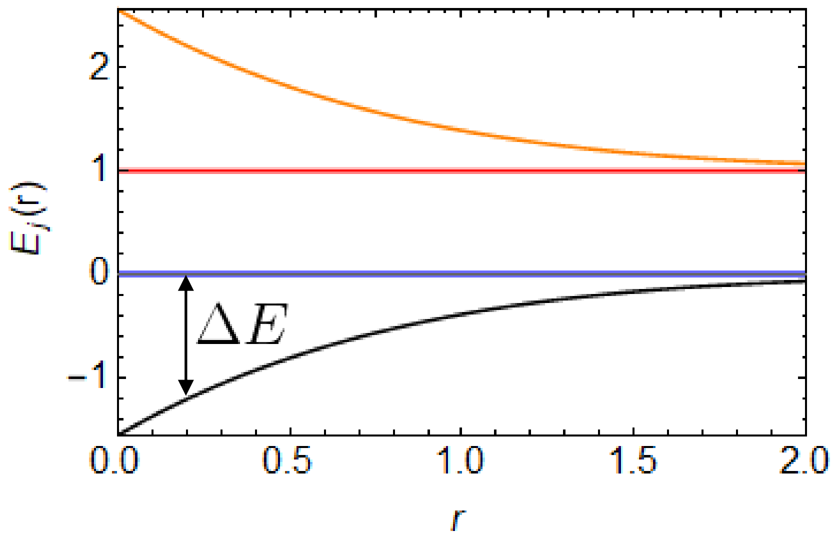

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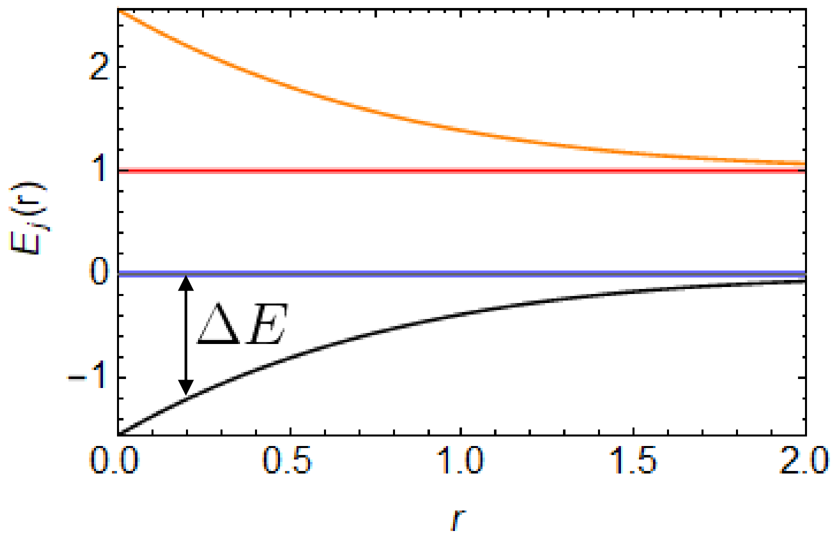

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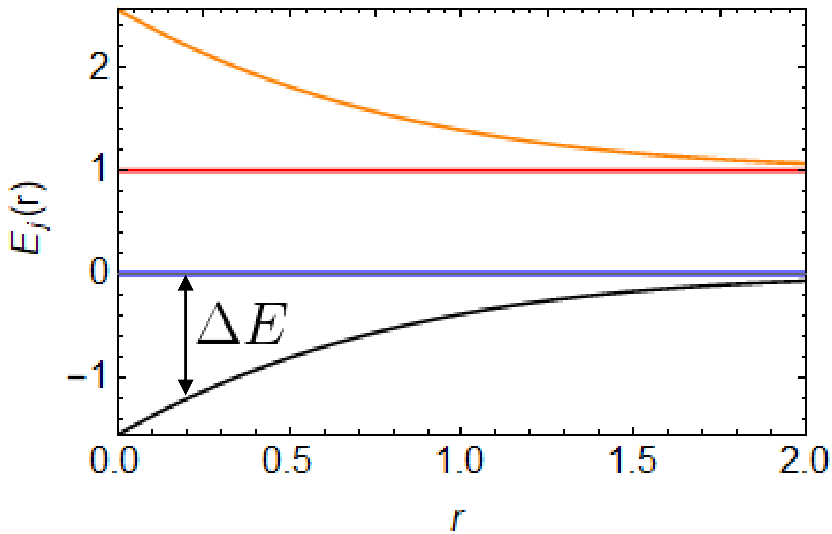

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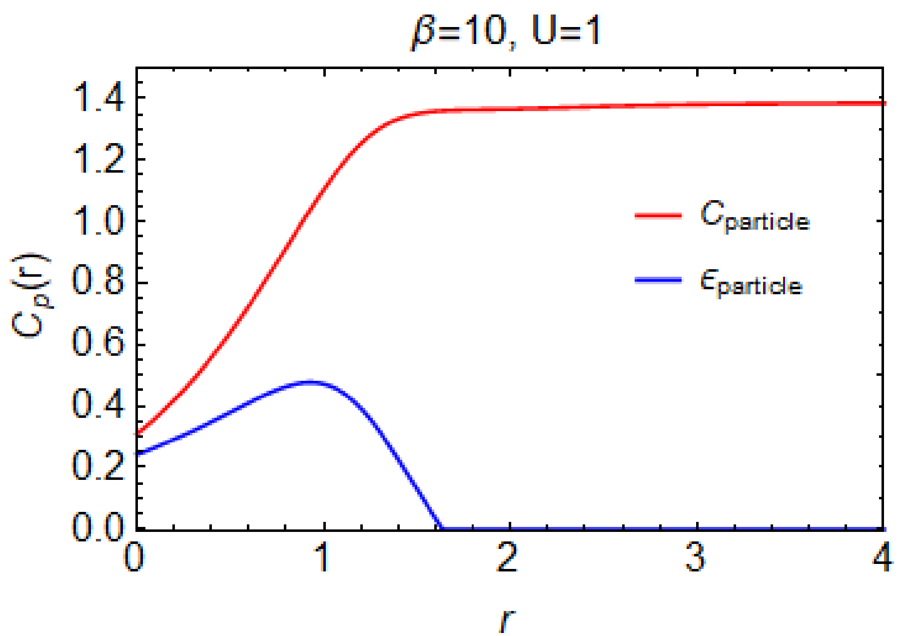
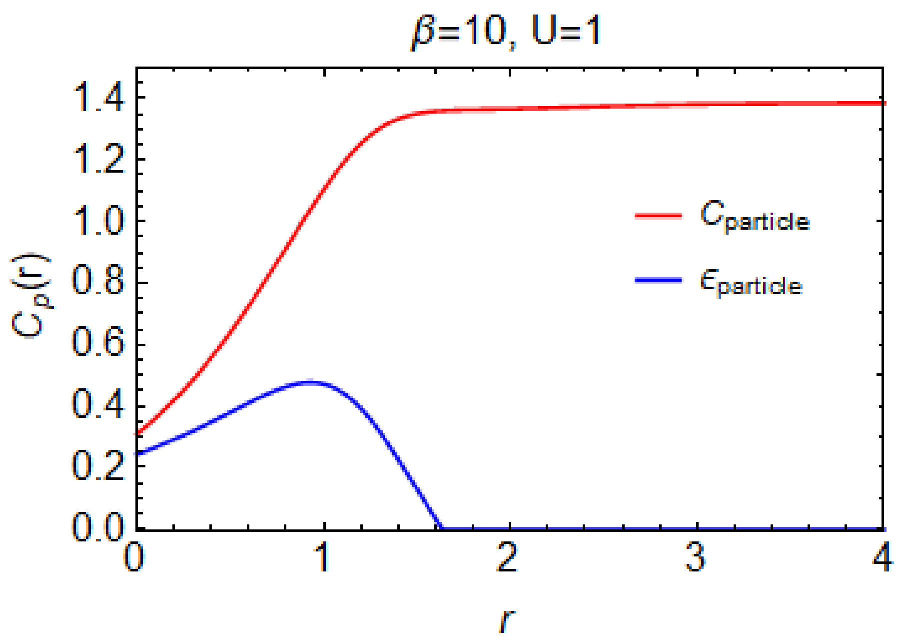
$$= \frac{1}{4}\sum_{\sigma,\sigma'=\uparrow,\downarrow} |L\sigma, R\sigma'\rangle\langle L\sigma, R\sigma'|$$

p



β=10, U=1
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
$C_p(r)$
r
C_{particle}
$\epsilon_{\text{particle}}$

p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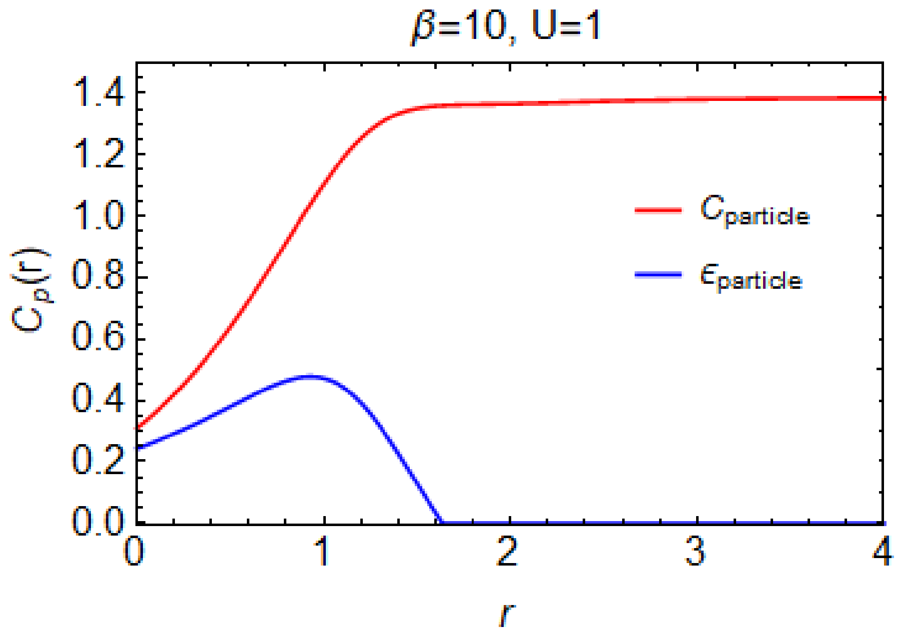
$$r \geq 1.6 :$$

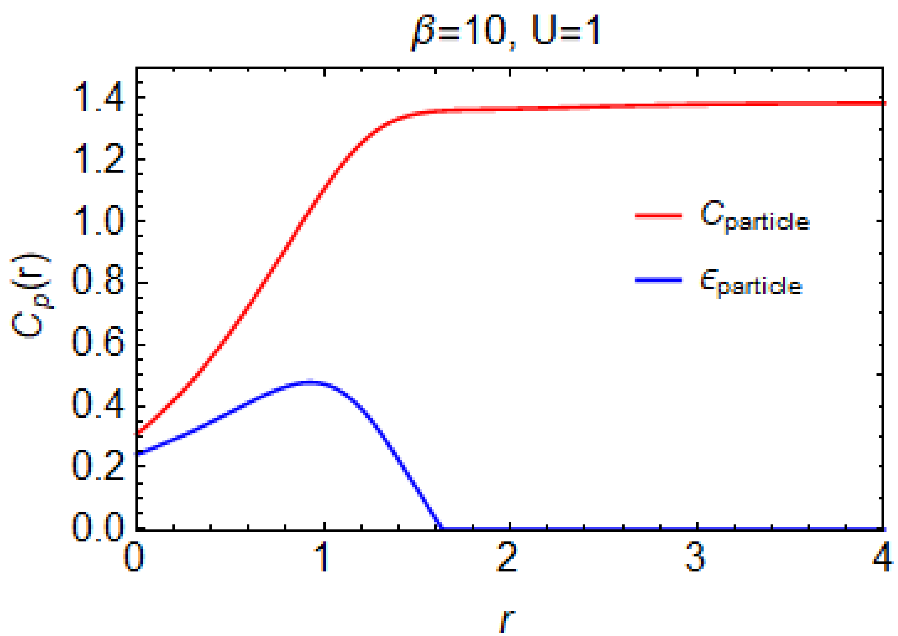
p



$$r \geq 1.6 :$$

$$\rho = \sum_j p_j \, |SD_j\rangle\langle SD_j|$$

p



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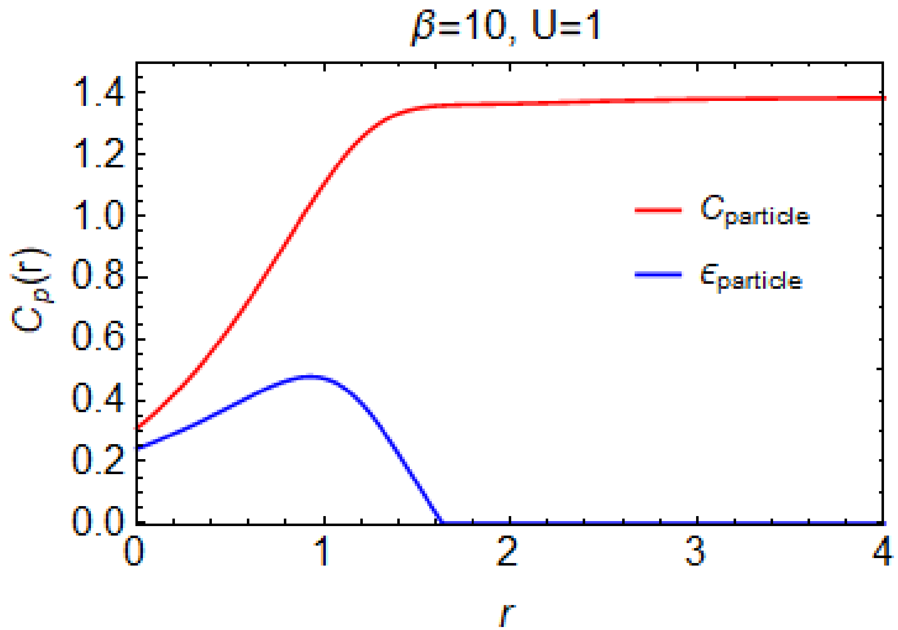
$$\rightarrow \text{particle correlation}$$

p



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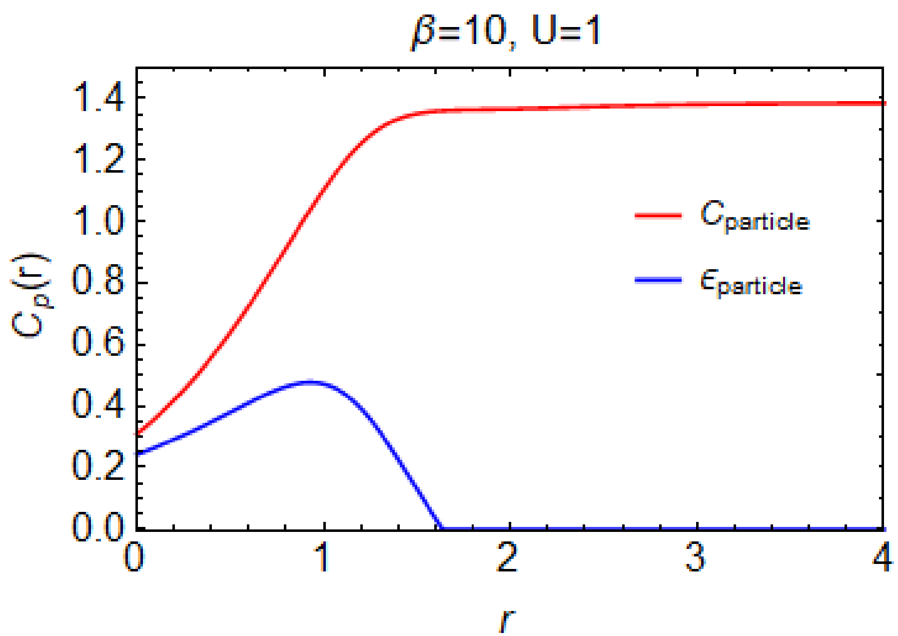
but no entanglement

p



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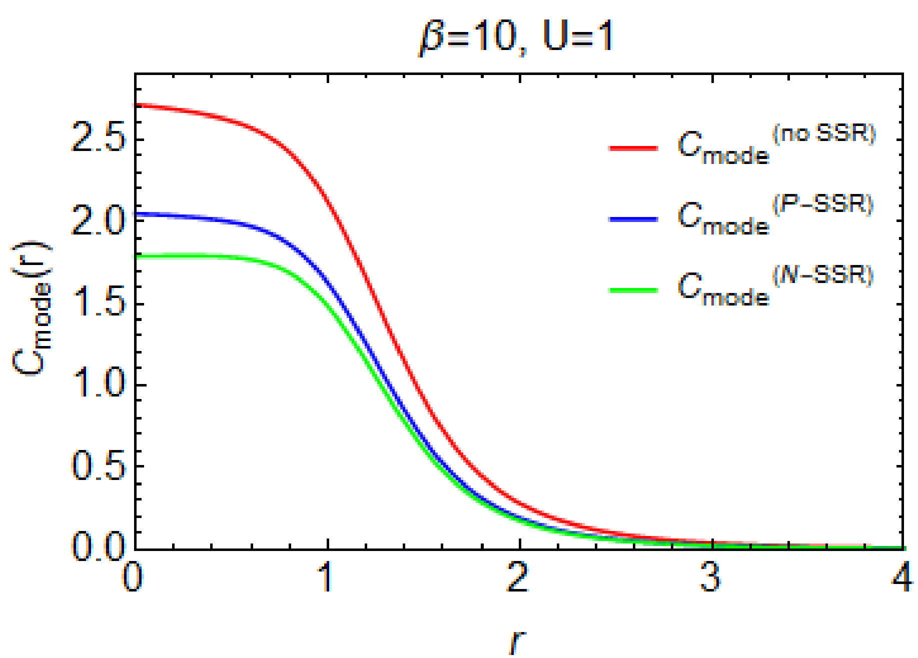
m



Thank you!