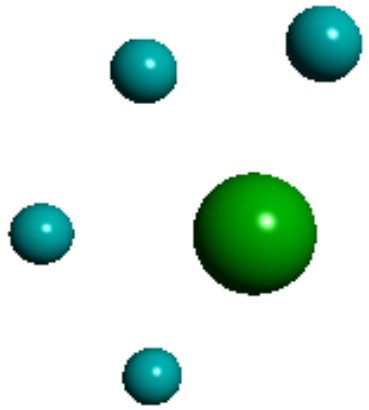
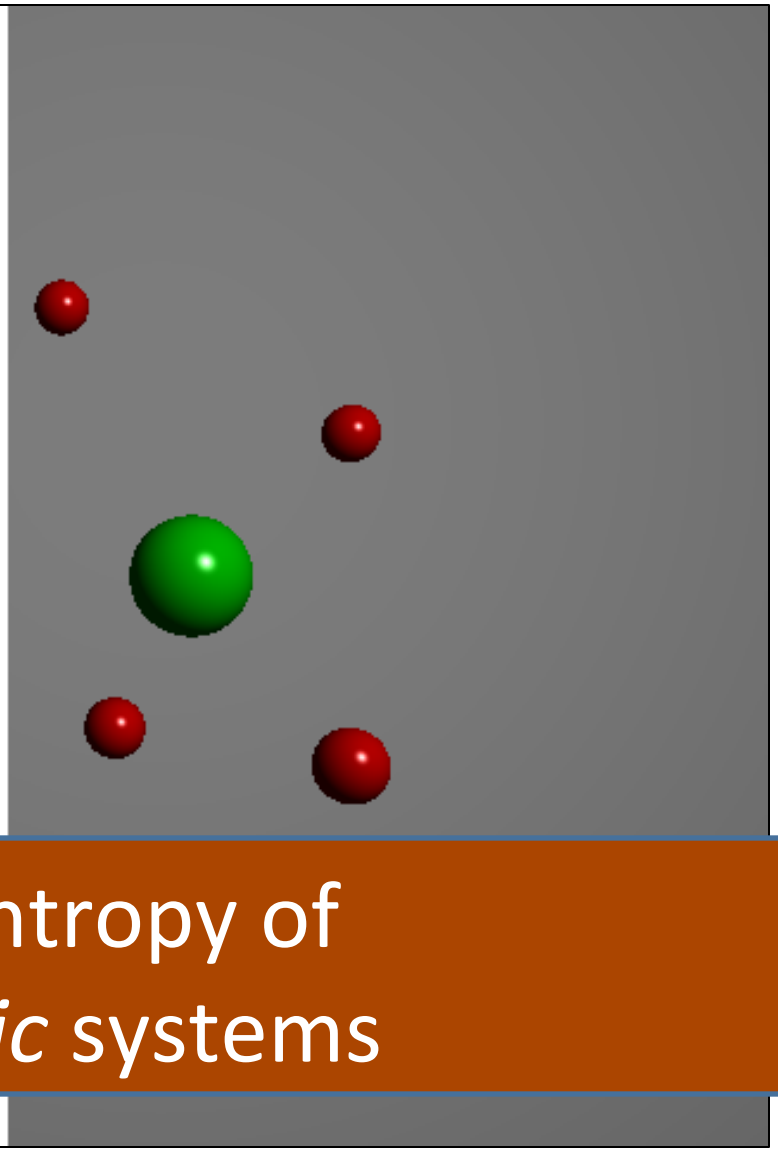
Norm Tubman
University of Illinois





Renyi Entropy of *coulombic* systems

Overview Entanglement research

Entanglement Applications

- Black Hole Physics
- Critical Scaling
- Quantum Information
- Topological phase transitions

Methods based on SRDMS

- DMRG (1993)
- DMET (2012)

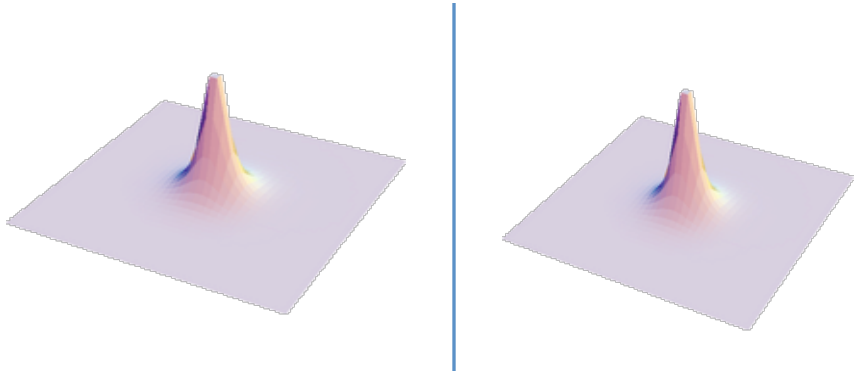
Calculating Entanglement

- Extended systems (2003)
- Single determinant (2004)
- Relationship to Widom (2006)
  Widom Conjecture (1978)
- Fluctuation methods (2006)
- Entanglement Spectrum (2000s)

Quantum Monte Carlo of Entanglement

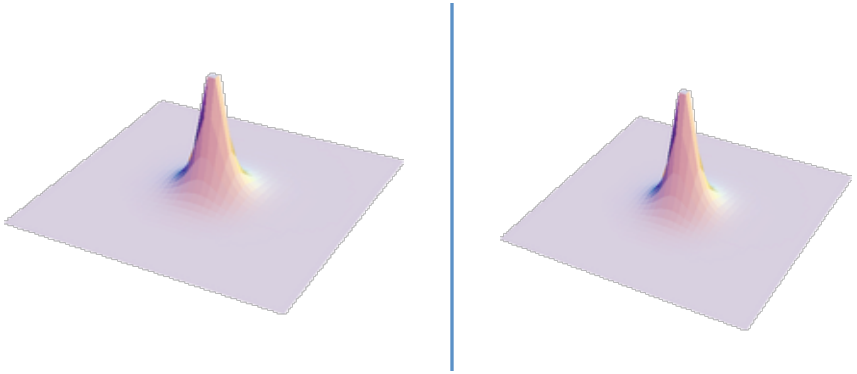
- Swap Operator (2010)
  Replica Trick

Basic Idea of Spatial Entanglement



$$|\Psi\rangle = \sum_n |a_n\rangle|b_n\rangle$$

Basic Idea of Spatial Entanglement



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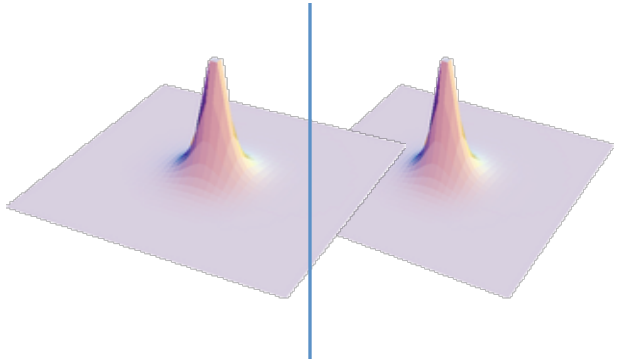
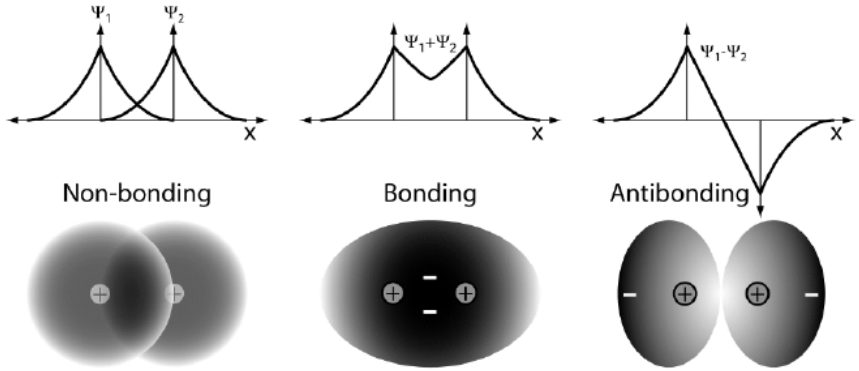


$$|\Psi\rangle \neq |a\rangle|b\rangle$$



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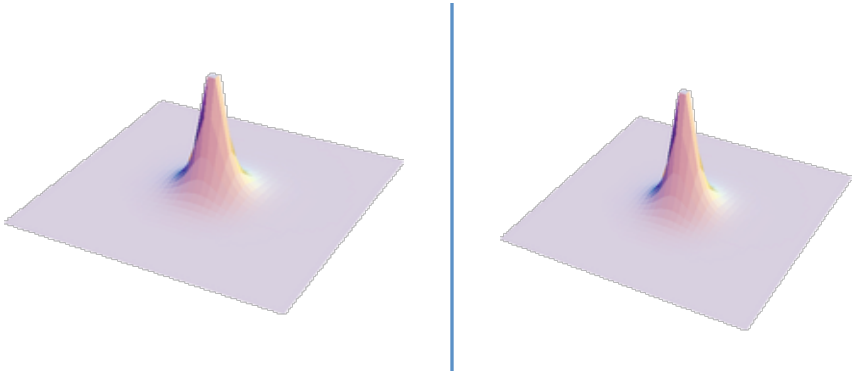

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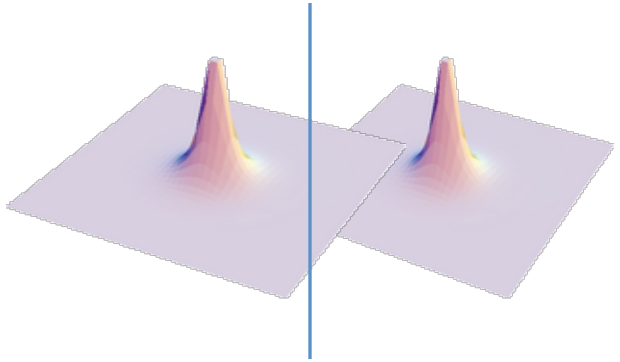

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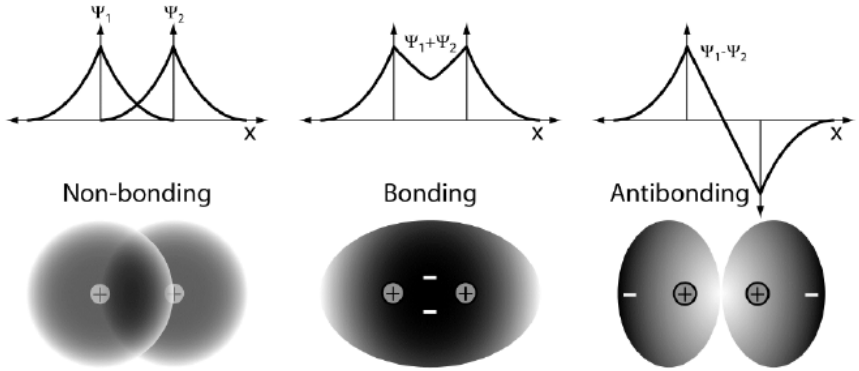

Even if a and b are multi-determinant

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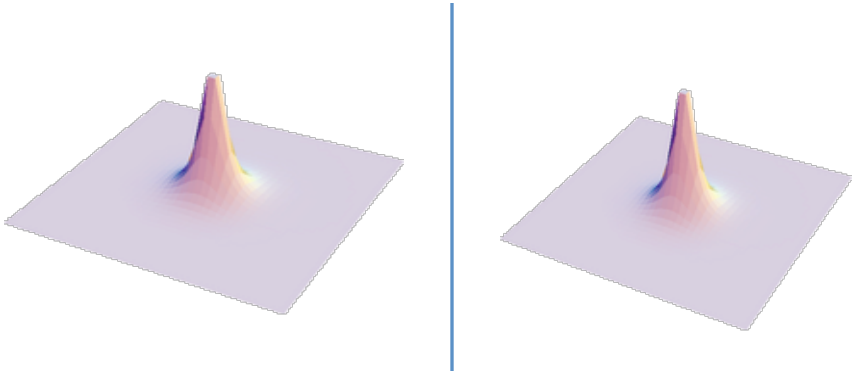
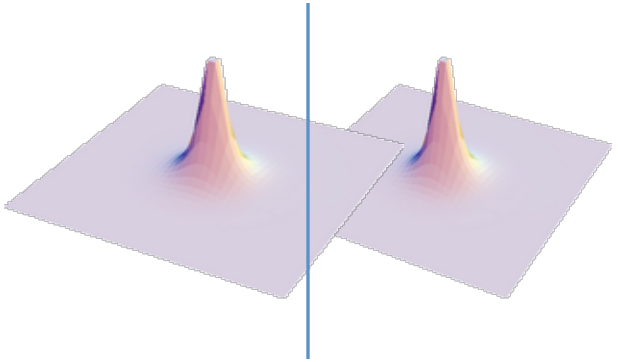


$$|\Psi\rangle = |a_n\rangle|b_n\rangle$$



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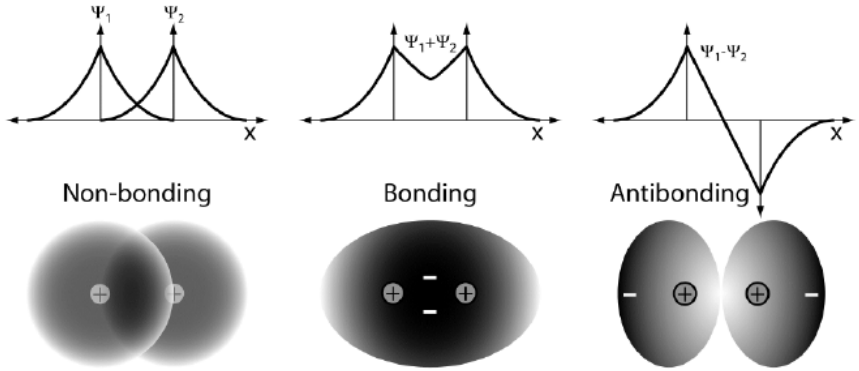

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$$|\Psi\rangle = \sum_n s_n |a_n\rangle|b_n\rangle$$

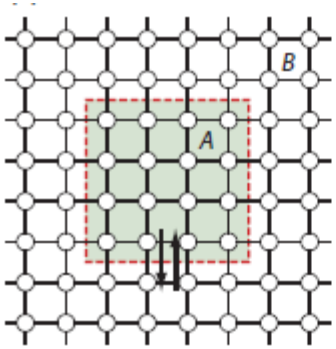
How many of these are important?
(States come from spatial rdm)

Introduction to Entanglement Entropy

Everything comes from spatial reduced density matrix $\rho_A = Tr_B(\rho_{AB})$

1-Particle Section $\gamma(\mathbf{x_1'}, \mathbf{x_1}) = \int \cdots \int \Psi(\mathbf{x_1'}, \mathbf{x_2} \cdots \mathbf{x_N}) \Psi(\mathbf{x_1}, \mathbf{x_2} \cdots \mathbf{x_N}) d\mathbf{x_2} \cdots d\mathbf{x_N}$

2-Particle Section $\gamma(\mathbf{x_1'}, \mathbf{x_1}, \mathbf{x_2'}, \mathbf{x_2}) = \int \cdots \int \Psi(\mathbf{x_1'}, \mathbf{x_2'} \cdots \mathbf{x_N}) \Psi(\mathbf{x_1}, \mathbf{x_2} \cdots \mathbf{x_N}) d\mathbf{x_3} \cdots d\mathbf{x_N}$



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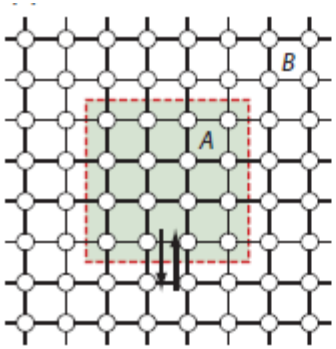
Three terms to distinguish between

1) Entanglement Spectrum
2) Entanglement Entropy
3) Renyi Entropies



Entanglement Entropy $S_1(A) = -\mathrm{Tr}(\rho_A \ln(\rho_A))$

Renyi Entropy $S_n(A) = \frac{1}{1-n} \ln[\mathrm{Tr}((\rho_A)^n)]$

Properties of Renyi entropies

1) Lower Bound

$S_n < S_m$ for 1> m > n

2) Same universal behavior as Von Neumann Entropy

Three methods to calculate entanglement

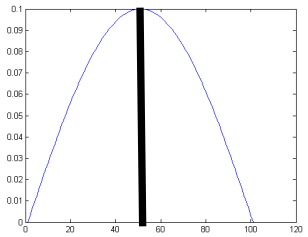
- Correlation Method : Exact for single det
- Fluctuation Method : Exact for single det
- Swap Operator : Exact for any wavefunction

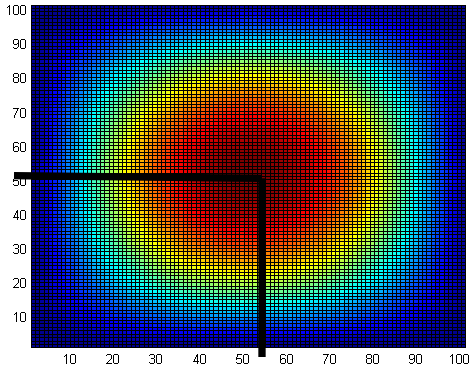
  Renyi entropy only*

Wavefunction from Correlation Method

The output from the correlation method generates N triplets of (Orbital A, Orbital B, eigenvalue)

Define Fermi operators $a_{\alpha,l}$ for the orbitals $\phi_{\alpha,l}$





ζ_1	$a^\dagger_{A,1}$	$a^\dagger_{B,1}$
ζ_2	$a^\dagger_{A,2}$	$a^\dagger_{B,2}$
ζ_3	$a^\dagger_{A,3}$	$a^\dagger_{B,3}$
ζ_4	$a^\dagger_{A,4}$	$a^\dagger_{B,4}$
ζ_5	$a^\dagger_{A,5}$	$a^\dagger_{B,5}$

$$|\psi\rangle = \prod_{l=1}^{N} (\sqrt{\zeta} a^\dagger_{A,l} + \sqrt{1-\zeta} a^\dagger_{B,l})|0\rangle$$

1 equally shared electron

$$\psi = \frac{1}{\sqrt{2}}|a_1> + \frac{1}{\sqrt{2}}|b_1>$$

2 equally shared electrons

$$\psi = \frac{1}{2}|a_1 a_2> + \frac{1}{2}|a_1 b_2> + \frac{1}{2}|a_2 b_1> + \frac{1}{2}|b_1 b_2>$$

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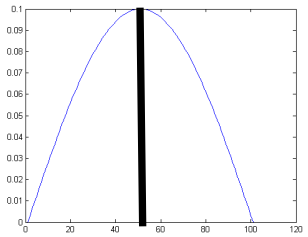

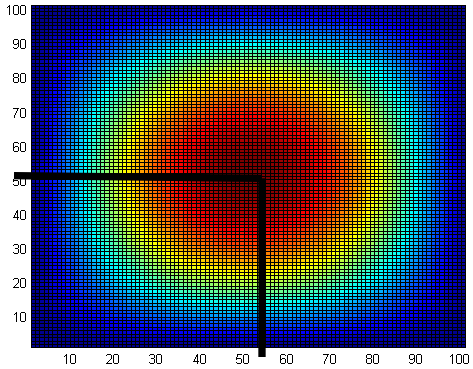

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How to calculate Entanglement: Swap

Through the replica trick, one can sample the trace of the spatial reduced density matrix.

$$Tr((\rho_A)^2) = \frac{\langle \Psi_T \otimes \Psi_T | swap_A | \Psi_T \otimes \Psi_T \rangle}{\langle \Psi_T \otimes \Psi_T | \Psi_T \otimes \Psi_T \rangle}.$$

Hastings PRL 2010

$$\begin{aligned}\langle \Psi_T \otimes \Psi_T | swap_A | \Psi_T \otimes \Psi_T \rangle &= \int d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_{2N} \Psi_T^*(R(\alpha_1,\beta_1))\Psi_T^*(R(\alpha_2,\beta_2))\Psi_T(R(\alpha_2,\beta_1))\Psi_T(R(\alpha_1,\beta_2)) \\ &= \int d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_{2N} |\Psi_T(R(\alpha_1,\beta_1))|^2 |\Psi_T(R(\alpha_2,\beta_2))|^2 \frac{\Psi_T(R(\alpha_2,\beta_1))\Psi_T(R(\alpha_1,\beta_2))}{\Psi_T(R(\alpha_1,\beta_1))\Psi_T(R(\alpha_2,\beta_2))}\end{aligned}$$

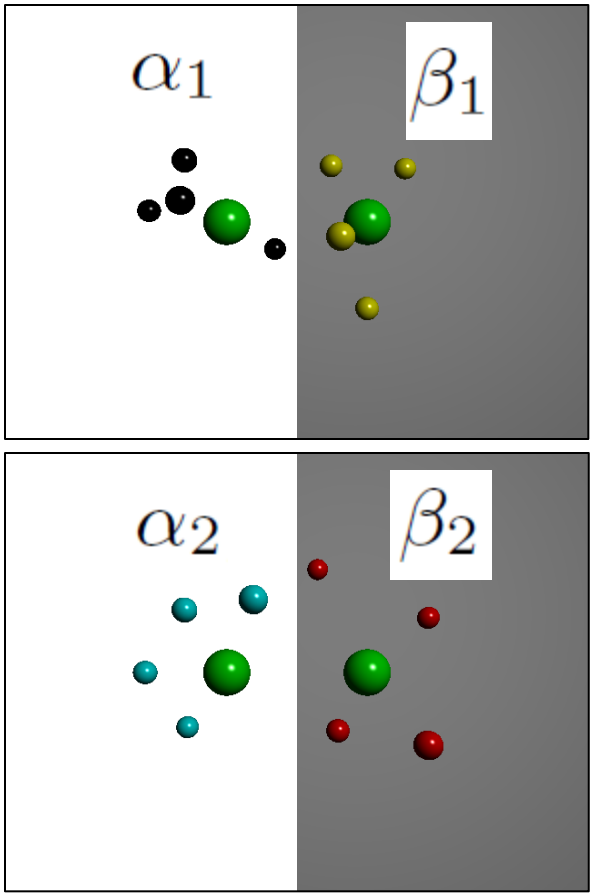
The QMC estimator can be determined by the application of the swap

$$O(\alpha_1,\alpha_2,\beta_1,\beta_2) = \frac{\Psi_T(R(\alpha_2,\beta_1))\Psi_T(R(\alpha_1,\beta_2))}{\Psi_T(R(\alpha_1,\beta_1))\Psi_T(R(\alpha_2,\beta_2))}$$

The estimator becomes the product of four wavefunction evaluations

How to calculate Entanglement: Swap

$$O(\alpha_1, \alpha_2, \beta_1, \beta_2) = \frac{\Psi_T(R(\alpha_2, \beta_1))\Psi_T(R(\alpha_1, \beta_2))}{\Psi_T(R(\alpha_1, \beta_1))\Psi_T(R(\alpha_2, \beta_2))}$$



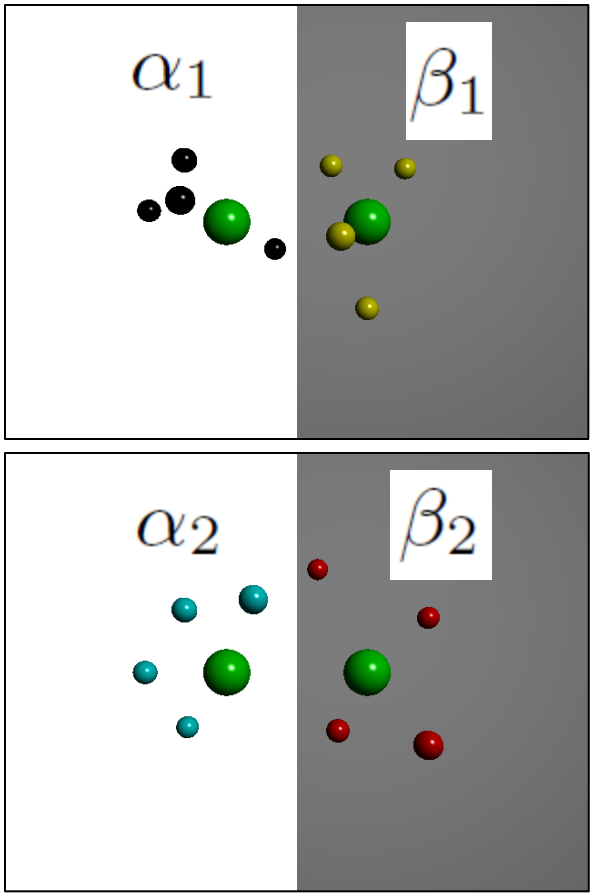
In Variational Monte Carlo, we generally sample a wavefunction with a 'walker' in 3N dimensions

We perform the swap after we have done all wave function optimizations

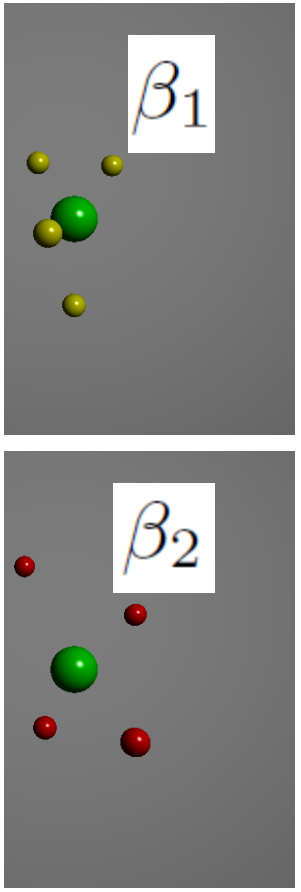
To calculate the swap,
start by sampling the extended Hilbert space of 6N dimensions

How to calculate Entanglement: Swap

$$O(\alpha_1, \alpha_2, \beta_1, \beta_2) = \frac{\Psi_T(R(\alpha_2, \beta_1))\Psi_T(R(\alpha_1, \beta_2))}{\Psi_T(R(\alpha_1, \beta_1))\Psi_T(R(\alpha_2, \beta_2))}$$



Create two new walkers,
keep all the coordinates the same
In region B



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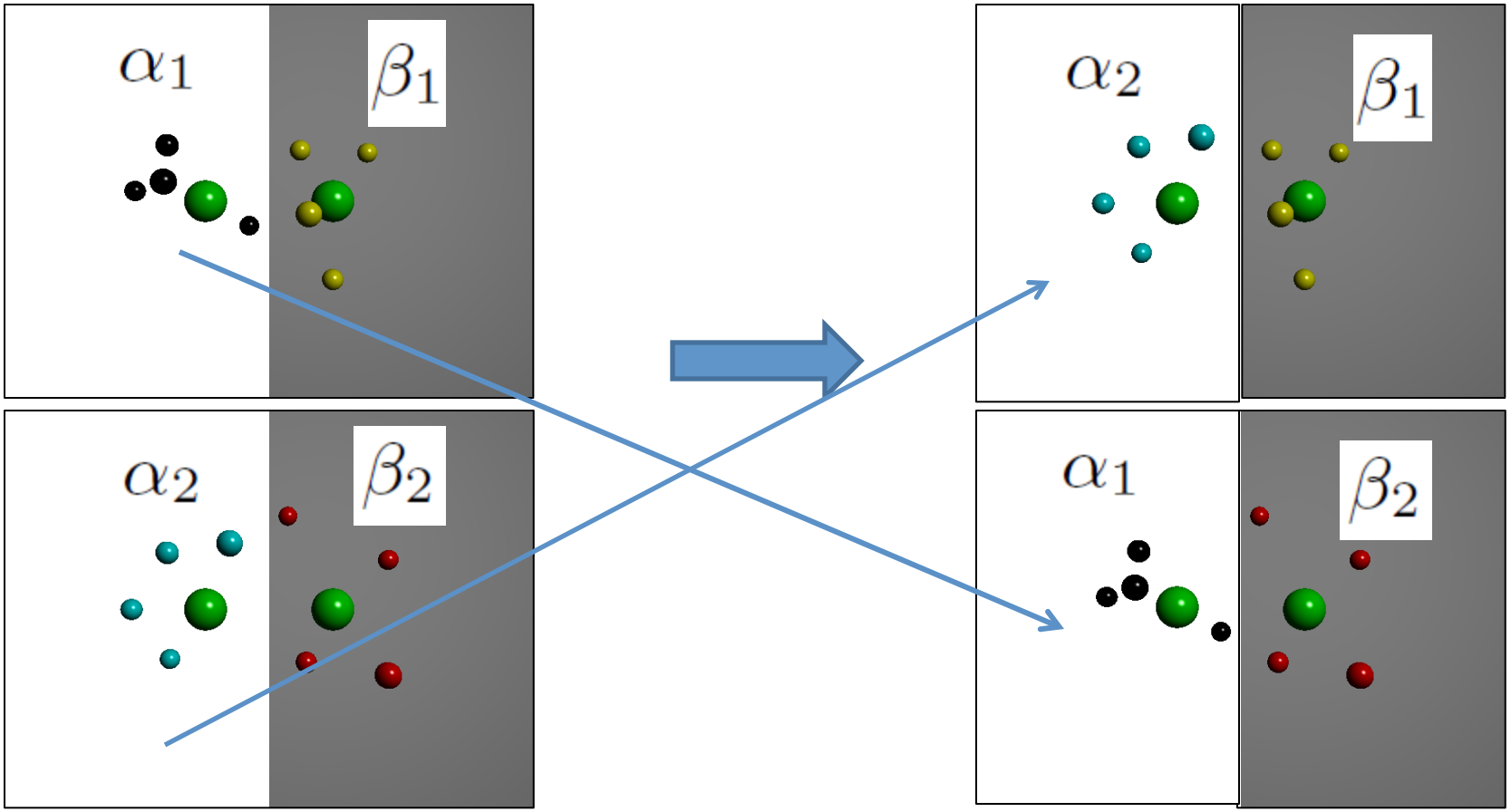

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An estimator value close to zero implies large entanglement
An estimator value close to one implies no entanglement

In VMC, all walkers are independent, so it is unnecessary to have two populations of walkers.
This come with one caveat: Do not swap a walker with itself

Entanglement of Molecules

Why study molecules

- The study of bonding is essentially a study of how electrons interact between two (or more) regions of space
- Entanglement gives properties of how wave functions partition between two (or more) regions of space

Bond order definitions?

IUPAC
GOLD BOOK

IUPAC > Gold Book > alphabetical index > B > **bond order**

PREVIOUS
bond orbital

NEXT
bond order p_{rs}

bond order

The electron population in the region between atoms A and B of a molecular entity at the expense of electron density in the immediate vicinity of the individual atomic centers. Different schemes of partitioning electron density give rise to different definitions of bond orders. In the framework of the Mulliken population analysis, bond order is associated with the total overlap population

$$q_{AB} = 2 \sum_{\mu}^{A} \sum_{\nu}^{B} P_{\mu\nu} S_{\mu\nu}$$

where $P_{\mu\nu}$ and $S_{\mu\nu}$ are respectively the elements of the density matrix and overlap matrix (see overlap integral).

Standard Results

(So one obtains the values 1, 0, 3, and 1 for H_2, He_2, N_2 and F_2, respectively.)

On Bond Orders and Valences in the *Ab Initio* Quantum Chemical Theory*

1986

I. MAYER

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

Reaching the Maximum Multiplicity of the Covalent Chemical Bond**

Björn O. Roos, Antonio C. Borin, and Laura Gagliardi*

2007

A Simple Definition of Ionic Bond Order

2008

D. B. Chesnut*

Department of Chemistry, Duke University, Durham, North Carolina 27708

Received August 9, 2008

A definition for the covalent and ionic bond index in a molecule

An approach based on Roby's atomic projection operators

Mark D. Gould · Christopher Taylor · Stephen K. Wolff · Graham S. Chandler · Dylan Jayatilaka

2008

Entanglement and bonding?

It is possible to determine entanglement just from the fluctuations of the system. This is exact for non-interacting wavefunctions.

$$S_1 = \lim_{K \Rightarrow \infty} \sum_{n=1}^{K+1} \alpha_n(K) f_n(\mu_n')$$

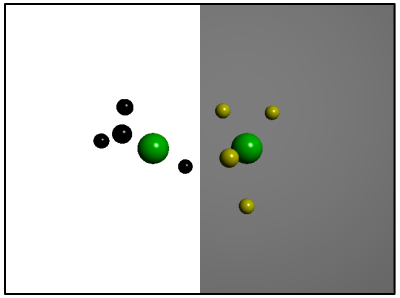
Song PRB 2011

Lower Bound $S_1 \geq S_{fluc}$

Klitch PRA 2006

$$\mu_1' = \int |\Psi(x_1 \cdots x_N)|^2 N_A dx_1 \cdots dx_N$$

$$\mu_2' = \int |\Psi(x_1 \cdots x_1)|^2 N_A^2 dx_1 \cdots dx_N$$



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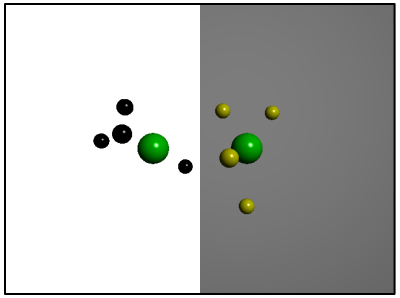

Ab-Inito bond order is related to the fluctuations of particles between regions A and B.

$$B_{AB} = -2\left\langle \left(\hat{N}_A - \langle \hat{N}_A \rangle\right)\left(\hat{N}_B - \langle \hat{N}_B \rangle\right)\right\rangle$$

Entanglement bonding properties

The bipartite density matrix of the ground state particle in a box wave function
Has two eigenvalues (1/2,1/2) which yields a value of ln(2) for the Renyi Entropy

$$|\Psi\rangle = \sum_n s_n |a_n\rangle |b_n\rangle \qquad N_{bond} = \frac{S_1}{2(ln(2))}$$

1) Comes from an N-body density matrix, spectrum contains all information
2) Rigorous definition of zero bonding

$$\psi = \psi_A \psi_B$$

3) Non-standard bonding situations
4) Correlations and fluctuations cause entanglement
5) Any space partitioning can be used
6) Gives close to integer values for simple bonding situations

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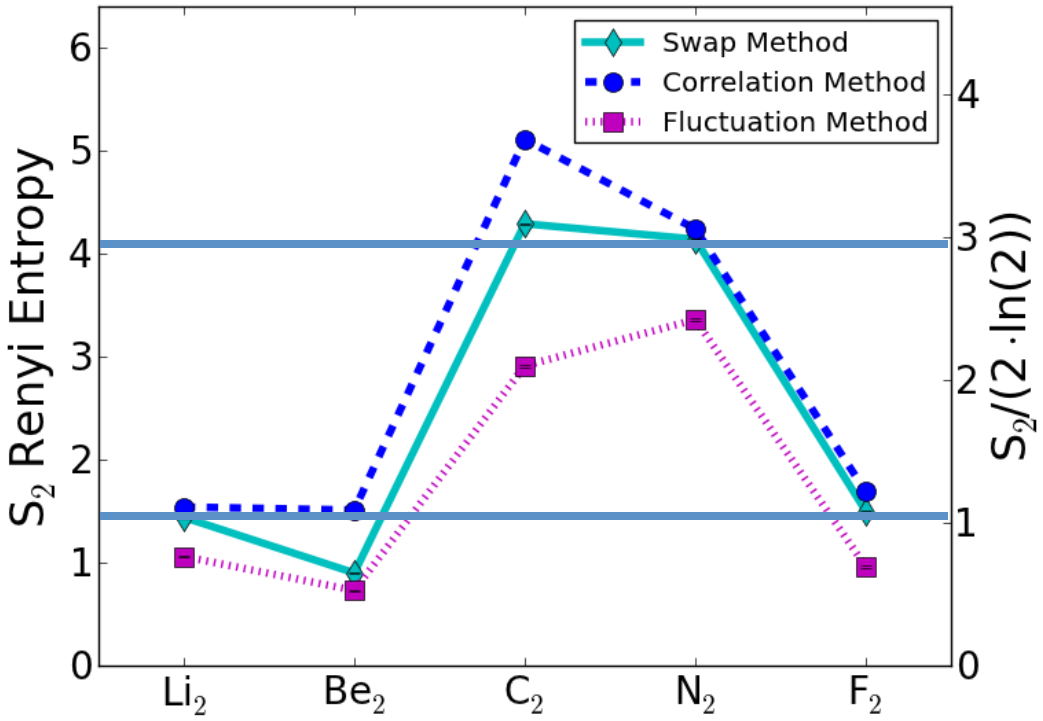
Molecular Results

All calculations are performed at equilibrium positions

Different quality wave functions tested for carbon:
-1) Hartree-Fock
-2) CASSCF (100-1000) dets
-3) Jastrow+CASSCF
-4) Jastrow+CASSCF+coeff opt (QMCPACK)

Swap method is unbiased QMC. Correlation and Fluctuations are approximate.

Singlet First Row Dimers



CASSCF wave functions

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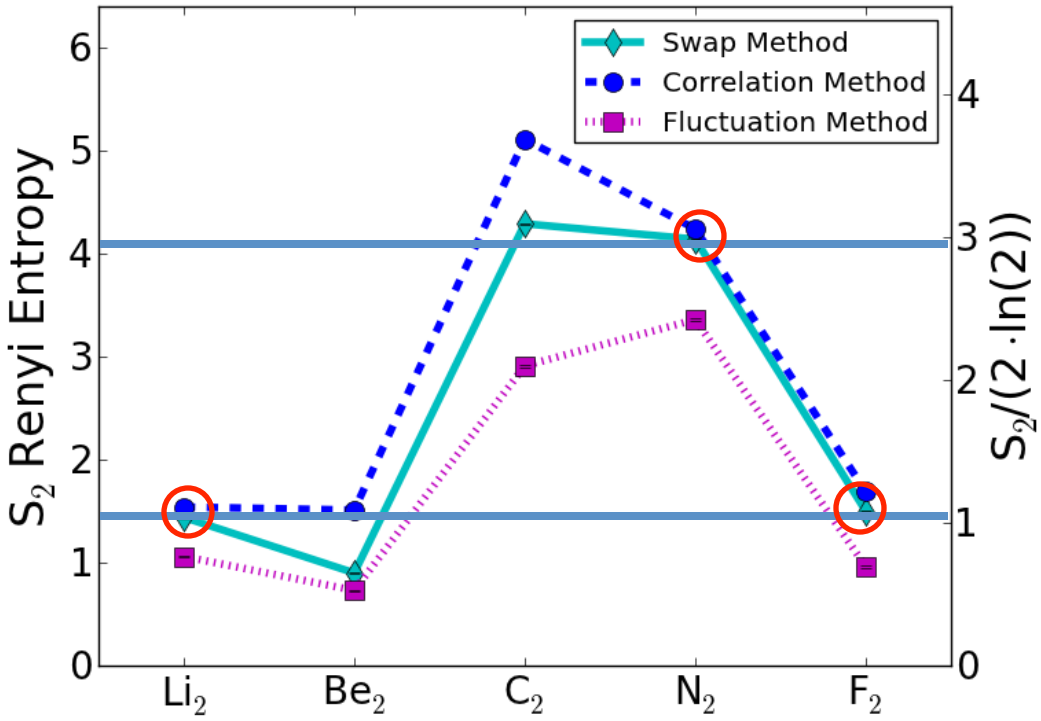
Singlet First Row Dimers



CASSCF wave functions

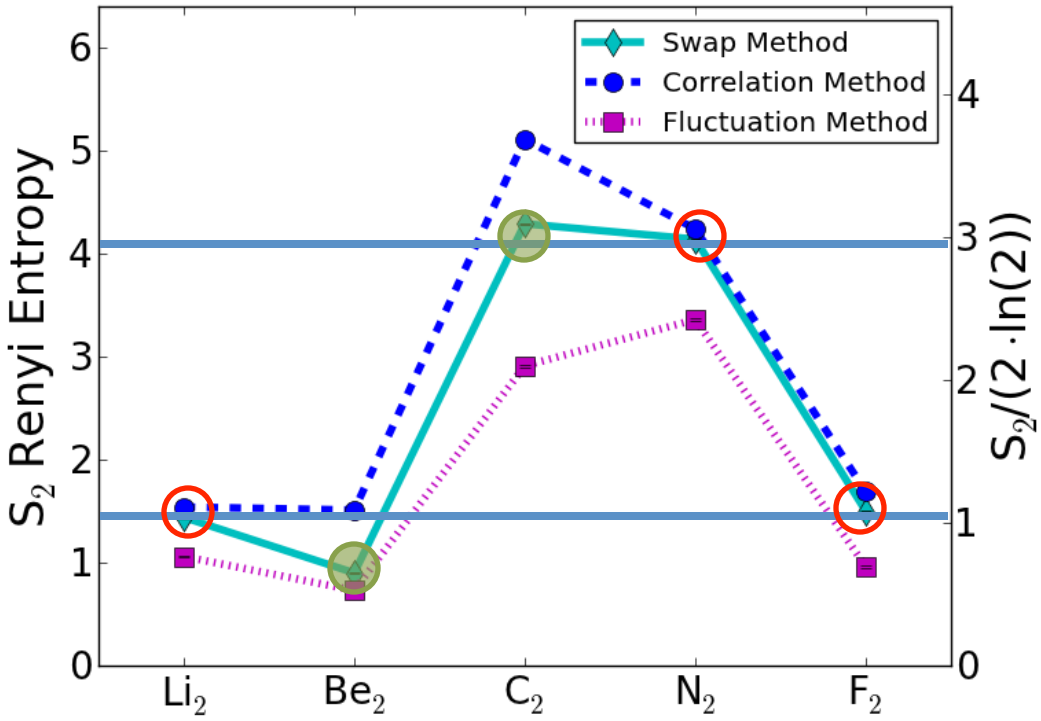
Molecular Results

All calculations are performed at equilibrium positions

Different quality wave functions tested for carbon:
-1) Hartree-Fock
-2) CASSCF (100-1000) dets
-3) Jastrow+CASSCF
-4) Jastrow+CASSCF+coeff opt (QMCPACK)

Swap method is unbiased QMC. Correlation and Fluctuations are approximate.

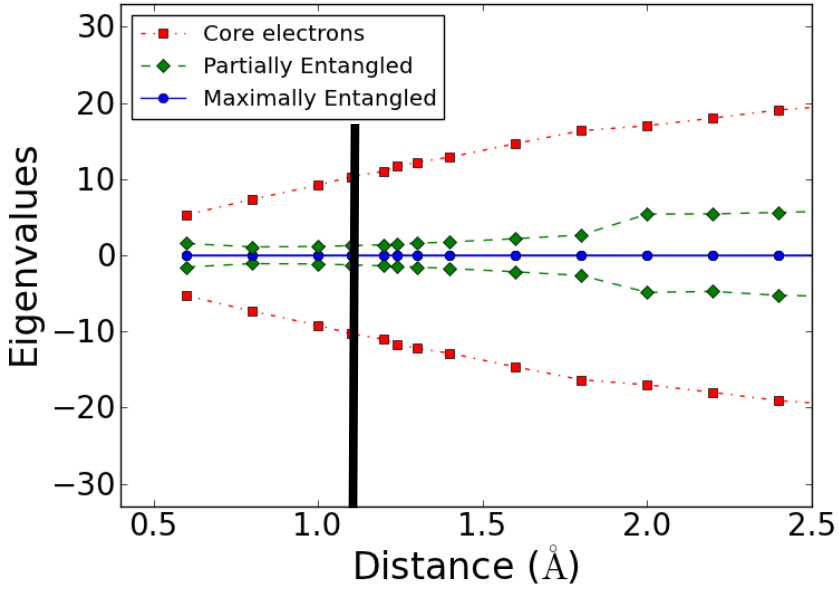
Singlet First Row Dimers



CASSCF wave functions

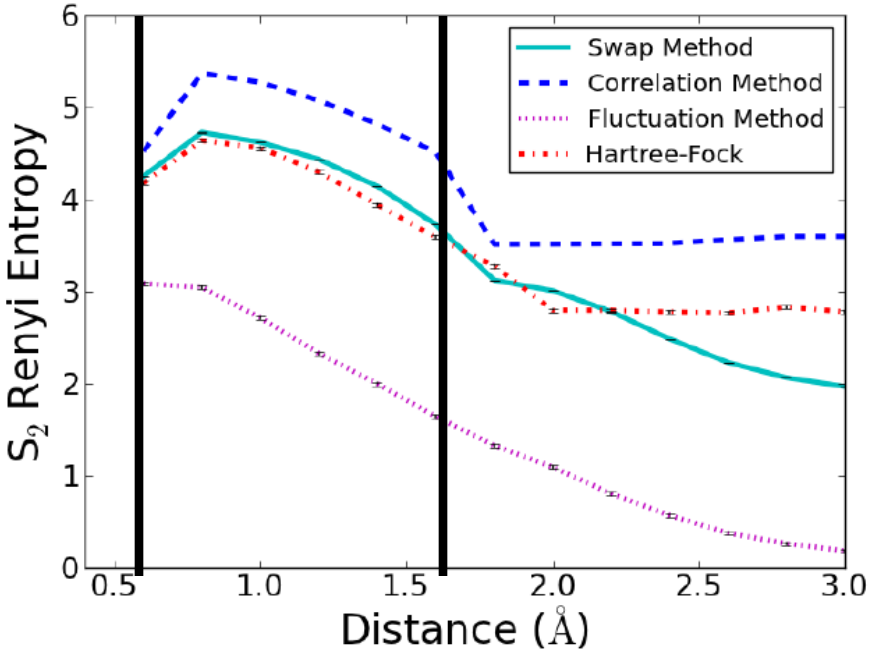
Bonding in C_2

Hartree-Fock Entanglement Hamiltonian

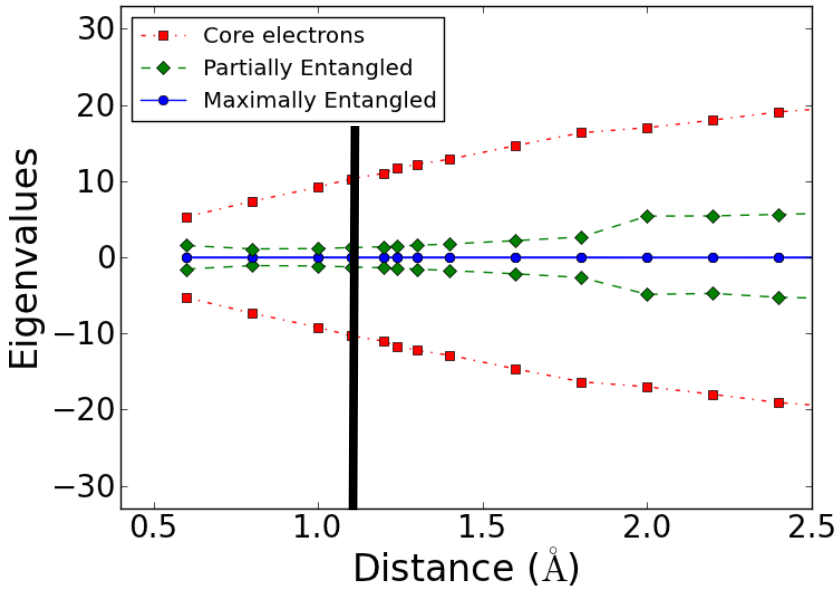


-There are 12 eigenvalues total at a given distance
-The eigenvalue line at zero is 4 times degenerate
-The other eigenvalues are doubly degenerate
-A zero eigenvalue represents a completely shared mode
-The further away from zero an eigenvalue line the less entanglement it contributes

Bonding in C_2



Hartree-Fock Entanglement Hamiltonian



Quadruple bonding in C_2 and analogous eight-valence electron species

Sason Shaik[1]*, David Danovich[1], Wei Wu[2], Peifeng Su[2], Henry S. Rzepa[3] and Philippe C. Hiberty[4]

Triple bonding is conventionally considered to be the limit for multiply bonded main group elements, despite higher metal–metal bond orders being frequently observed for transition metals and lanthanides/actinides. Here, using high-level theoretical methods, we show that C_2 and its isoelectronic molecules CN^+, BN and CB^- (each having eight valence electrons) are bound by a quadruple bond. The bonding comprises not only one σ- and two π-bonds, but also one weak 'inverted' bond, which can be characterized by the interaction of electrons in two outwardly pointing *sp* hybrid orbitals. A simple way of assessing the energy of the fourth bond is proposed and is found to be ~12–17 kcal mol^{-1} for the isoelectronic species studied, and thus stronger than a hydrogen bond. In contrast, the analogues of C_2 that contain higher-row elements, such as Si_2 and Ge_2, exhibit only double bonding.

Nature Chemistry 2012

-Core electrons non-factor
-All valence electrons important
-Interacting spectrum would be useful

Entanglement of Fermi Liquids

Entanglement in condensed matter systems

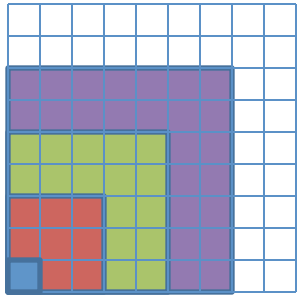
In condensed matter systems, the entanglement scaling laws have been studied extensively.

area law $S_N = a\ell + sub$ Gapped systems

topological $S_N = a\ell - \gamma + sub$

critical $S_N = a\ell - c_N + sub$

Fermi surface $S_N = c\ell ln(\ell) + sub$



- Entanglement has been used to study different phases and identify quantum critical points
- Subleading terms are thought also describe important physics

Widom Conjecture and other Fermi Liquid predictions

The Widom conjecture has been used to describe the entanglement of gapless systems with free fermions

$$S \sim \frac{L^{d-1}\log L}{(2\pi)^{d-1}}\frac{1}{12}\int_{\partial\Omega}\int_{\partial\Gamma}|n_x\cdot n_p|dS_x dS_p$$

Entanglement Entropy of Fermions in Any Dimension and the Widom Conjecture

Dimitri Gioev[1,*] and Israel Klich[2,†]
[1]*Courant Institute, New York University, New York, New York 10012, USA and Department of Mathematics, University of Rochester, Rochester, New York 14627, USA*
[2]*Department of Physics, California Institute of Technology, Pasadena, California 91125, USA*
(Received 10 May 2005; published 14 March 2006)

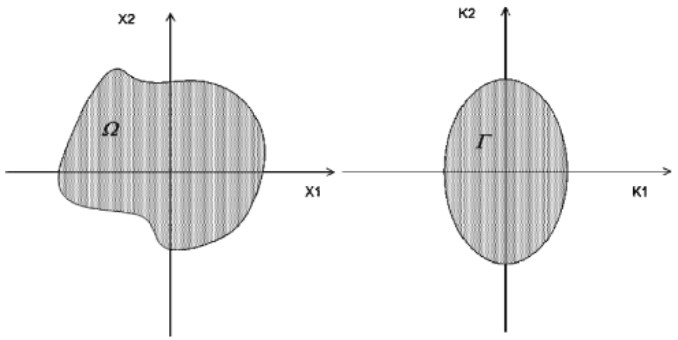
Entanglement Entropy and the Fermi Surface

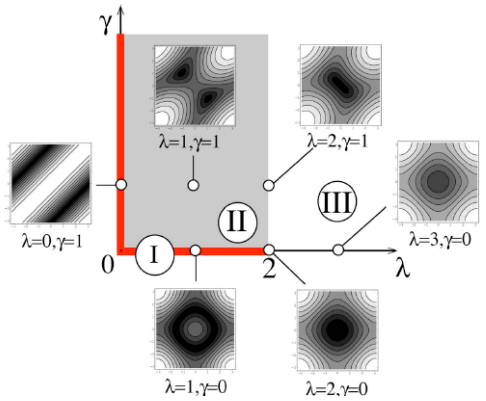
Brian Swingle*
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
(Received 11 March 2010; published 30 July 2010)

Entanglement Entropy of Fermi Liquids via Multidimensional Bosonization

Wenxin Ding,[1] Alexander Seidel,[2] and Kun Yang[1]
[1]*National High Magnetic Field Laboratory and Department of Physics, Florida State University, Tallahassee, Florida 32306, USA*
[2]*Department of Physics and Center for Materials Innovation, Washington University, St. Louis, Missouri 63136, USA*
(Received 6 November 2011; published 20 March 2012)

The logarithmic violations of the area law, i.e., an "area law" with logarithmic correction of the form





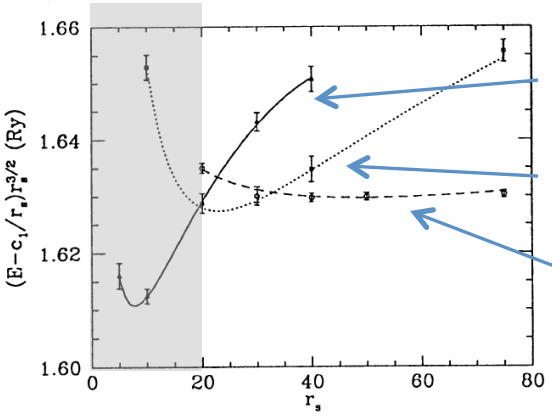
Li PRB 2006

Properties of Entanglement

We considered two Hamiltonians for the 2D electron gas

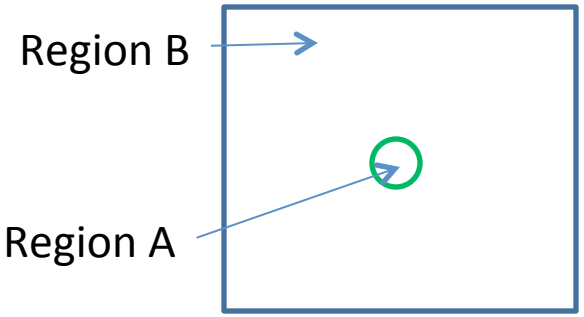
$$H_{HEG} = -\sum_i \frac{\nabla^2}{2} + \sum_{i<j} r_{ij}^{-1} + C(r_s)$$

$$H_{MPT} = -\sum_i \frac{\nabla^2}{2} + V_0 \sum_{i<j} cosh^{-2}(r_{ij})$$



Wave function: Slater-Jastrow
But we also tested Slater-Jastrow-Backflow

Results



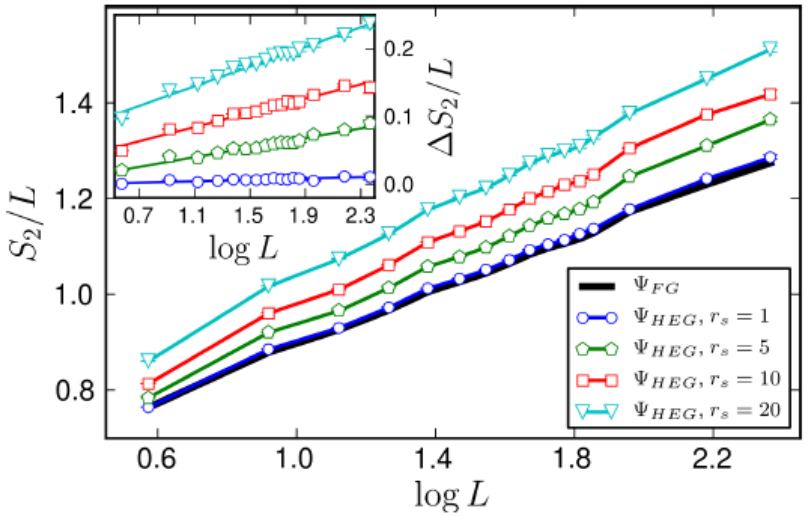
Finite size effects tested with 50, 137, 261 electrons

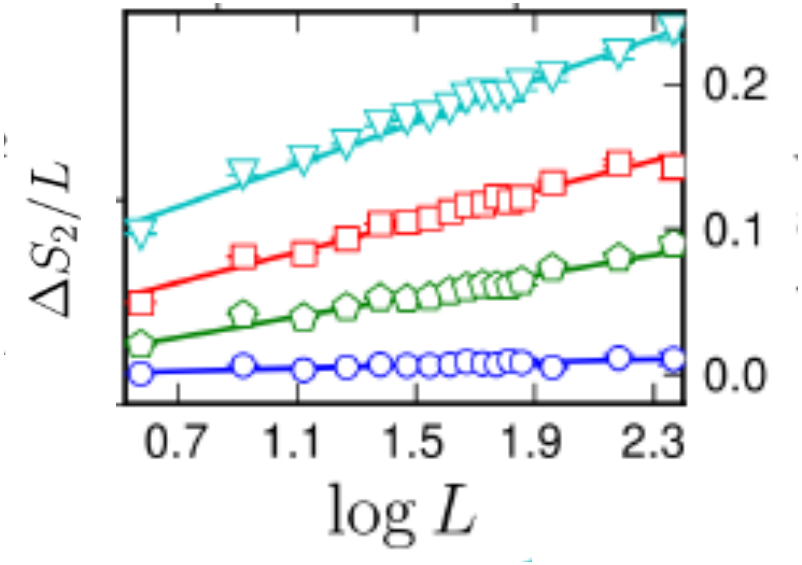
Largest entangled region 36 electrons out of 261

Data is plotted such that all non-interacting data falls on the same line $L \rightarrow L/(\sqrt{\pi} r_s)$

Leading terms do not follow the Widom conjecture at low densities

Sub-leading terms oscillate and decay





Conclusions

- We report one of the first calculations to calculate entanglement entropy for *ab initio* systems with coulomb interactions.
- Spatial density matrix contains information about composite systems. Natural way to calculate bonding properties?
- Renormalization of the scaling laws occur when interactions are introduced in a Fermi-liquid
- Many possibilities to expand analysis to other bonding situations, extended systems, and new methods

The End