Many-Electron States

Erik Koch
German Research School for Simulation Sciences, Jülich

Martin Schoeller
IDENTICAL
Portraits of Twins
teNeues Verlag, 2012

Identical Twins

Diane Arbus:
Identical Twins,
Roselle, NJ, 1967

Martin Schoeller
IDENTICAL: Portraits of Twins

twinsdays.org

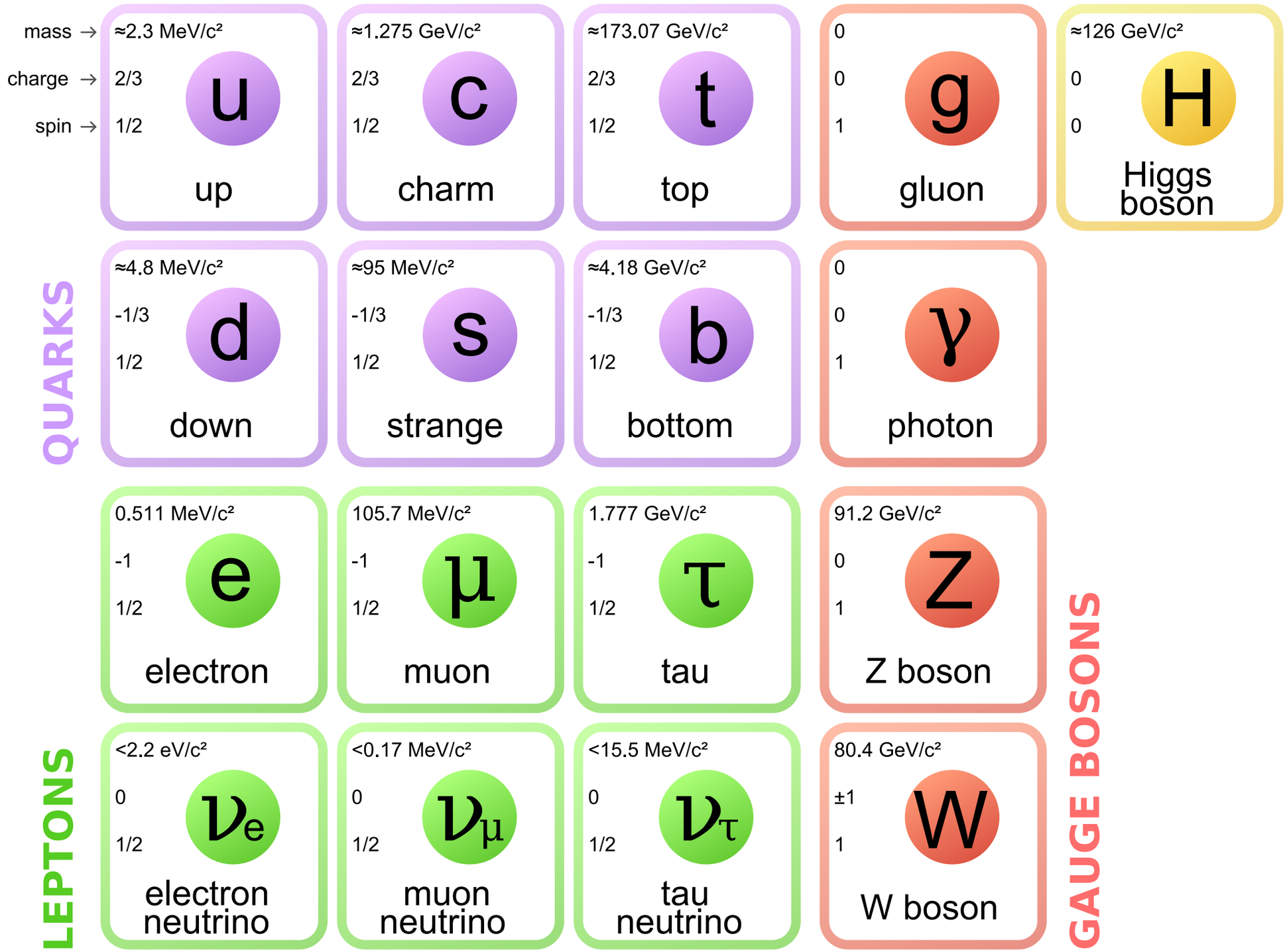
Twins Days Festival in Twinsburg, Ohio

The World's Largest Annual Gathering of Twins! Next Festival: Aug 1-3, 2014

Welcome

The Twins Days Festival in Twinsburg, Ohio is the largest annual gathering of twins (& other multiples) in the world! Twins Days takes place on the **first full weekend of August** each year. For 2014, that's **August 1, 2, and 3**. Mark your calendars now, and make your plans to attend!

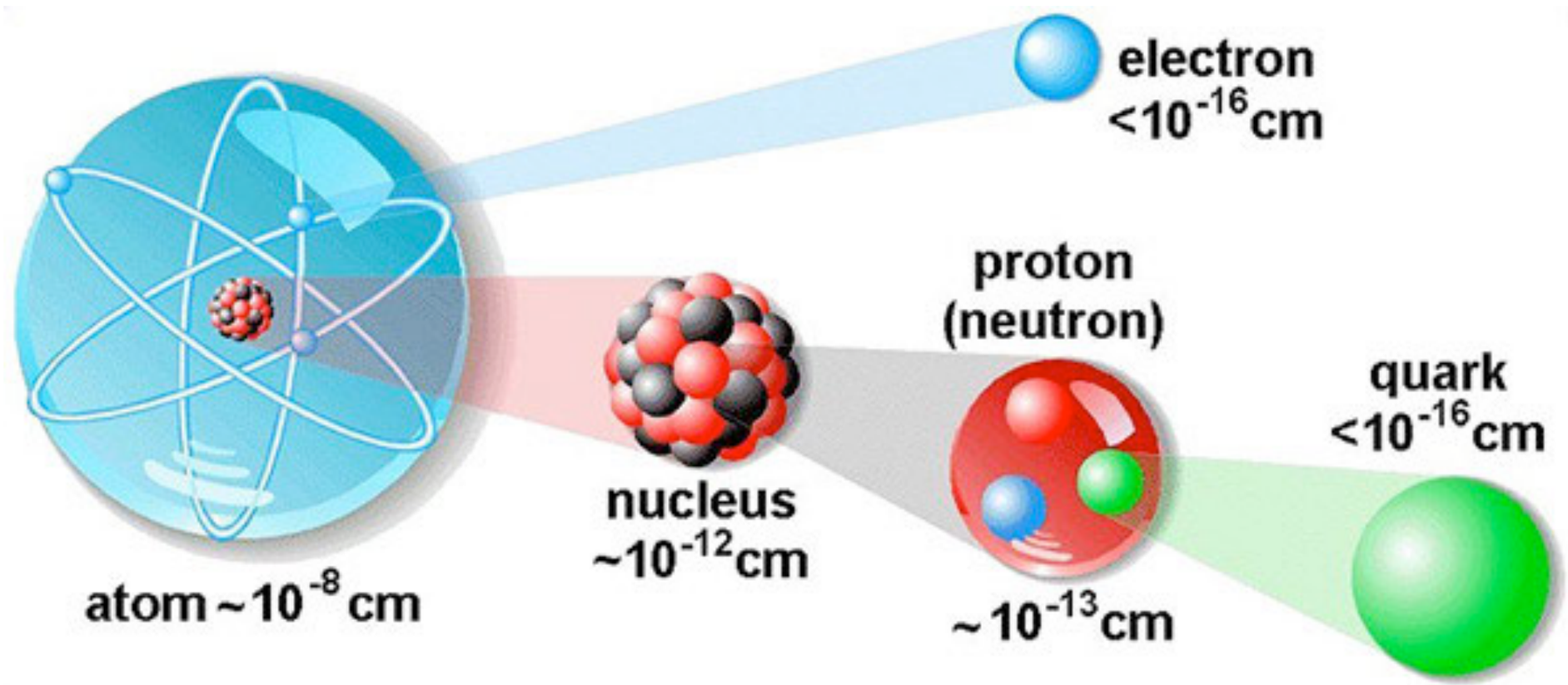
Standard Model: Identical Particles



en.wikipedia.org/wiki/Standard_Model

indistinguishable particles

fundamental particles change over time/length-scale/energy



https://community.emc.com/people/ble/blog/2011/11

emergence of distinguishability

uncertainty:

quantum particles can usually not be distinguished by their position

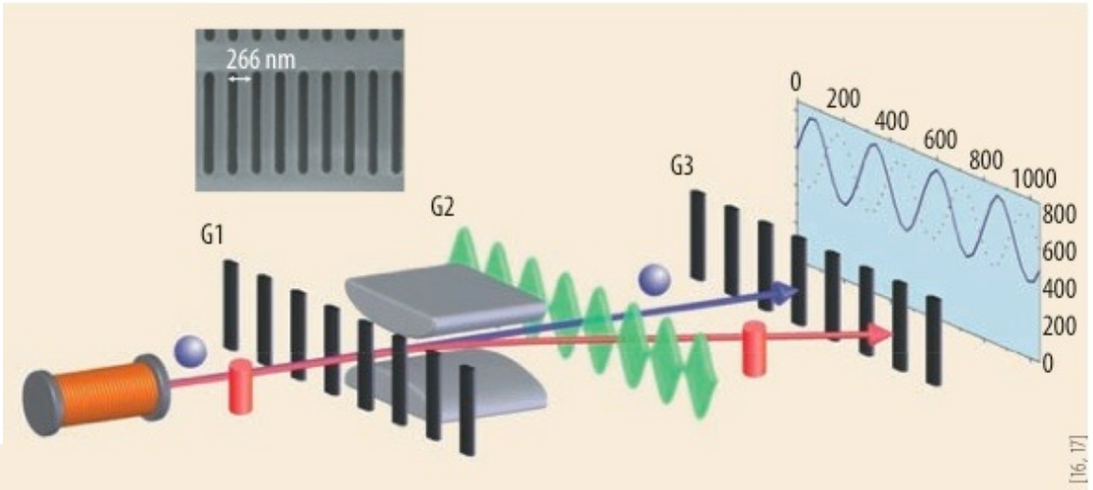
Interferometrie mit komplexen Molekülen

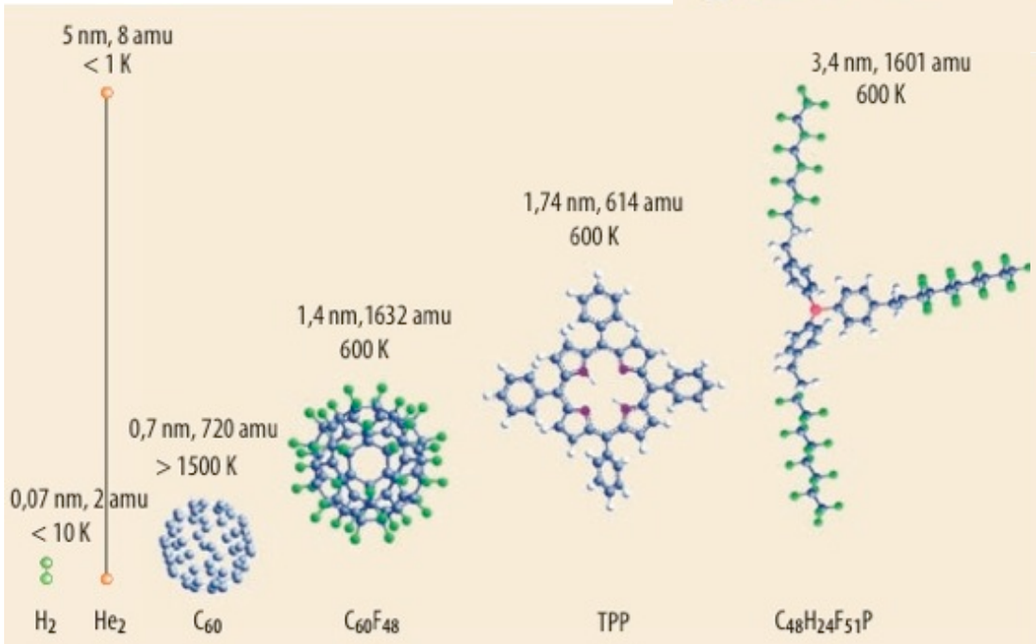
Physik Journal **9** Okt. 2010, p. 37

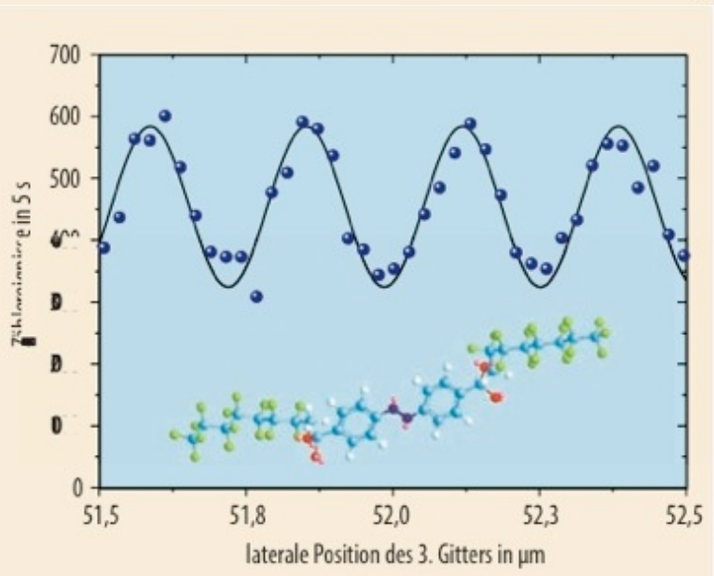
Wie man Einblick in das Innenleben von quantenmechanisch delokalisierten Molekülen gewinnt

Markus Arndt, Stefan Gerlich, Klaus Hornberger und Marcel Mayor

not just electrons behave as waves ...







indistinguishability and statistics

N-particle systems described by wave-function with
N particle degrees of freedom (tensor space):

$\Psi(x_1, ..., x_N)$

introduces **labeling** of particles

indistinguishable particles: no observable exists to distinguish them
in particular no observable can depend on labeling of particles

consider permutations *P* of particle labels

$$P\Psi(x_1, x_2) = \Psi(x_2, x_1) \text{ with } |\Psi(x_1, x_2)|^2 = |\Psi(x_2, x_1)|^2$$

$$\rightsquigarrow \; P\Psi(x_1, x_2) = e^{i\phi}\Psi(x_1, x_2)$$

when $P^2 = \mathrm{Id} \Rightarrow e^{i\phi} = \pm 1$ (Ψ (anti)symmetric under permuation)

antisymmetric: $\Psi(x_1, x_2 \to x_1) = 0$ (Pauli principle)

spin-statistics connection

bosons (integer spin): symmetric wave-function

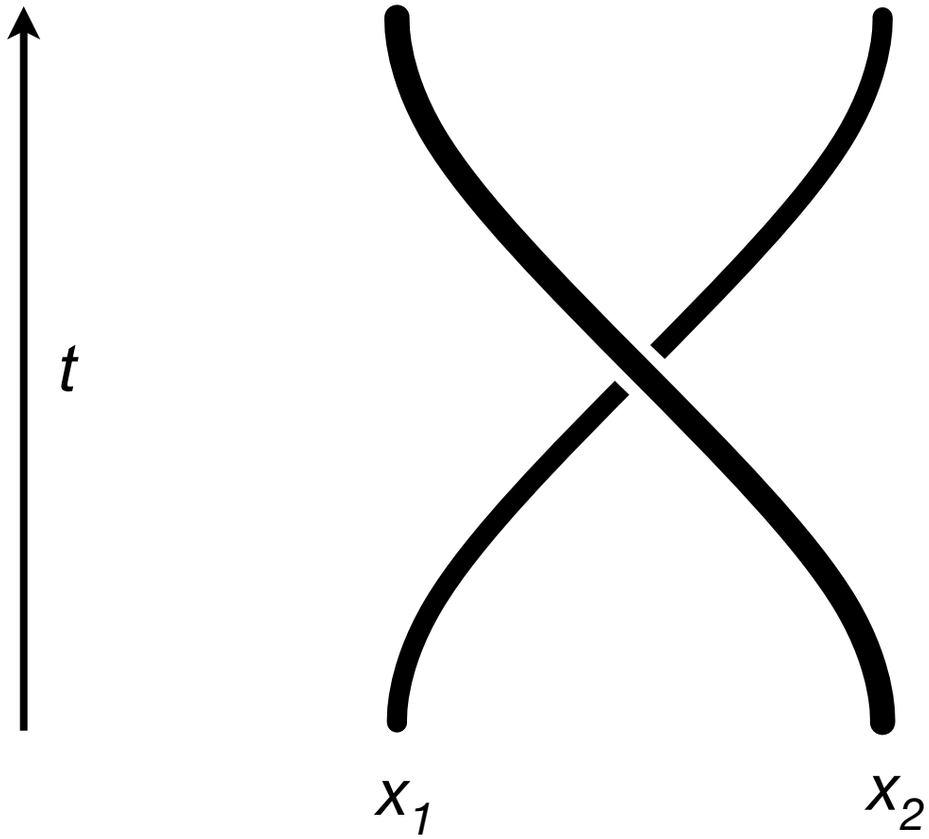
fermions (half-integer spin): anti-symmetric wave-function

Feynman Lectures III, 4-1:

Why is it that particles with half-integral spin are Fermi particles whose amplitudes add with the minus sign, whereas particles with integral spin are Bose particles whose amplitudes add with the positive sign? We apologize for the fact that we cannot give you an elementary explanation. An explanation has been worked out by Pauli from complicated arbuments of quantum field theory and relativity. He has shown that the two must necessarily go together, but we have not been able to find a way of reproducing his arguments on an elementary level. It appears to be one of the few places in physics where there is a rule which can be stated very simply, but for which no one has found a simple and easy explanation. The explanation is deep down in relativistic quantum mechanics. This probably means that we do not have a complete understanding of the fundamental principle involved. For the moment, you will just have to take it as one of the rules of the world.

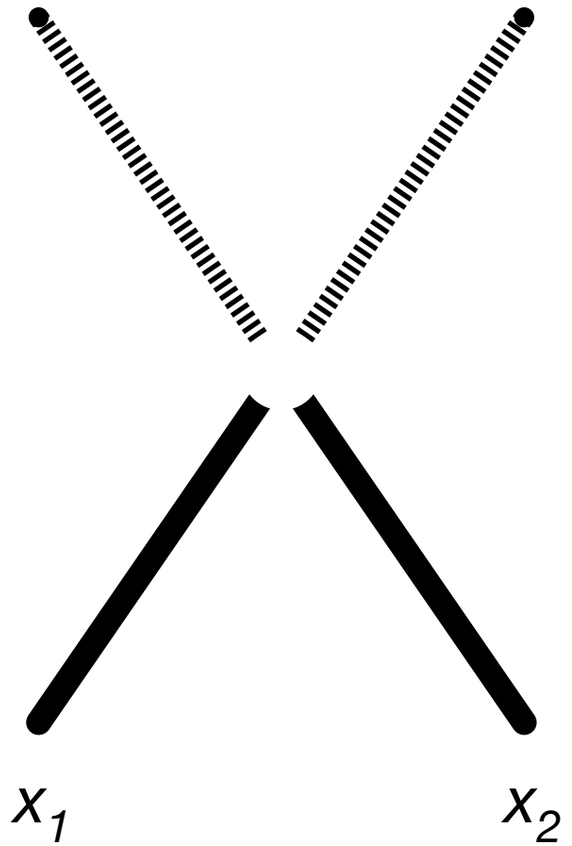
permutations in lower dimensions

M. Berry *et al.*: spin-statistics connection from geometric phase when permuting particles along paths?



2 dimensional

$P^2 \neq$ Id: *braiding* statistics: anyons



1 dimensional

fermions cannot pass

2-particle wave-function: distinguishable

two particles in (different) ortho-normal single-particle states $\varphi_a(x)$ and $\varphi_b(x)$

$$\psi_{12}(x_1, x_2) = \varphi_a(x_1)\varphi_b(x_2) \quad \text{or} \quad \psi_{21}(x_1, x_2) = \varphi_b(x_1)\varphi_a(x_2)$$

expectation value of particle distance: $M = (x_1\text{-}x_2)^2$

$$\left\langle (x_1 - x_2)^2 \right\rangle = \left\langle x_1^2 \right\rangle - 2\left\langle x_1 x_2 \right\rangle + \left\langle x_2^2 \right\rangle$$

normalized

$$\begin{aligned}
\left\langle x_1^2 \right\rangle_{12} &= \int dx_1\, x_1^2 |\varphi_a(x_1)|^2 \int dx_2 \quad |\varphi_b(x_2)|^2 = \left\langle x^2 \right\rangle_a \cdot \quad 1 \\
\left\langle x_2^2 \right\rangle_{12} &= \int dx_1 \quad |\varphi_a(x_1)|^2 \int dx_2\, x_2^2 |\varphi_b(x_2)|^2 = \quad 1 \quad \cdot \left\langle x^2 \right\rangle_b \\
\left\langle x_1 x_2 \right\rangle_{12} &= \int dx_1\, x_1 |\varphi_a(x_1)|^2 \int dx_2\, x_2 |\varphi_b(x_2)|^2 = \left\langle x \right\rangle_a \cdot \left\langle x \right\rangle_b
\end{aligned}$$

$$\left\langle (x_1 - x_2)^2 \right\rangle_{12} = \left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b - 2\left\langle x \right\rangle_a \left\langle x \right\rangle_b$$

$$= \left\langle (x_2 - x_1)^2 \right\rangle_{12} = \left\langle (x_1 - x_2)^2 \right\rangle_{21}$$

observable does not distinguish particles

2-particle wave-function: indistinguishable

symmetric / anti-symmetric wave-function

$$\psi_{\pm}(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\psi_{12}(x_1, x_2) \pm \psi_{21}(x_1, x_2)\right)$$

cross-terms between product wave-functions

observable does not distinguish particles

$$\langle M\rangle_{\pm} = \frac{1}{2}\Big(\langle M\rangle_{12} \pm \langle\psi_{12}|M|\psi_{21}\rangle \pm \langle\psi_{21}|M|\psi_{12}\rangle + \langle M\rangle_{21} \Big) = \langle M\rangle_{12} \pm \langle\psi_{12}|M|\psi_{21}\rangle$$

particle permutation: **exchange-terms**

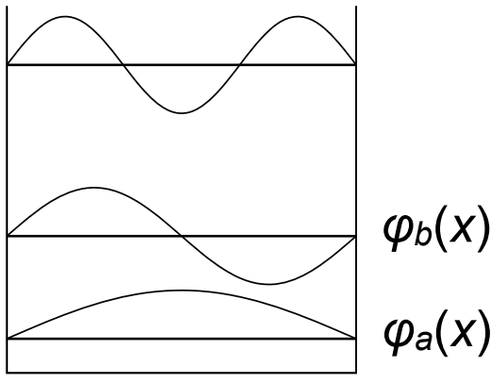
orthogonal

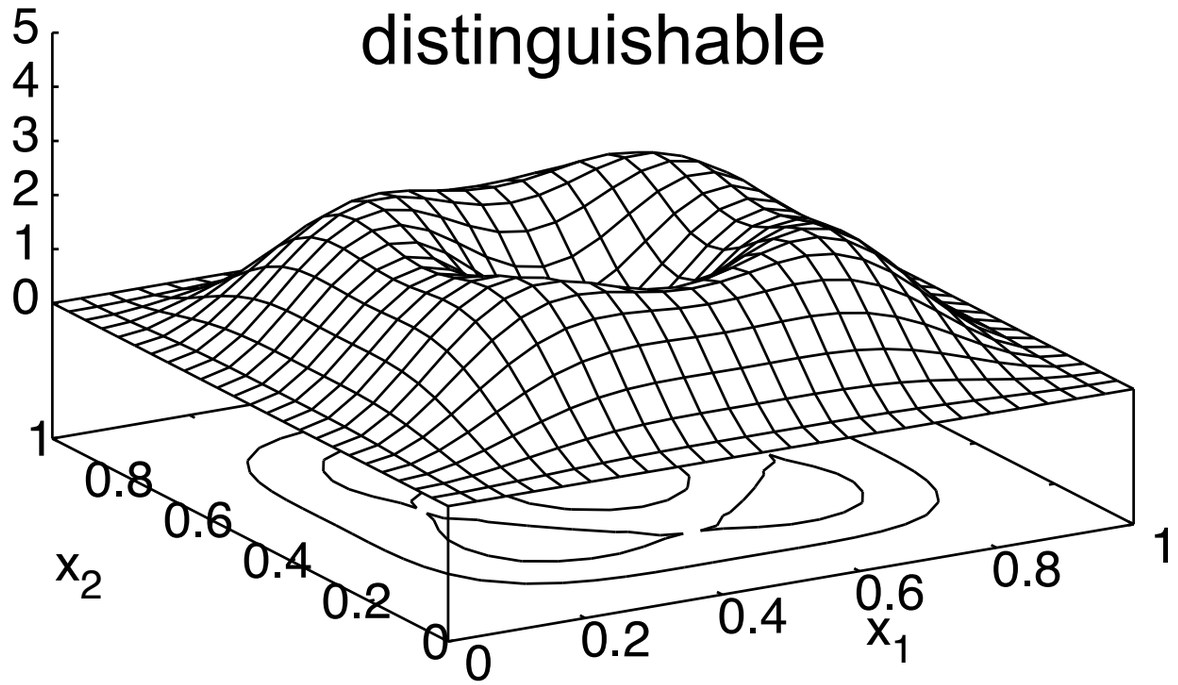
$$\begin{aligned}
\langle\psi_{12}|x_1^2|\psi_{21}\rangle &= \int dx_1\, x_1^2 \overline{\varphi_a(x_1)}\varphi_b(x_1) \int dx_2 \quad \overline{\varphi_b(x_2)}\varphi_a(x_2) = \langle x^2\rangle_{ab} \cdot \quad 0 \\
\langle\psi_{12}|x_2^2|\psi_{21}\rangle &= \int dx_1 \quad \overline{\varphi_a(x_1)}\varphi_b(x_1) \int dx_2\, x_2^2 \overline{\varphi_b(x_2)}\varphi_a(x_2) = \quad 0 \quad \cdot \langle x^2\rangle_{ba} \\
\langle\psi_{12}|x_1 x_2|\psi_{21}\rangle &= \int dx_1\, x_1 \overline{\varphi_a(x_1)}\varphi_b(x_1) \int dx_2\, x_2 \overline{\varphi_b(x_2)}\varphi_a(x_2) = \langle x\rangle_{ab} \cdot \langle x\rangle_{ba}
\end{aligned}$$

$$\left\langle (x_1 - x_2)^2 \right\rangle_{\pm} = \left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b - 2\left\langle x \right\rangle_a \left\langle x \right\rangle_b \mp \mathbf{2}\left|\langle \mathbf{x} \rangle_{\mathrm{ab}}\right|^2$$

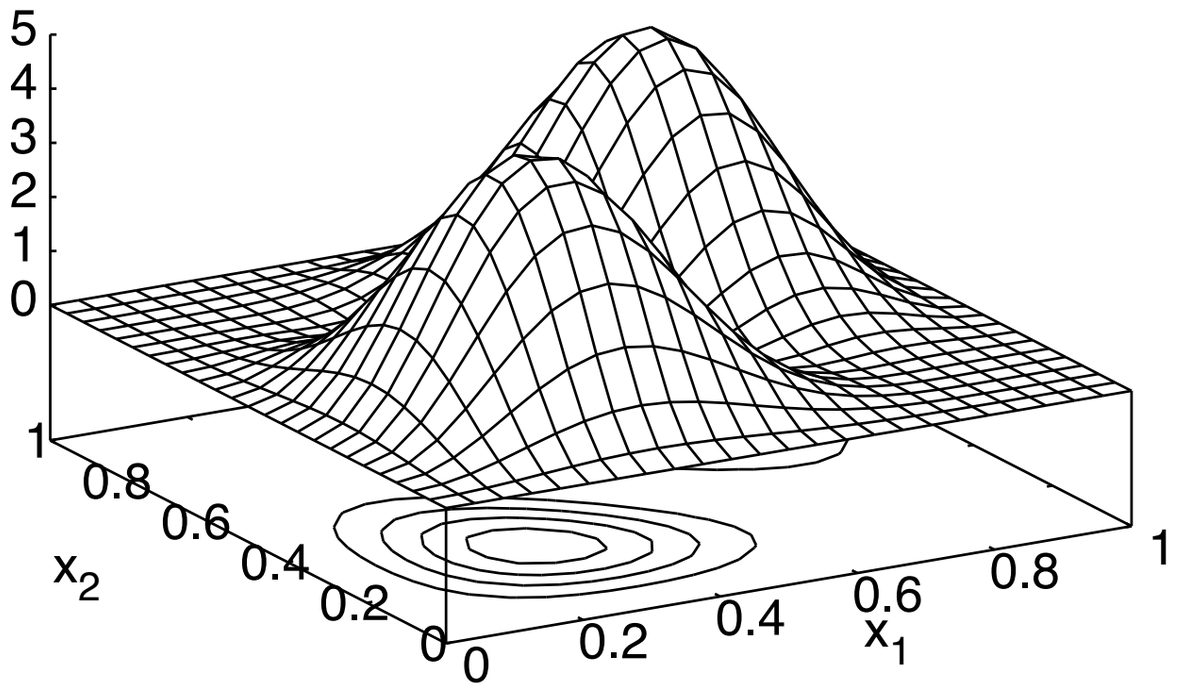
Bosons prefer company
Fermions keep their distance

probability density for 2 particles in a box

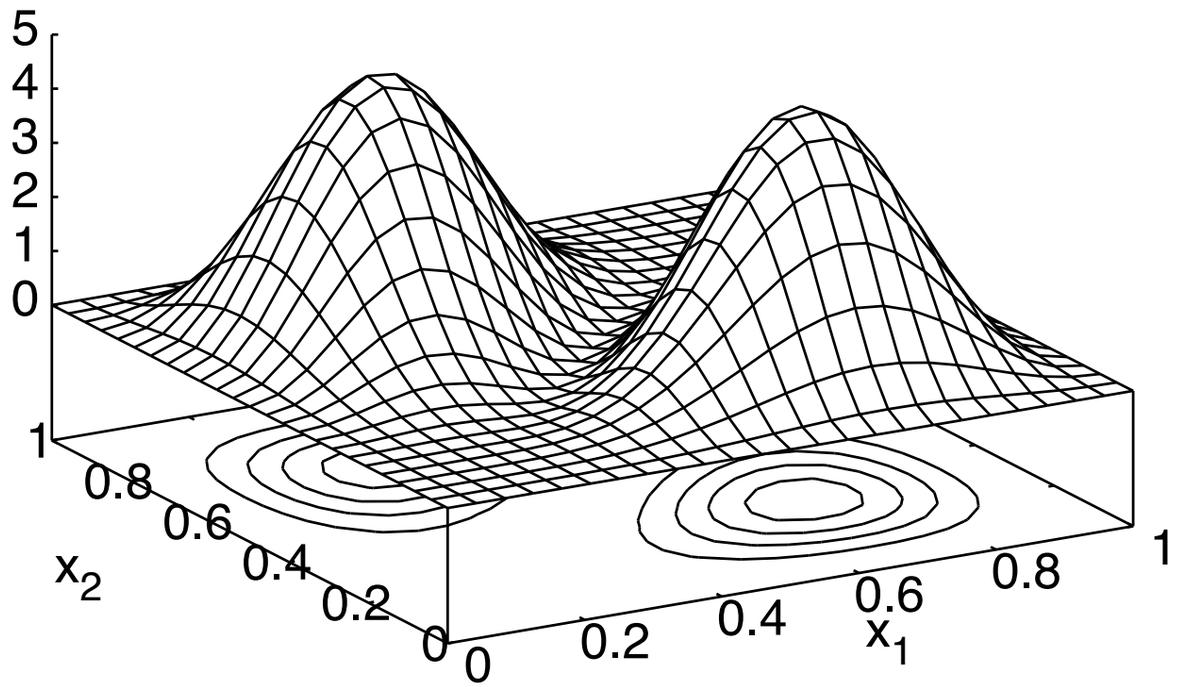




symmetric



anti-symmetric



How about electrons on the moon?

in principle we need to antisymmetrize the
wave-function for all electrons in the universe

really?

product states of states with zero overlap will not give an exchange contribution

$$\langle \psi_{12} | M | \psi_{21} \rangle = \int dx_1\, dx_2\, \overline{\varphi_a(x_1)\varphi_b(x_2)}\, M(x_1, x_2)\, \varphi_b(x_1)\varphi_a(x_2)$$

zero overlap makes electrons actually distinguishable by their coordinate

in practice:

can exclude electrons with negligible overlap from antisymmetrization

more practical example: **spin**
need not antisymmetrize electrons of different spin
when we are only interested in observables that do not change spin

Do we need the wave-function?

observable for N indistinguishable particles

$$M(\mathbf{x}) = M_0 + \sum_i M_1(x_i) + \frac{1}{2!}\sum_{i\neq j} M_2(x_i, x_j) + \frac{1}{3!}\sum_{i\neq j\neq k} M_3(x_i, x_j, x_k) + \cdots$$

$$= M_0 + \sum_i M_1(x_i) + \sum_{i<j} M_2(x_i, x_j) + \sum_{i<j<k} M_3(x_i, x_j, x_k) + \cdots$$

operators must be symmetric in particle coordinates,
if not they could be used to distinguish particles...

we use the wave-function as a **tool** for calculating observables

expectation values

expectation value

$$\langle M_1 \rangle = \int dx_1 \cdots dx_N \, \overline{\psi(x_1, \ldots, x_N)} \sum_i M_1(x_i) \, \psi(x_1, \ldots, x_N)$$

$$= N \int dx_1 \, M_1(x_1) \underbrace{\int dx_2 \cdots dx_N \, \overline{\psi(x_1, \ldots, x_N)} \, \psi(x_1, \ldots, x_N)}_{= \Gamma^{(1)}(x_1)}$$

for non-local operators, e.g. $M(x) = -\frac{1}{2} \Delta$

$$\langle M_1 \rangle = \int dx_1 \cdots dx_N \, \overline{\psi(x_1, \ldots, x_N)} \sum_i M_1(x_i) \, \psi(x_1, \ldots, x_N)$$

$$= N \int dx_1 \lim_{x_1' \to x_1} M_1(x_1) \underbrace{\int dx_2 \cdots dx_N \, \overline{\psi(x_1', \ldots, x_N)} \, \psi(x_1, \ldots, x_N)}_{= \Gamma^{(1)}(x_1'; x_1)}$$

reduced density matrices

p-body density matrix of *N*-electron state
for evaluation of expectation values of M_p

$$\Gamma^{(p)}(x'_1,\ldots,x'_p;x_1,\ldots,x_p) =$$

$$\binom{N}{p}\int dx_{p+1}\cdots dx_N\,\overline{\Psi(x'_1,\ldots,x'_p,x_{p+1},\ldots,x_N)}\,\Psi(x_1,\ldots,x_p,x_{p+1},\ldots,x_N)$$

Hermitean ($x'\leftrightarrow x$) and antisymmetric under permutations of the x_i (or x_i')

normalization sum-rule $\int dx_1\cdots dx_p\,\Gamma^{(p)}(x_1,\ldots,x_p;x_1,\ldots,x_p) = \binom{N}{p}$

allows evaluation of expectation values of observables M_q with $q \le p$:
recursion relation

$$\Gamma^{(p)}(x'_1,\ldots,x'_p;x_1,\ldots,x_p) = \frac{p+1}{N-p}\int dx_{p+1}\Gamma^{(p+1)}(x'_1,\ldots,x'_p,x_{p+1};x_1,\ldots,x_p,x_{p+1})$$

Coulson's challenge

external potential $$\langle V \rangle = \left\langle \psi \left| \sum_i V(r_i) \right| \psi \right\rangle = \int dx\, V(r)\, \Gamma^{(1)}(x;x)$$

kinetic energy $$\langle T \rangle = \left\langle \psi \left| -\frac{1}{2} \sum_i \Delta_{r_i} \right| \psi \right\rangle = -\frac{1}{2} \int dx\, \Delta_r\, \Gamma^{(1)}(x';x) \Big|_{x'=x}$$

Coulomb repulsion $$\langle U \rangle = \left\langle \psi \left| \sum_{i<j} \frac{1}{|r_i - r_j|} \right| \psi \right\rangle = \int dx\, dx'\, \frac{\Gamma^{(2)}(x,x';x,x')}{|r-r'|}$$

minimize $E_{tot} = \langle T \rangle + \langle V \rangle + \langle U \rangle$ as a function of the
2-body density matrix $\Gamma^{(2)}(x_1',x_2';\, x_1,x_2)$
instead of the N-electron wave-function $\Psi(x_1,\ldots,\, x_N)$

representability problem:

what function $\Gamma(x_1',x_2';\, x_1,x_2)$ is a fermionic 2-body density-matrix?

exchange-correlation hole

electron density: $\Gamma(x; x) = n(x)$

conditional electron density: $2\Gamma(x, x'; x, x') = n(x, x')$

electron density at *x'* given that an electron is at *x*

Coulomb repulsion $\langle U \rangle = \int dx\, dx'\, \frac{\Gamma^{(2)}(x, x'; x, x')}{|r - r'|} = \frac{1}{2} \int dx\, dx' \frac{n(x, x')}{|r - r'|}$

rewrite in terms of Hartree energy

(how $\langle U \rangle$ differs from mean-field)

$$n(x, x') = n(x)n(x')\, g(x, x') = n(x)n(x') + n(x)n(x')\, (g(x, x') - 1)$$

pair correlation function

Hartree term

exchange-correlation hole

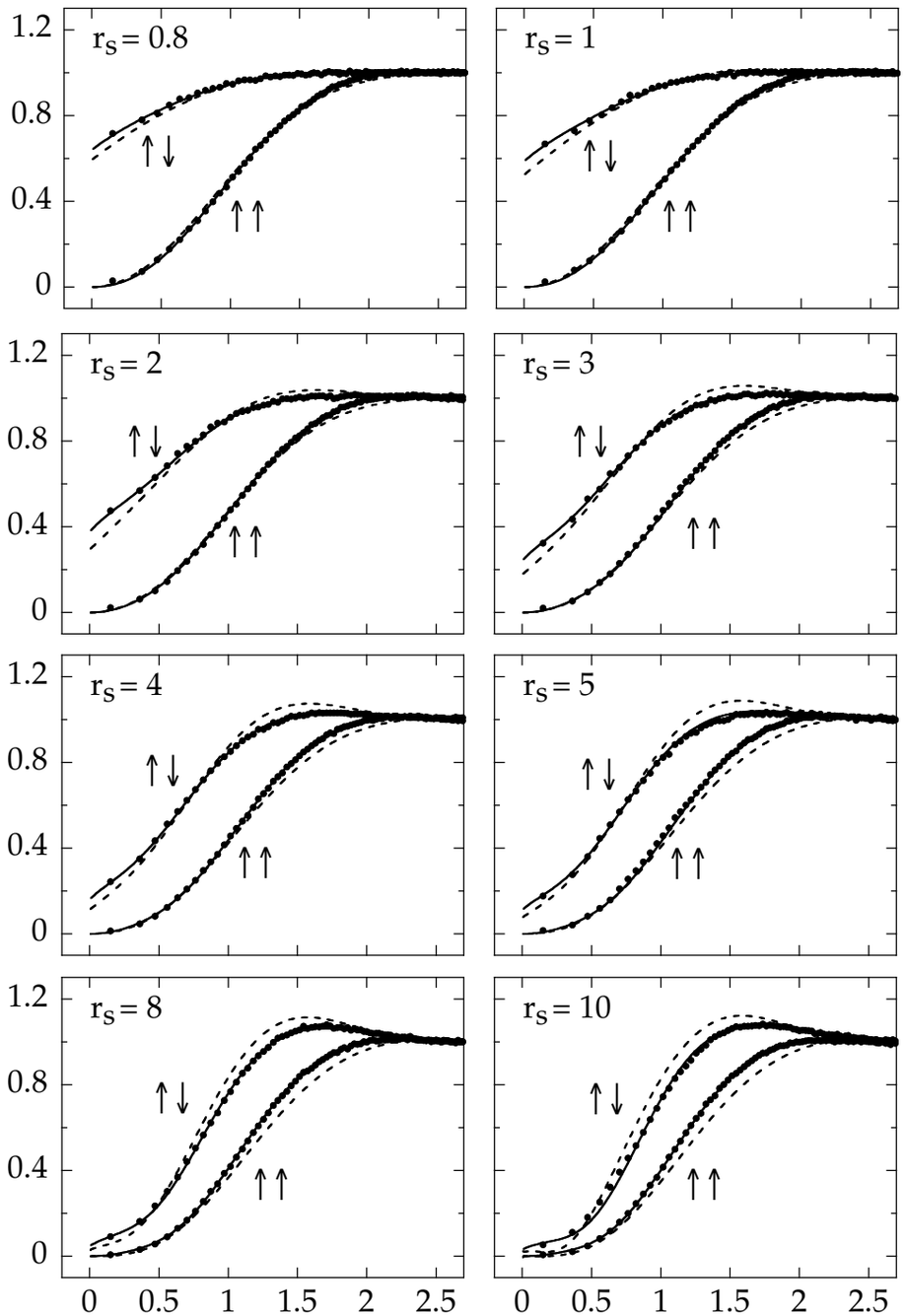
sum rule

$$\int dx'\, n(x, x') = n(x)\, (N - 1)$$

$$\int dx'\, n(x')\, \big(g(x, x') - 1\big) = -1$$

exchange-correlation holes from QMC

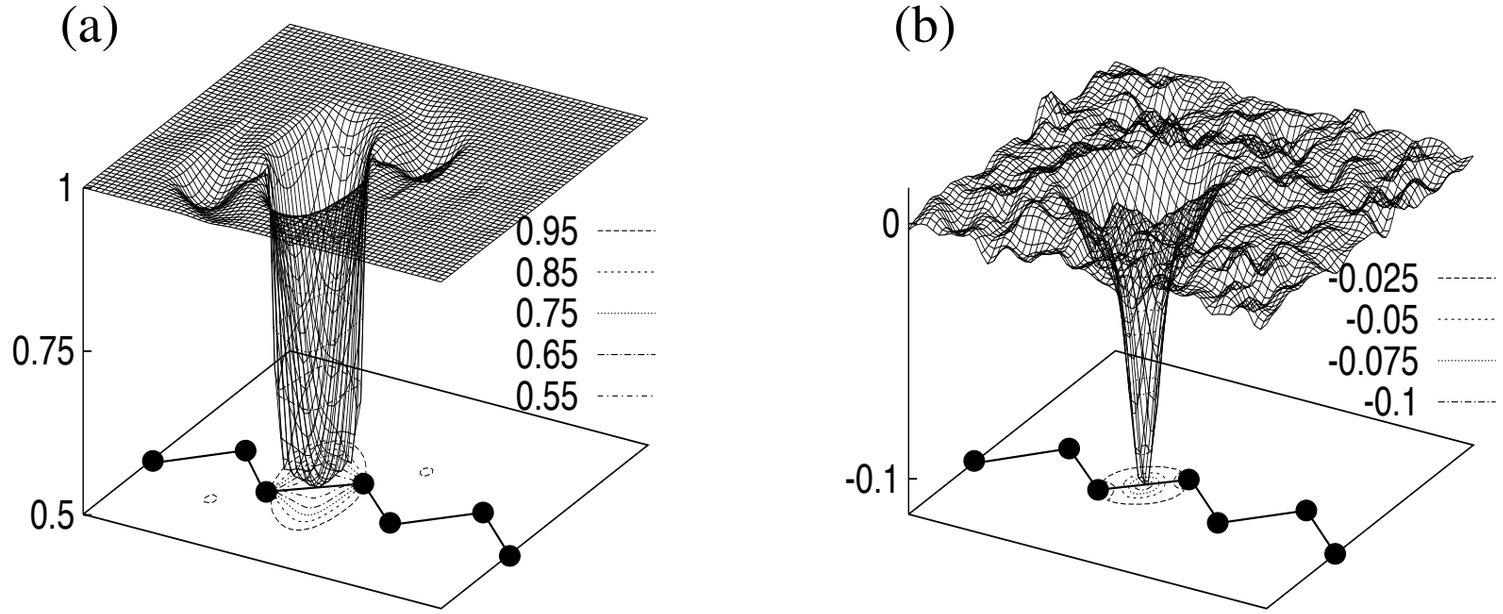
homogeneous electron gas $g_{xc}^{\sigma\sigma'}(r/r_s)$



G. Ortiz, M. Harris, P. Ballone, Phys. Rev. Lett. 82, 5317 (1999)
P. Gori-Giorgi, F. Sacchetti, G.B. Bachelet, Phys. Rev. B 61, 7353 (2000)

(110) plane of Si, electron at bond center

$g_x^{\mathrm{VMC}}(\vec{r})$ $\qquad$ $g_c^{\mathrm{VMC}}(\vec{r})$



R.Q. Hood, M.Y. Chou, A.J. Williamson, G. Rajagopal, R.J. Needs, W.M.C. Foulkes, Phys. Rev. B 57, 8972 (1998)

antisymmetric wave-functions

(anti)symmetrization of N-body wave-function: $N!$ operations

$$\mathcal{S}_\pm \, \psi(x_1, \ldots, x_N) := \frac{1}{\sqrt{N!}} \sum_P (\pm 1)^P \psi\left(x_{p(1)}, \ldots, x_{p(N)}\right)$$

antisymmetrization of products of single-particle states

$$\mathcal{S}_- \, \varphi_{\alpha_1}(x_1) \cdots \varphi_{\alpha_N}(x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

much more efficient: scales only polynomially in N

Slater determinant: $\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N)$

Slater determinants

$$\Phi_{\alpha_1 \cdots \alpha_N}(\mathbf{x}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

simple examples

N=1: $\Phi_{\alpha_1}(x_1) = \varphi_{\alpha_1}(x_1)$

N=2: $\Phi_{\alpha_1\alpha_2}(x) = \frac{1}{\sqrt{2}}\left(\varphi_{\alpha_1}(x_1)\varphi_{\alpha 2}(x_2) - \varphi_{\alpha_2}(x_1)\varphi_{\alpha_1}(x_2)\right)$

expectation values need only one antisymmetrized wave-function:

$$\int d\mathbf{x}\, \overline{(\mathcal{S}_\pm \Psi_a(\mathbf{x}))}\, M(\mathbf{x})\, (\mathcal{S}_\pm \Psi_b(\mathbf{x})) = \int d\mathbf{x} \left(\sqrt{N!}\, \overline{\Psi_a(\mathbf{x})}\right) M(\mathbf{x})\, (\mathcal{S}_\pm \Psi_b(\mathbf{x}))$$

remember: $M(x_1, \ldots, x_N)$ symmetric in arguments

corollary: overlap of Slater determinants:

$$\int dx_1 \cdots dx_N\, \overline{\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N)}\, \Phi_{\beta_1 \cdots \beta_N}(x_1, \ldots, x_N) = \det\left(\langle \varphi_{\alpha_n} | \varphi_{\beta_m} \rangle\right)$$

basis of Slater determinants

$$\int dx_1 \cdots dx_N \, \overline{\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N)} \, \Phi_{\beta_1 \cdots \beta_N}(x_1, \ldots, x_N) = \det\Big(\langle \varphi_{\alpha_n} | \varphi_{\beta_m} \rangle \Big)$$

Slater determinants of ortho-normal orbitals $\varphi_a(x)$ are normalized

a Slater determinant with two identical orbital indices vanishes (Pauli principle)

Slater determinants that only differ in the order of the orbital indices are (up to a sign) identical

define **convention for ordering indices**, e.g. $\alpha_1 < \alpha_2 < \ldots < \alpha_N$

given K ortho-normal orbitals $\{ \varphi_a(x) \mid \alpha \in \{1, \ldots, K\} \}$

the $K! \,/\, N! \, (K-N)!$ Slater determinants

$$\left\{ \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N) \,\middle|\, \alpha_1 < \alpha_2 < \cdots < \alpha_N \in \{1, \ldots, K\} \right\}$$

are an ortho-normal basis of the N-electron Hilbert space

reduced density-matrices: *p*=1

Laplace expansion

$$\Phi_{\alpha_1\cdots\alpha_N}(x_1,\ldots,x_N) = \frac{1}{\sqrt{N}}\sum_{n=1}^{N}(-1)^{1+n}\,\varphi_{\alpha_n}(x_1)\,\Phi_{\alpha_{i\neq n}}(x_2,\ldots,x_N)$$

$$\Gamma^{(1)}(x';x) = \frac{1}{N}\sum_{n,m}(-1)^{n+m}\,\overline{\varphi_{\alpha_n}(x')}\,\varphi_{\alpha_m}(x)\,\frac{\det(\langle\varphi_{\alpha_{j\neq n}}|\varphi_{\alpha_{k\neq m}}\rangle)}{\det(\langle\varphi_{\alpha_j}|\varphi_{\alpha_k}\rangle)}$$

for ortho-normal orbitals

$$\Gamma^{(1)}(x';x) = \sum_n \overline{\varphi_{\alpha_n}(x')}\,\varphi_{\alpha_n}(x) \quad \text{and} \quad n(x) = \sum_n |\varphi_n(x)|^2$$

reduced density-matrices

expansion of determinant in product of determinants

$$\Phi_{\alpha_1\cdots\alpha_N}(\mathbf{x}) = \frac{1}{\sqrt{\binom{N}{p}}} \sum_{n_1<n_2<\cdots<n_p} (-1)^{1+\sum_i n_i} \Phi_{\alpha_{n_1}\cdots\alpha_{n_p}}(x_1,\ldots,x_p)\Phi_{\alpha_{i\notin\{n_1,\ldots,n_p\}}}(x_{p+1},\ldots,x_N)$$

p-electron Slater det $(N-p)$-electron Slater det

express p-body density matrix in terms of p-electron Slater determinants:

$$\Gamma^{(1)}(x';x) = \sum_n \overline{\varphi_{\alpha_n}(x')}\,\varphi_{\alpha_n}(x) \quad \text{and} \qquad n(x) = \sum_n |\varphi_n(x)|^2$$

$$\Gamma^{(2)}(x_1'x_2';x_1,x_2) = \sum_{n<m} \overline{\Phi_{\alpha_n,\alpha_m}(x_1',x_2')}\,\Phi_{\alpha_n,\alpha_m}(x_1,x_2)$$

$$\text{and} \quad n(x_1,x_2) = \sum_{n,m} |\Phi_{\alpha_n,\alpha_m}(x_1,x_2)|^2$$

in particular $$n(x_1,x_2) = \sum_{n,m} \left| \frac{1}{\sqrt{2}} \Big(\varphi_{\alpha_n}(x_1)\varphi_{\alpha_m}(x_2) - \varphi_{\alpha_m}(x_2)\varphi_{\alpha_n}(x_1) \Big) \right|^2$$

$$= \sum_{n,m} \Big(|\varphi_{\alpha_n}(x_1)|^2 |\varphi_{\alpha_m}(x_2)|^2 - \overline{\varphi_{\alpha_n}(x_1)}\varphi_{\alpha_m}(x_1)\,\overline{\varphi_{\alpha_m}(x_2)}\varphi_{\alpha_n}(x_2) \Big)$$

exchange hole

pair correlation function for Slater determinant $\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N)$

$$g(x_1, x_2) = 1 - \frac{\sum_{n,m} \overline{\varphi_{\alpha_n}(x_1)} \varphi_{\alpha_m}(x_1)\, \overline{\varphi_{\alpha_m}(x_2)} \varphi_{\alpha_n}(x_2)}{n(x_1)\, n(x_2)}$$

homogeneous electron gas: $\varphi_{k\sigma}(x) = \frac{1}{\sqrt{2\pi}}\, e^{ik\cdot x}\, \chi_\sigma \quad$ with $|k| \le k_F$

$$g(0, \sigma; r, \sigma) - 1 = -\frac{1}{(n/2)^2} \frac{1}{(2\pi)^6} \int_{|k|,|k'| \le k_F} d^3k\, d^3k'\, e^{i(k-k')\cdot r}$$

translation invariance
only same spin

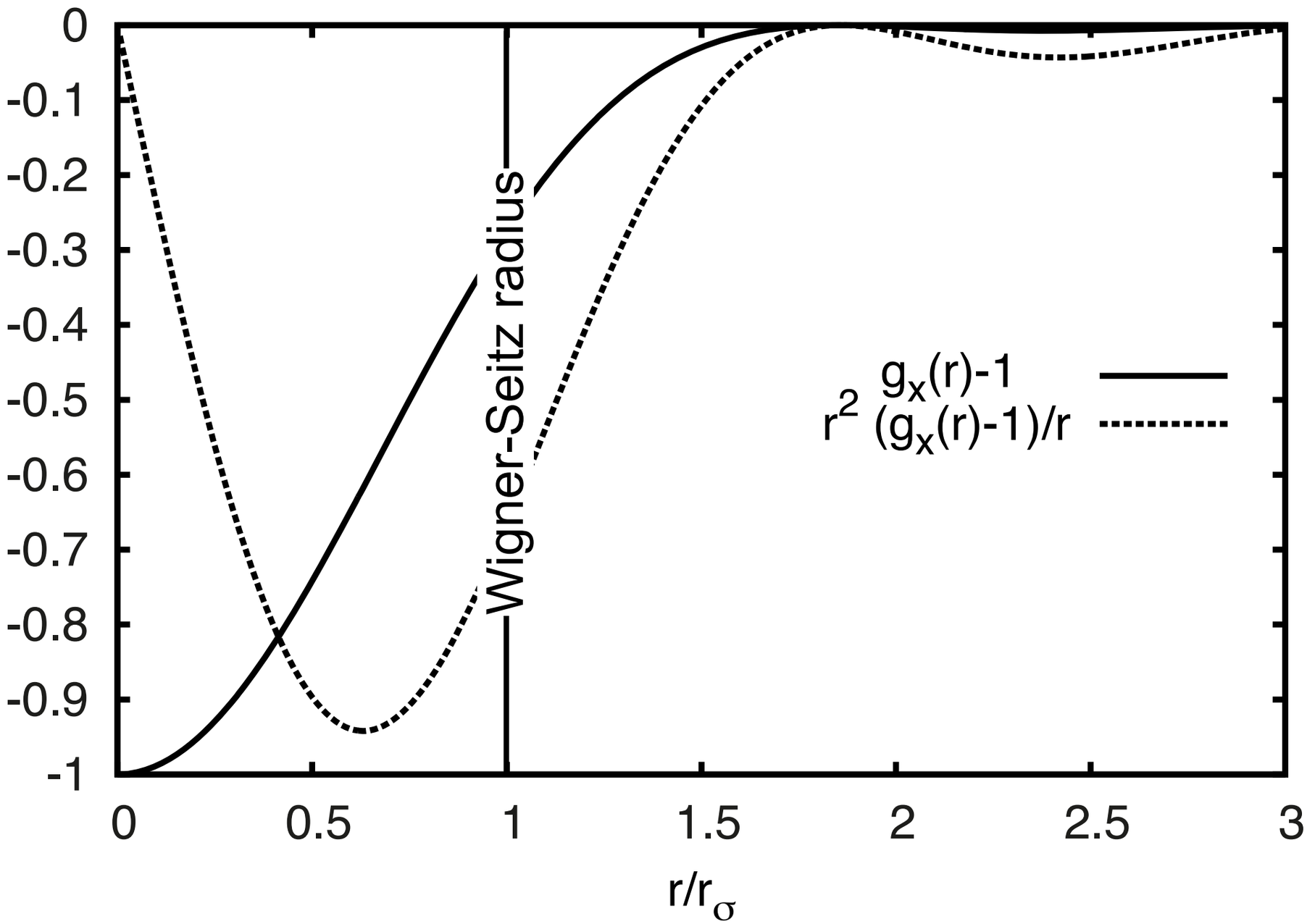
$$= -\left(\frac{3}{4\pi k_F^3}\right)^2 \left| 2\pi \int_0^{k_F} dk\, k^2 \int_{-1}^{1} d\cos\theta\, e^{ikr\cos\theta} \right|^2$$

$$= -9\, \frac{\big(\sin(k_F r) - k_F r \cos(k_F r)\big)^2}{(k_F r)^6}$$

exchange hole
for electrons of same spin

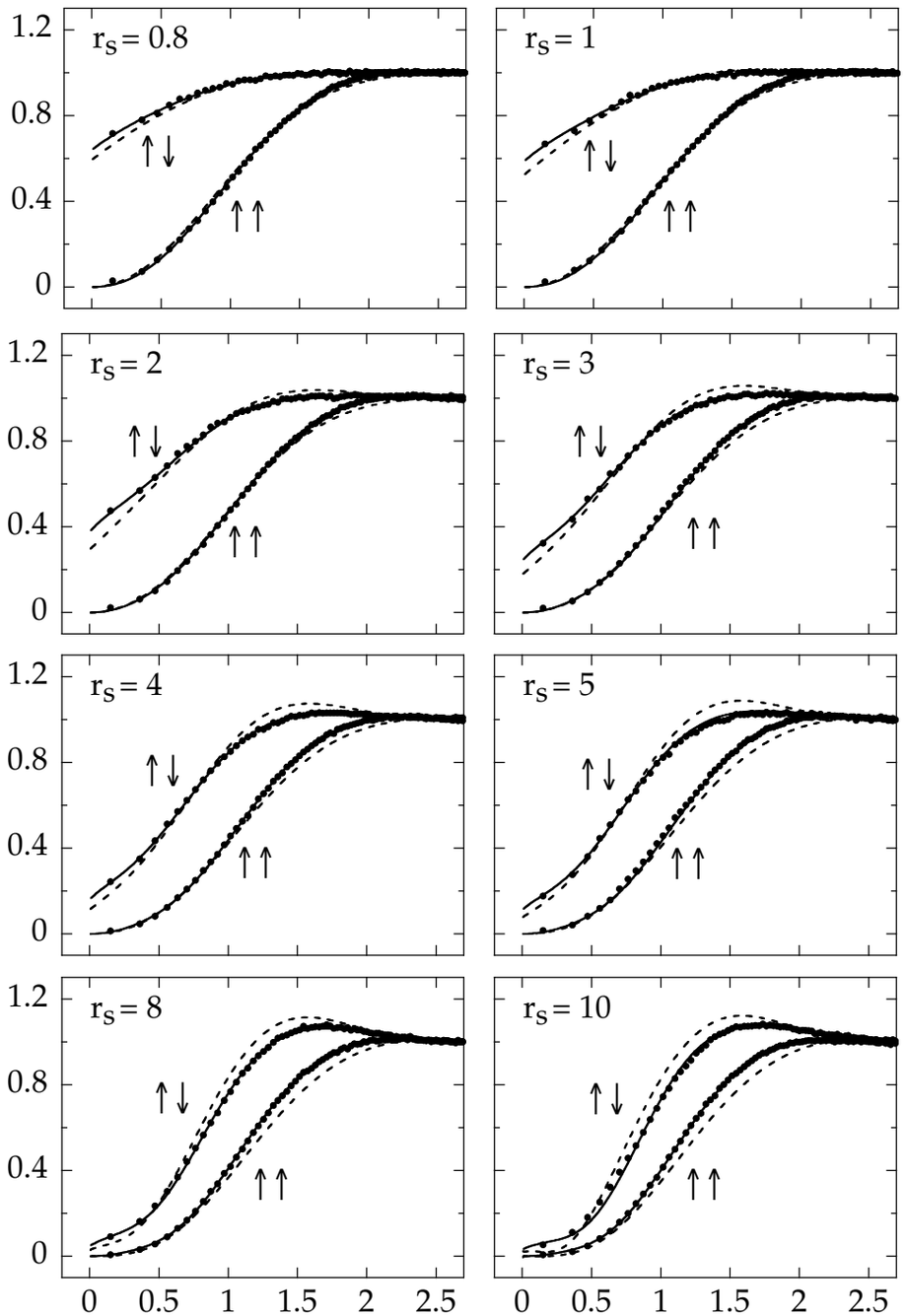
exchange hole

$$g(0,\sigma;r,\sigma) - 1 = -9\,\frac{\left(\sin(k_F r) - k_F r\cos(k_F r)\right)^2}{(k_F r)^6}$$



exchange-correlation holes from QMC

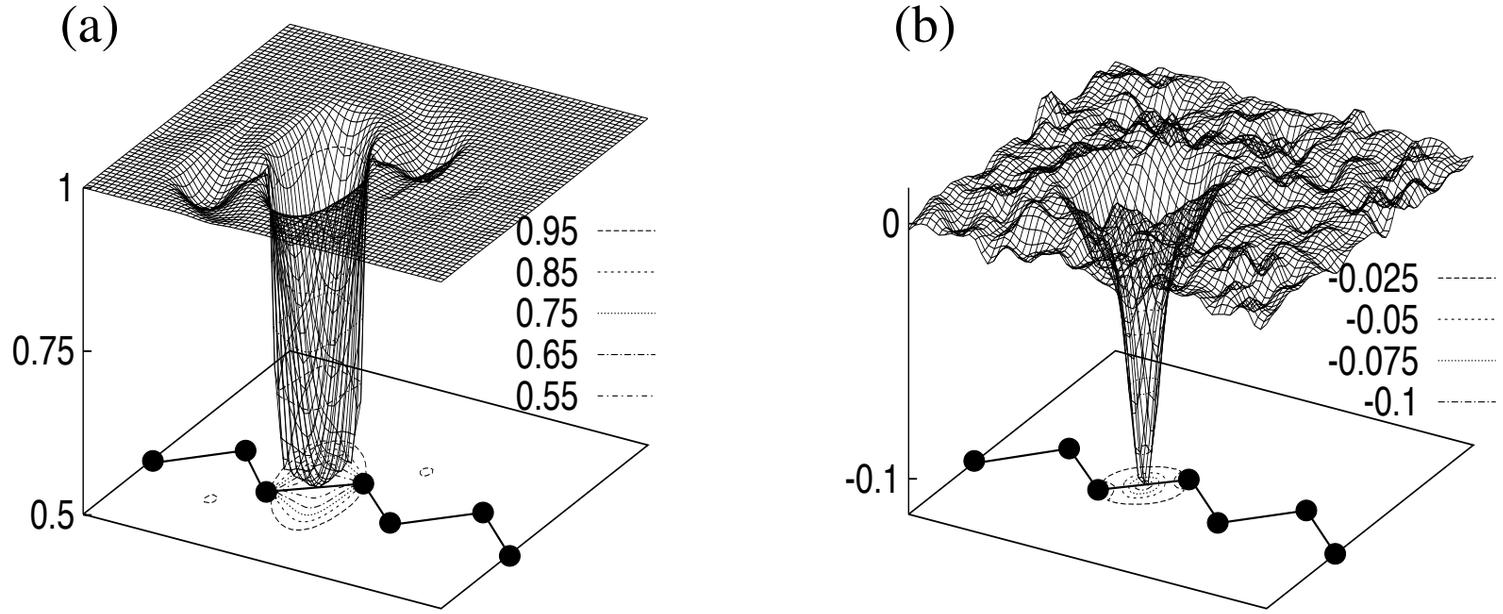
homogeneous electron gas $g_{xc}^{\sigma\sigma'}(r/r_s)$



G. Ortiz, M. Harris, P. Ballone, Phys. Rev. Lett. 82, 5317 (1999)
P. Gori-Giorgi, F. Sacchetti, G.B. Bachelet, Phys. Rev. B 61, 7353 (2000)

(110) plane of Si, electron at bond center

$g_x^{\mathrm{VMC}}(\vec{r})$ $\qquad$ $g_c^{\mathrm{VMC}}(\vec{r})$



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Slater determinants

Hartree-Fock method:

know how to represent 2-body density matrix derived from Slater determinant

$$\Gamma^{(2)}(x_1' x_2'; x_1, x_2) = \sum_{n<m} \overline{\Phi_{\alpha_n,\alpha_m}(x_1', x_2')}\, \Phi_{\alpha_n,\alpha_m}(x_1, x_2)$$

minimize (á la Coulson)

could generalize reduced density matrices by introducing density matrices for expectation values between different Slater determinants

see e.g. Per-Olov Löwdin, Phys. Rev. **97**, 1474 (1955)

still, always have to deal with determinants and signs.

there must be a better way...

second quantization: motivation

keeping track of all these signs...

Slater determinant $\Phi_{\alpha\beta}(x_1, x_2) = \frac{1}{\sqrt{2}} \left(\varphi_\alpha(x_1)\varphi_\beta(x_2) - \varphi_\beta(x_1)\varphi_\alpha(x_2)\right)$

corresponding Dirac state $|\alpha, \beta\rangle = \frac{1}{\sqrt{2}} \left(|\alpha\rangle|\beta\rangle - |\beta\rangle|\alpha\rangle\right)$

use operators $|\alpha, \beta\rangle = c_\beta^\dagger c_\alpha^\dagger |0\rangle$

position of operators encodes signs

$$c_\beta^\dagger c_\alpha^\dagger |0\rangle = |\alpha, \beta\rangle = -|\beta, \alpha\rangle = -c_\alpha^\dagger c_\beta^\dagger |0\rangle$$

product of operators changes sign when commuted: anti-commutation

anti-commutator $\{A, B\} := A\,B + B\,A$

second quantization: motivation

specify *N*-electron states using operators

N=0: $|0\rangle$ (vacuum state)

normalization: $\langle 0|0\rangle = 1$

N=1: $|\alpha\rangle = c_\alpha^\dagger|0\rangle$ (creation operator adds one electron)

normalization: $\langle\alpha|\alpha\rangle = \langle 0|c_\alpha c_\alpha^\dagger|0\rangle$

overlap: $\langle\alpha|\beta\rangle = \langle 0|c_\alpha c_\beta^\dagger|0\rangle$

adjoint of creation operator removes one electron: annihilation operator

$$c_\alpha|0\rangle = 0 \text{ and } c_\alpha c_\beta^\dagger = \pm c_\beta^\dagger c_\alpha + \langle\alpha|\beta\rangle$$

N=2: $|\alpha,\beta\rangle = c_\beta^\dagger c_\alpha^\dagger|0\rangle$

antisymmetry: $c_\alpha^\dagger c_\beta^\dagger = -c_\beta^\dagger c_\alpha^\dagger$

second quantization: formalism

vacuum state $|0\rangle$

and

set of operators c_α related to single-electron states $\varphi_\alpha(x)$

defined by:

$$c_\alpha|0\rangle = 0 \qquad \left\{c_\alpha, c_\beta\right\} = 0 = \left\{c_\alpha^\dagger, c_\beta^\dagger\right\}$$

$$\langle 0|0\rangle = 1 \qquad \left\{c_\alpha, c_\beta^\dagger\right\} = \langle\alpha|\beta\rangle$$

second quantization: field operators

creation/annihilation operators in real-space basis

$\hat{\psi}^\dagger(x)$ with $x = (r, \sigma)$ creates electron of spin σ at position r

$$\text{then} \quad c_\alpha^\dagger = \int dx\, \varphi_\alpha(x) \hat{\psi}^\dagger(x)$$

put electron at x with amplitude $\varphi_a(x)$

$\{\varphi_{\alpha_n}(x)\}$ complete orthonormal set $\sum_j \overline{\varphi_{\alpha_j}(x)}\, \varphi_{\alpha_j}(x') = \delta(x - x')$

$$\hat{\psi}(x) = \sum_n \varphi_{\alpha_n}(x)\, c_{\alpha_n}$$

they fulfill the standard anti-commutation relations

$$\left\{\hat{\psi}(x), \hat{\psi}(x')\right\} = 0 = \left\{\hat{\psi}^\dagger(x), \hat{\psi}^\dagger(x')\right\}$$
$$\left\{\hat{\psi}(x), \hat{\psi}^\dagger(x')\right\} = \delta(x - x')$$

second quantization: Slater determinants

$$\Phi_{\alpha_1\alpha_2\ldots\alpha_N}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \left\langle 0 \left| \hat{\psi}(x_1)\hat{\psi}(x_2)\ldots\hat{\psi}(x_N)\, c^\dagger_{\alpha_N} \ldots c^\dagger_{\alpha_2} c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

proof by induction

N=0: $\Phi() = \langle 0|0\rangle = 1$

N=1: $\left\langle 0 \left| \hat{\psi}(x_1)\, c^\dagger_{\alpha_1} \right| 0 \right\rangle = \left\langle 0 \left| \varphi_{\alpha_1}(x_1) - c^\dagger_{\alpha_1}\hat{\psi}(x_1) \right| 0 \right\rangle = \varphi_{\alpha_1}(x_1)$

using $\{\hat{\psi}(x), c^\dagger_\alpha\} = \int dx'\, \varphi_\alpha(x') \left\{\hat{\psi}(x), \hat{\psi}^\dagger(x')\right\} = \varphi_\alpha(x)$

N=2: $\left\langle 0 \left| \hat{\psi}(x_1)\hat{\psi}(x_2)\, c^\dagger_{\alpha_2} c^\dagger_{\alpha_1} \right| 0 \right\rangle$

$$= \left\langle 0 \left| \hat{\psi}(x_1) \left(\varphi_{\alpha_2}(x_2) - c^\dagger_{\alpha_2}\hat{\psi}(x_2)\right) c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

$$= \left\langle 0 \left| \hat{\psi}(x_1) c^\dagger_{\alpha_1} \right| 0 \right\rangle \varphi_{\alpha_2}(x_2) - \left\langle 0 \left| \hat{\psi}(x_1) c^\dagger_{\alpha_2} \hat{\psi}(x_2) c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

$$= \varphi_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_2) - \varphi_{\alpha_2}(x_1)\varphi_{\alpha_1}(x_2)$$

second quantization: Slater determinants

general N: commute $\Psi(x_N)$ to the right

$$\left\langle 0 \left| \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1}) \hat{\psi}(x_N)\, c^\dagger_{\alpha_N} c^\dagger_{\alpha_{N-1}} \ldots c^\dagger_{\alpha_1} \right| 0 \right\rangle \;=$$

$$+ \quad \left\langle 0 \left| \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1})\, c^\dagger_{\alpha_{N-1}} \ldots c^\dagger_{\alpha_1} \right| 0 \right\rangle \quad \varphi_{\alpha_N}(x_N)$$

$$- \quad \left\langle 0 \left| \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1}) \prod_{n \neq N-1} c^\dagger_{\alpha_n} \right| 0 \right\rangle \quad \varphi_{\alpha_{N-1}}(x_N)$$

$$\vdots$$

$$(-1)^N \quad \left\langle 0 \left| \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1})\, c^\dagger_{\alpha_N} \quad \ldots \quad c^\dagger_{\alpha_2} \right| 0 \right\rangle \quad \varphi_{\alpha_1}(x_N)$$

Laplace expansion in terms of *N-1* dim determinants wrt last line of

$$= \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

second quantization: Dirac notation

product state $c^\dagger_{\alpha_N} \cdots c^\dagger_{\alpha_2} c^\dagger_{\alpha_1} |0\rangle$

corresponds to

Slater determinant $\Phi_{\alpha_1 \alpha_2 \ldots \alpha_N}(x_1, x_2, \ldots, x_N)$

as

Dirac state $|\alpha\rangle$

corresponds to

wave-function $\varphi_\alpha(x)$

second quantization: expectation values

expectation value of *N*-body operator wrt *N*-electron Slater determinants

$$\int dx_1 \cdots dx_N \, \overline{\Phi_{\beta_1 \cdots \beta_N}(x_1, \cdots, x_N)} M(x_1, \cdots, x_N) \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \cdots, x_N)$$

$$= \left\langle 0 \left| c_{\beta_1} \cdots c_{\beta_N} \, \hat{M} \, c^\dagger_{\alpha_N} \cdots c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

$$\int dx_1 \cdots dx_N \frac{1}{\sqrt{N!}} \left\langle 0 \left| c_{\beta_1} \cdots c_{\beta_N} \, \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \right| 0 \right\rangle M(x_1, \cdots, x_N) \frac{1}{\sqrt{N!}} \left\langle 0 \left| \hat{\psi}(x_1) \cdots \hat{\psi}(x_N) \, c^\dagger_{\alpha_N} \cdots c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

$$= \left\langle 0 \left| c_{\beta_1} \cdots c_{\beta_N} \, \frac{1}{N!} \int dx_1 \cdots dx_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) M(x_1, \cdots, x_N) \hat{\psi}(x_1) \cdots \hat{\psi}(x_N) \, c^\dagger_{\alpha_N} \cdots c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

$|0\rangle\langle 0| = \mathbb{1}$ on 0-electron space

collecting field-operators to obtain *M* in second quantization:

$$\hat{M} = \frac{1}{N!} \int dx_1 \cdots x_N \, \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \, M(x_1, \cdots, x_N) \, \hat{\psi}(x_1) \cdots \hat{\psi}(x_N)$$

apparently dependent on number *N* of electrons!

second quantization: zero-body operator

zero-body operator $M_0(x_1,\ldots x_N)$=1 independent of particle coordinates

second quantized form for operating on N-electron states:

$$\hat{M}_0 = \frac{1}{N!}\int dx_1 dx_2 \cdots x_N \, \hat{\psi}^\dagger(x_N)\cdots\hat{\psi}^\dagger(x_2)\hat{\psi}^\dagger(x_1)\,\hat{\psi}(x_1)\hat{\psi}(x_2)\cdots\hat{\psi}(x_N)$$

$$= \frac{1}{N!}\int \quad dx_2 \cdots x_N \, \hat{\psi}^\dagger(x_N)\cdots\hat{\psi}^\dagger(x_2) \qquad \hat{N} \qquad \hat{\psi}(x_2)\cdots\hat{\psi}(x_N)$$

$$= \frac{1}{N!}\int \quad dx_2 \cdots x_N \, \hat{\psi}^\dagger(x_N)\cdots\hat{\psi}^\dagger(x_2) \qquad 1 \qquad \hat{\psi}(x_2)\cdots\hat{\psi}(x_N)$$

$$\vdots$$

$$= \frac{1}{N!}\, 1\cdot 2 \;\cdots\; N = 1$$

only(!) when operating on N-electron state

using $\int dx\, \hat{\psi}^\dagger(x)\hat{\psi}(x) = \hat{N}$

result independent of N

second quantization: one-body operators

one-body operator $M(x_1, \ldots, x_N) = \sum_j M_1(x_j)$

$$\hat{M}_1 = \frac{1}{N!} \int dx_1 \cdots dx_N \, \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \sum_j M_1(x_j) \; \hat{\psi}(x_1) \cdots \hat{\psi}(x_N)$$

$$= \frac{1}{N!} \sum_j \int dx_j \, \hat{\psi}^\dagger(x_j) \, M_1(x_j) \, (N-1)! \; \hat{\psi}(x_j)$$

$$= \frac{1}{N} \sum_j \int dx_j \, \hat{\psi}^\dagger(x_j) \, M_1(x_j) \, \hat{\psi}(x_j)$$

$$= \int dx \quad \hat{\psi}^\dagger(x) \;\; M_1(x) \;\; \hat{\psi}(x)$$

result independent of N

expand in complete orthonormal set of orbitals

$$\hat{M}_1 = \sum_{n,m} \int dx \, \overline{\varphi_{\alpha_n}(x)} \, M(x) \, \varphi_{\alpha_m}(x) \; c^\dagger_{\alpha_n} c_{\alpha_m} = \sum_{n,m} \langle \alpha_n | M_1 | \alpha_m \rangle \; c^\dagger_{\alpha_n} c_{\alpha_m}$$

second quantization: two-body operators

two-body operator $M(x_1, \ldots, x_N) = \sum_{i<j} M_2(x_i, x_j)$

$$\hat{M}_2 = \frac{1}{N!} \int dx_1 \cdots dx_N \, \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \sum_{i<j} M_2(x_i, x_j) \; \hat{\psi}(x_1) \cdots \hat{\psi}(x_N)$$

$$= \frac{1}{N!} \sum_{i<j} \int dx_i dx_j \, \hat{\psi}^\dagger(x_j) \hat{\psi}^\dagger(x_i) \, M_2(x_i, x_j) \, (N-2)! \; \hat{\psi}(x_i) \hat{\psi}(x_j)$$

$$= \frac{1}{N(N-1)} \sum_{i<j} \int dx_i dx_j \, \hat{\psi}^\dagger(x_j) \hat{\psi}^\dagger(x_i) \, M_2(x_i, x_j) \, \hat{\psi}(x_i) \hat{\psi}(x_j)$$

$$= \frac{1}{2} \int dx \; dx' \; \hat{\psi}^\dagger(x') \; \hat{\psi}^\dagger(x) \;\; M_2(x, x') \;\; \hat{\psi}(x) \; \hat{\psi}(x')$$

result independent of N

expand in complete orthonormal set of orbitals

$$\hat{M}_2 = \frac{1}{2} \sum_{n,n',m,m'} \int dx dx' \, \overline{\varphi_{\alpha_{n'}}(x') \varphi_{\alpha_n}(x)} \, M_2(x, x') \, \varphi_{\alpha_m}(x) \varphi_{\alpha_{m'}}(x') \; c^\dagger_{\alpha_{n'}} c^\dagger_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}}$$

$$= \frac{1}{2} \sum_{n,n',m,m'} \langle \alpha_n \alpha_{n'} | M_2 | \alpha_m \alpha_{m'} \rangle \; c^\dagger_{\alpha_{n'}} c^\dagger_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}}$$

electron-hole transformation

consider spin-orbital $\varphi_a(x)$

$|0\rangle$ vacuum state

$c^\dagger_{\alpha\uparrow}|0\rangle$ single-electron state

$c^\dagger_{\alpha\downarrow}|0\rangle$

$c^\dagger_{\alpha\downarrow}c^\dagger_{\alpha\uparrow}|0\rangle$ two-electron state

$= |\text{full}\rangle$ orbital full

Pauli principle: $c^\dagger_{\alpha\sigma}|\text{full}\rangle = 0$

idea: $|\text{full}\rangle$ looks like vacuum state if we rename operators: $h_{\alpha\sigma} = c^\dagger_{\alpha\sigma}$

hole-operators

isomorphism

vacuum state $|0\rangle$

and

set of operators c_α related to single-electron states $\varphi_\alpha(x)$

defined by:

$$c_\alpha|0\rangle = 0 \qquad \{c_\alpha, c_\beta\} = 0 = \{c_\alpha^\dagger, c_\beta^\dagger\}$$

$$\langle 0|0\rangle = 1 \qquad \{c_\alpha, c_\beta^\dagger\} = \langle\alpha|\beta\rangle$$

algebra unchanged if we choose hole operators such that

$$\{h_\alpha, h_\beta^\dagger\} = \{c_{\bar\alpha}^\dagger, c_{\bar\beta}\} = \langle\bar\beta|\bar\alpha\rangle = \langle\alpha|\beta\rangle$$

e.g. complex conjugate orbitals: $h_\delta = c_{\bar\delta}^\dagger$ with $\varphi_{\bar\delta}(x) = \overline{\varphi_\delta(x)}$

examples

atomic shells

$$|\text{full shell}\rangle = d^\dagger_{-2\downarrow} d^\dagger_{-1\downarrow} \cdots d^\dagger_{2\downarrow} d^\dagger_{-2\uparrow} d^\dagger_{-1\uparrow} \cdots d^\dagger_{2\uparrow} |0\rangle = \prod_{\sigma} \prod_{m=2}^{-2} d^\dagger_{m\sigma} |0\rangle$$

removing electron with (m, σ) from completely filled shell ($L=0$, $S=0$)
changes $L_z=0 \rightarrow -m$ and $S_z=0 \rightarrow -\sigma$

$$h^\dagger_{m\sigma} = d_{-m,-\sigma}$$

electron band

$$|\text{full band}\rangle = \prod_{\sigma} \prod_{k} b^\dagger_{k\sigma} |0\rangle$$

removing electron with (k, σ) from completely filled band ($K=0$, $S=0$)
changes $K=0 \rightarrow -k$ and $S_z=0 \rightarrow -\sigma$

$$h^\dagger_{k\sigma} = b_{-k,-\sigma}$$

Hubbard model

two sites

$$H = -t \sum_{\sigma} \left(c_{2\sigma}^{\dagger} c_{1\sigma} + c_{1\sigma}^{\dagger} c_{2\sigma} \right) + U \sum_{i \in \{1,2\}} n_{i\uparrow} n_{i\downarrow}$$

N=1: basis $\left\{ c_{1\uparrow}^{\dagger} |0\rangle, c_{2\uparrow}^{\dagger} |0\rangle \right\}$

$$\left\langle 0 \right| \begin{pmatrix} c_{1\uparrow} \\ c_{2\uparrow} \end{pmatrix} H \begin{pmatrix} c_{1\uparrow}^{\dagger} & c_{2\uparrow}^{\dagger} \end{pmatrix} \left| 0 \right\rangle = \begin{pmatrix} 0 & -t \\ -t & 0 \end{pmatrix}$$

$$|\pm\rangle = \frac{1}{\sqrt{2}} \left(c_{1\uparrow}^{\dagger} \pm c_{2\uparrow}^{\dagger} \right) |0\rangle = c_{\pm\uparrow}^{\dagger} |0\rangle \quad \text{with } \varepsilon_{\pm} = \mp t$$

Hubbard model

two sites

$$H = -t \sum_{\sigma} \left(c_{2\sigma}^{\dagger} c_{1\sigma} + c_{1\sigma}^{\dagger} c_{2\sigma} \right) + U \sum_{i \in \{1,2\}} n_{i\uparrow} n_{i\downarrow}$$

N=2: $N_\uparrow = 1 = N_\downarrow$

$$\left\langle 0 \right| \begin{pmatrix} c_{1\uparrow} c_{2\downarrow} \\ c_{2\uparrow} c_{1\downarrow} \\ c_{1\uparrow} c_{1\downarrow} \\ c_{2\uparrow} c_{2\downarrow} \end{pmatrix} H \begin{pmatrix} c_{2\downarrow}^{\dagger} c_{1\uparrow}^{\dagger} & c_{1\downarrow}^{\dagger} c_{2\uparrow}^{\dagger} & c_{1\downarrow}^{\dagger} c_{1\uparrow}^{\dagger} & c_{2\downarrow}^{\dagger} c_{2\uparrow}^{\dagger} \end{pmatrix} \left| 0 \right\rangle = \begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & -t & -t \\ -t & -t & U & 0 \\ -t & -t & 0 & U \end{pmatrix}$$

ground state

$$\varepsilon_{\mathrm{gs}} = \frac{U - \sqrt{U^2 + 16t^2}}{2} \qquad \tan\theta = 4t/U$$

$$|\mathrm{gs}\rangle = \frac{1}{\sqrt{2}} \left(\cos\tfrac{\Theta}{2}\, c_{2\downarrow}^{\dagger} c_{1\uparrow}^{\dagger} + \cos\tfrac{\Theta}{2}\, c_{1\downarrow}^{\dagger} c_{2\uparrow}^{\dagger} + \sin\tfrac{\Theta}{2}\, c_{1\downarrow}^{\dagger} c_{1\uparrow}^{\dagger} + \sin\tfrac{\Theta}{2}\, c_{2\downarrow}^{\dagger} c_{2\uparrow}^{\dagger} \right) |0\rangle$$

cannot be factorized for U>0; approaches maximally entangled state for $\Theta \to 0$

Hubbard model

two sites

$$H = -t \sum_{\sigma} \left(c^{\dagger}_{2\sigma} c_{1\sigma} + c^{\dagger}_{1\sigma} c_{2\sigma} \right) + U \sum_{i \in \{1,2\}} n_{i\uparrow} n_{i\downarrow}$$

N=2: $N_{\uparrow} = 1 = N_{\downarrow}$ $\qquad \tan\theta = 4t/U$

$$|\mathrm{gs}\rangle = \frac{1}{\sqrt{2}} \left(\cos\tfrac{\Theta}{2}\, c^{\dagger}_{2\downarrow} c^{\dagger}_{1\uparrow} + \cos\tfrac{\Theta}{2}\, c^{\dagger}_{1\downarrow} c^{\dagger}_{2\uparrow} + \sin\tfrac{\Theta}{2}\, c^{\dagger}_{1\downarrow} c^{\dagger}_{1\uparrow} + \sin\tfrac{\Theta}{2}\, c^{\dagger}_{2\downarrow} c^{\dagger}_{2\uparrow} \right) |0\rangle$$

$$\rightarrow \frac{1}{\sqrt{2}} \left(c^{\dagger}_{2\downarrow} c^{\dagger}_{1\uparrow} + c^{\dagger}_{1\downarrow} c^{\dagger}_{2\uparrow} \right)$$ strongly correlated limit $\Theta \rightarrow 0$

cannot be factorized in Hilbert space

factorized Fock-space wave-function:

$$|\mathrm{VB}\rangle = \left(1 + c^{\dagger}_{2\downarrow} c^{\dagger}_{1\uparrow}\right) \left(1 + c^{\dagger}_{1\downarrow} c^{\dagger}_{2\uparrow}\right) |0\rangle$$

$$= \underbrace{|0\rangle}_{N=0} + \underbrace{\left(c^{\dagger}_{2\downarrow} c^{\dagger}_{1\uparrow} + c^{\dagger}_{1\downarrow} c^{\dagger}_{2\uparrow} \right) |0\rangle}_{N_{\uparrow}=1=N_{\downarrow}} + \underbrace{c^{\dagger}_{2\downarrow} c^{\dagger}_{1\downarrow} c^{\dagger}_{2\uparrow} c^{\dagger}_{1\uparrow} |0\rangle}_{N=4}$$

Hubbard model

$$H = -t \sum_{ij,\sigma} c^\dagger_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

generalize product wave-function to more sites?

$$|\mathrm{VB?}\rangle = \prod_{\langle ij \rangle} \left(1 + c^\dagger_{j\downarrow} c^\dagger_{i\uparrow} + c^\dagger_{i\downarrow} c^\dagger_{j\uparrow}\right) |0\rangle$$

product over distinct bonds to avoid double occupancies

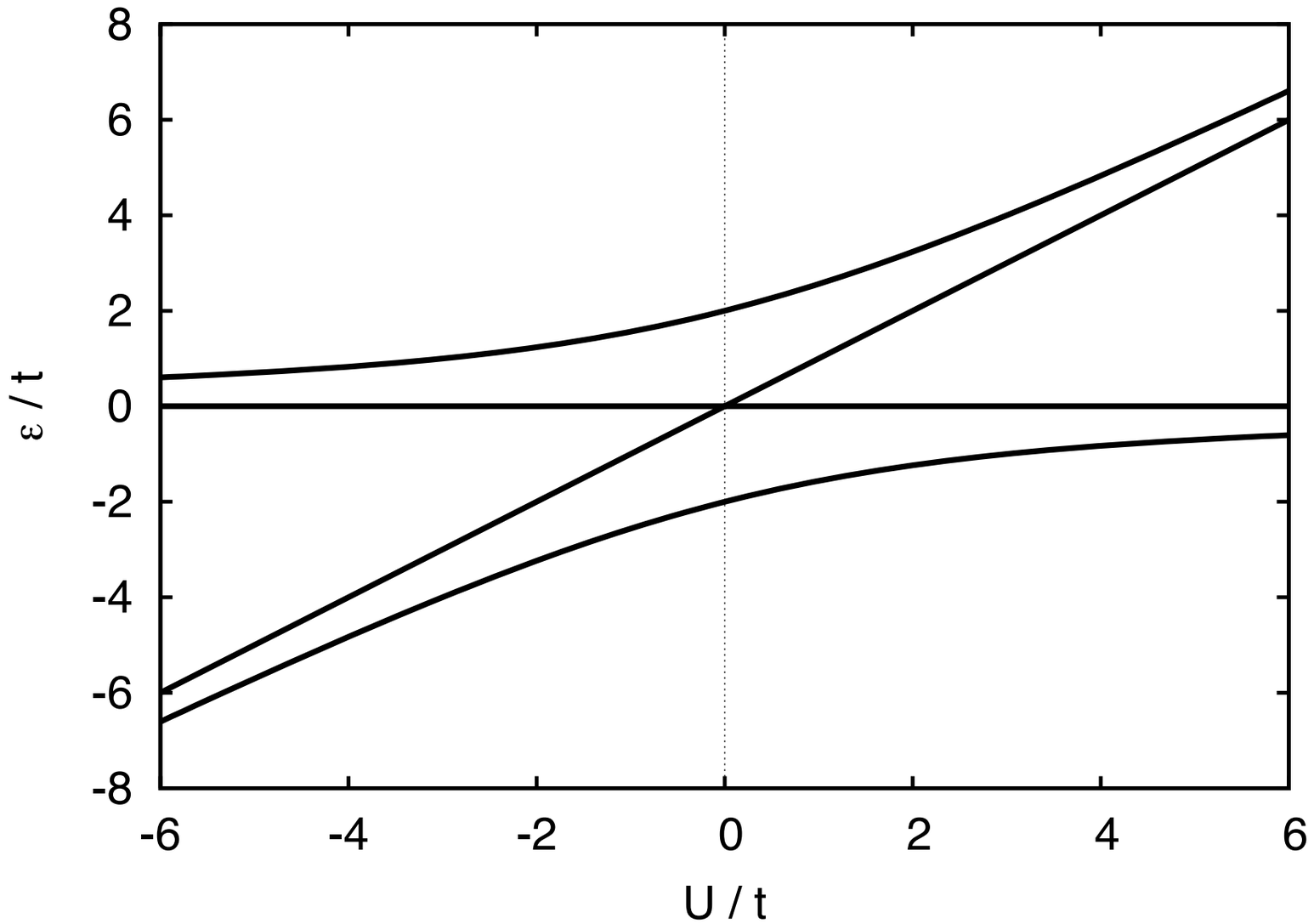
in general there is no unique partitioning of a lattice into bonds

Hubbard model

two sites

$$H = -t \sum_{\sigma} \left(c^{\dagger}_{2\sigma} c_{1\sigma} + c^{\dagger}_{1\sigma} c_{2\sigma} \right) + U \sum_{i \in \{1,2\}} n_{i\uparrow} n_{i\downarrow}$$

spectrum $N_{\uparrow} = 1 = N_{\downarrow}$



Hubbard model

two sites

$$H = -t \sum_{\sigma} \left(c^{\dagger}_{2\sigma} c_{1\sigma} + c^{\dagger}_{1\sigma} c_{2\sigma} \right) + U \sum_{i \in \{1,2\}} n_{i\uparrow} n_{i\downarrow}$$

N=2: $N_{\uparrow} = 1 = N_{\downarrow}$ U<0 $\tan\theta = 4t/U$

$$|\mathrm{gs}\rangle = \frac{1}{\sqrt{2}} \left(\cos\tfrac{\Theta}{2}\, c^{\dagger}_{2\downarrow} c^{\dagger}_{1\uparrow} + \cos\tfrac{\Theta}{2}\, c^{\dagger}_{1\downarrow} c^{\dagger}_{2\uparrow} + \sin\tfrac{\Theta}{2}\, c^{\dagger}_{1\downarrow} c^{\dagger}_{1\uparrow} + \sin\tfrac{\Theta}{2}\, c^{\dagger}_{2\downarrow} c^{\dagger}_{2\uparrow} \right) |0\rangle$$

$$\rightarrow \frac{1}{\sqrt{2}} \left(c^{\dagger}_{1\downarrow} c^{\dagger}_{1\uparrow} + c^{\dagger}_{2\downarrow} c^{\dagger}_{2\uparrow} \right)$$

local pairing limit $\Theta \rightarrow \pi$

factorized Fock-space wave-function:

$$|\mathrm{pair}\rangle = \frac{1}{2} \left(1 + c^{\dagger}_{2\downarrow} c^{\dagger}_{2\uparrow} \right) \left(1 + c^{\dagger}_{1\downarrow} c^{\dagger}_{1\uparrow} \right) |0\rangle$$

readily generalizes: $$|\mathrm{pair}\rangle = \prod_{i} \frac{1}{\sqrt{2}} \left(1 + c^{\dagger}_{i\downarrow} c^{\dagger}_{i\uparrow} \right) |0\rangle$$

BCS model

$$H_{\mathrm{BCS}} = \sum_{k\sigma} \varepsilon_k \, c^\dagger_{k\sigma} c_{k\sigma} + \sum_{k,k'} V_{k,k'} \, c^\dagger_{-k'\downarrow} c^\dagger_{k'\uparrow} c_{k\uparrow} c_{-k\downarrow}$$

interaction term scatters (Cooper) pairs of electrons ($k\uparrow$, $-k\downarrow$) → ($k'\uparrow$, $-k'\downarrow$)

model with just two k-points: $k = 0$ and $k = \pi$

$$H = \sum_{k\in\{0,\pi\},\sigma} \varepsilon_k \, n_{k\sigma} - I \left(c^\dagger_{\pi\downarrow} c^\dagger_{\pi\uparrow} c_{0\uparrow} c_{0\downarrow} + c^\dagger_{0\downarrow} c^\dagger_{0\uparrow} c_{\pi\uparrow} c_{\pi\downarrow} \right)$$

note: here $k = -k$

Hubbard model

two sites

$$H = \sum_{k\in\{0,\pi\},\sigma} \varepsilon_k\, n_{k\sigma} - I\left(c^\dagger_{\pi\downarrow}c^\dagger_{\pi\uparrow}c_{0\uparrow}c_{0\downarrow} + c^\dagger_{0\downarrow}c^\dagger_{0\uparrow}c_{\pi\uparrow}c_{\pi\downarrow}\right)$$

N=2: $N_\uparrow = 1 = N_\downarrow$

$$\left\langle 0\right| \begin{pmatrix} c_{0\uparrow}c_{\pi\downarrow} \\ c_{\pi\uparrow}c_{0\downarrow} \\ c_{0\uparrow}c_{0\downarrow} \\ c_{\pi\uparrow}c_{\pi\downarrow} \end{pmatrix} H \begin{pmatrix} c^\dagger_{\pi\downarrow}c^\dagger_{0\uparrow} & c^\dagger_{0_\downarrow}c^\dagger_{\pi\uparrow} & c^\dagger_{0\downarrow}c^\dagger_{0\uparrow} & c^\dagger_{\pi\downarrow}c^\dagger_{\pi\uparrow} \end{pmatrix} \left|0\right\rangle = \begin{pmatrix} \varepsilon_0+\varepsilon_\pi & 0 & 0 & 0 \\ 0 & \varepsilon_0+\varepsilon_\pi & 0 & 0 \\ 0 & 0 & 2\varepsilon_0 & -I \\ 0 & 0 & -I & 2\varepsilon_\pi \end{pmatrix}$$

ground state

$$\varepsilon_{\text{gs}} = \frac{\varepsilon_0+\varepsilon_\pi}{2} - \sqrt{I^2+(\varepsilon_\pi-\varepsilon_0)^2} \qquad \tan\theta = (\varepsilon_\pi-\varepsilon_0)/I$$

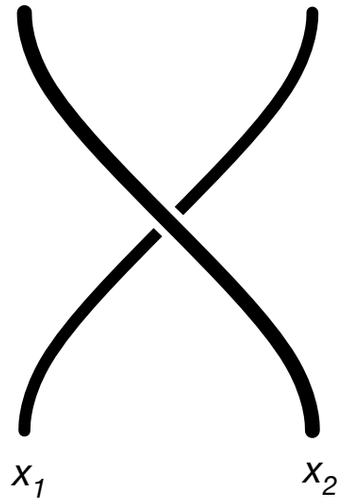
$$|\text{gs}\rangle = \left(\cos\tfrac{\Theta}{2}\, c^\dagger_{0\downarrow}c^\dagger_{0\uparrow} + \sin\tfrac{\Theta}{2}\, c^\dagger_{\pi\downarrow}c^\dagger_{\pi\uparrow}\right)|0\rangle$$

factorized Fock-space wave-function:

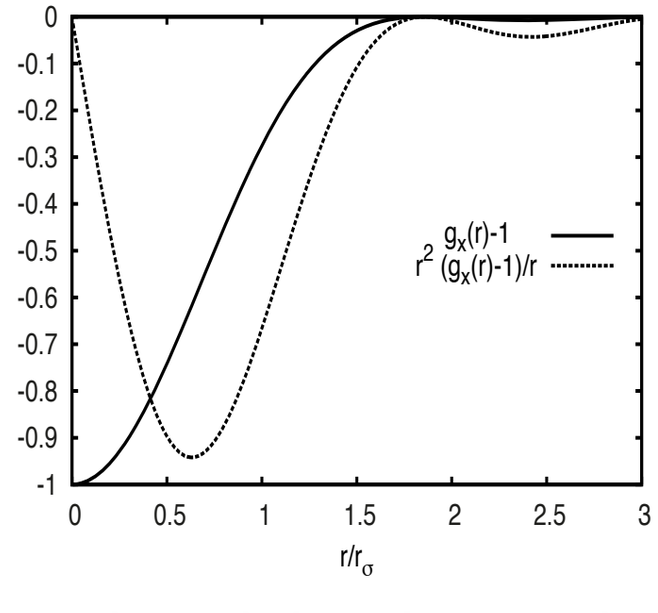
$$|\text{BCS}\rangle = \prod_{k\in\{0,\pi\}} \frac{1}{\sqrt{1+\cos^2\Theta_k/2}}\left(1+\cos\tfrac{\Theta_k}{2}\, c^\dagger_{-k\downarrow}c^\dagger_{k\uparrow}\right)|0\rangle$$

summary

for quantum particles
indistinguishability
is the norm



spin-statistics connection
exotic statistics



reduced density matrices
pair correlations

$$c_\alpha|0\rangle = 0 \qquad \{c_\alpha, c_\beta\} = 0 = \{c_\alpha^\dagger, c_\beta^\dagger\}$$
$$\langle 0|0\rangle = 1 \qquad \{c_\alpha, c_\beta^\dagger\} = \langle\alpha|\beta\rangle$$

$$\frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

(anti)symmetrization is hard
Slater determinants to the rescue

second quantization:
keeping track of signs

$$H = -t\sum_{ij,\sigma} c_{i\sigma}^\dagger c_{j\sigma} + U\sum_i n_{i\uparrow}n_{i\downarrow}$$
$$|\mathrm{BCS}\rangle = \prod_{k\in\{0,\pi\}} \frac{1}{\sqrt{1+\cos^2\Theta_k/2}}\left(1+\cos\tfrac{\Theta_k}{2}\, c_{-k\downarrow}^\dagger c_{k\uparrow}^\dagger\right)|0\rangle$$

second quantization:
operators and states in Fock-space