Many-Electron States

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Identical Twins

Diane Arbus:
Identical Twins,
Roselle, NJ, 1967
Welcome

The Twins Days Festival in Twinsburg, Ohio is the largest annual gathering of twins (and 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!
indistinguishable particles

fundamental particles change over time/length-scale/energy
emergence of distinguishability

uncertainty:
quantum particles can usually not be distinguished by their position

Interferometrie mit komplexen Molekülen

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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

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

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

when $P^2 = \text{Id} \Rightarrow e^{i\phi} = \pm 1$ ($\Psi$ (anti)symmetric under permutation)

antisymmetric: $\Psi(x_1, x_2 \rightarrow x_1) = 0$ (Pauli principle)
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 arguments 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?

$P^2 \neq \text{Id}$: braiding statistics: anyons

2-dimensional

1-dimensional

fermions cannot pass
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: \(M = (x_1-x_2)^2\)

\[\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle - 2 \langle x_1 x_2 \rangle + \langle x_2^2 \rangle\]

normalized

\[\langle x_1^2 \rangle_{12} = \int dx_1 x_1^2 |\varphi_a(x_1)|^2 \quad \int dx_2 |\varphi_b(x_2)|^2 = \langle x^2 \rangle_a \cdot 1\]

\[\langle x_2^2 \rangle_{12} = \int dx_1 |\varphi_a(x_1)|^2 \quad \int dx_2 x_2^2 |\varphi_b(x_2)|^2 = 1 \cdot \langle x^2 \rangle_b\]

\[\langle x_1 x_2 \rangle_{12} = \int dx_1 x_1 |\varphi_a(x_1)|^2 \quad \int dx_2 x_2 |\varphi_b(x_2)|^2 = \langle x \rangle_a \cdot \langle x \rangle_b\]

\[\langle (x_1 - x_2)^2 \rangle_{12} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b\]

\[= \langle (x_2 - x_1)^2 \rangle_{12} = \langle (x_1 - x_2)^2 \rangle_{21}\]

observable does not distinguish particles
2-particle wave-function: indistinguishable

symmetric / anti-symmetric wave-function

\[ \psi_\pm(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_{12}(x_1, x_2) \pm \psi_{21}(x_1, x_2)) \]

cross-terms between product wave-functions

\[ \langle M \rangle_\pm = \frac{1}{2} \left( \langle M \rangle_{12} \pm \langle \psi_{12} | M | \psi_{21} \rangle \pm \langle \psi_{21} | M | \psi_{12} \rangle + \langle M \rangle_{21} \right) = \langle M \rangle_{12} \pm \langle \psi_{12} | M | \psi_{21} \rangle \]

particle permutation: exchange-terms

\[ \langle \psi_{12} | x_1^2 | \psi_{21} \rangle = \int dx_1 x_1^2 \varphi_a(x_1) \varphi_b(x_1) \int dx_2 \varphi_b(x_2) \varphi_a(x_2) = \langle x^2 \rangle_{ab} \cdot 0 \]
\[ \langle \psi_{12} | x_2^2 | \psi_{21} \rangle = \int dx_1 \varphi_a(x_1) \varphi_b(x_1) \int dx_2 x_2^2 \varphi_b(x_2) \varphi_a(x_2) = 0 \cdot \langle x^2 \rangle_{ba} \]
\[ \langle \psi_{12} | x_1 x_2 | \psi_{21} \rangle = \int dx_1 x_1 \varphi_a(x_1) \varphi_b(x_1) \int dx_2 x_2 \varphi_b(x_2) \varphi_a(x_2) = \langle x \rangle_{ab} \cdot \langle x \rangle_{ba} \]

\[ \langle (x_1 - x_2)^2 \rangle_\pm = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2 \]

Bosons prefer company
Fermions keep their distance
probability density for 2 particles in a box

\[ \varphi_b(x) \]
\[ \varphi_a(x) \]

\textit{distinguishable}

\textit{symmetric}

\textit{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

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

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

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

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

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

$$= \Gamma^{(1)}(x_1)$$

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

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

$$= N \int dx_1 \lim_{x_1' \to x_1} M_1(x_1) \int dx_2 \cdots dx_N \overline{\psi(x_1', \ldots, x_N)} \psi(x_1, \ldots, x_N)$$

$$= \Gamma^{(1)}(x_1'; x_1)$$
reduced density matrices

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

\[
\Gamma^{(p)}(x'_1, \ldots, x'_p; x_1, \ldots, x_p) = \binom{N}{p} \int dx_{p+1} \cdots dx_N \frac{\psi(x'_1, \ldots, x'_p, x_{p+1}, \ldots, x_N)}{\psi(x_1, \ldots, x_p, x_{p+1}, \ldots, x_N)}
\]

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 $q \leq p$:

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

\[ \langle T \rangle = \left\langle \psi \left| -\frac{1}{2} \sum_i \Delta r_i \right| \psi \right\rangle = -\frac{1}{2} \int dx \, \Delta r \, \Gamma^{(1)}(x'; x) \bigg|_{x'=x} \]

Coulomb repulsion

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

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

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

(rewrite in terms of Hartree energy)

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

pair correlation function

Hartree term

exchange-correlation hole

sum rule

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

$$\int dx' \, n(x') \, (g(x, x') - 1) = -1$$
exchange-correlation holes from QMC

homogeneous electron gas \( g^{\sigma\sigma'}_{xc}(r/r_s) \)

G. Ortiz, M. Harris, P. Ballone, Phys. Rev. Lett. 82, 5317 (1999)

(110) plane of Si, electron at bond center

\( g^{\text{VMC}}_x(\vec{r}) \) (a)

\( g^{\text{VMC}}_c(\vec{r}) \) (b)

antisymmetric wave-functions

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

$$S_{\pm} \psi(x_1, \ldots, x_N) := \frac{1}{\sqrt{N!}} \sum_{P} (\pm 1)^P \psi(x_{p(1)}, \ldots, x_{p(N)})$$

antisymmetrization of products of single-particle states

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

much more efficient: scales only polynomially in $N$

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

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

simple examples

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

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

expectation values need only one antisymmetrized wave-function:

\[
\int d\mathbf{x} \left( S_{\pm} \psi_a(\mathbf{x}) \right) M(\mathbf{x}) \left( S_{\pm} \psi_b(\mathbf{x}) \right) = \int d\mathbf{x} \left( \sqrt{N!} \psi_a(\mathbf{x}) \right) M(\mathbf{x}) \left( S_{\pm} \psi_b(\mathbf{x}) \right)
\]

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

corollary: overlap of Slater determinants:

\[
\int d\mathbf{x}_1 \cdots d\mathbf{x}_N \Phi_{\alpha_1 \ldots \alpha_N}(x_1, \ldots, x_N) \Phi_{\beta_1 \ldots \beta_N}(x_1, \ldots, x_N) = \det \left( \langle \varphi_{\alpha_n} | \varphi_{\beta_m} \rangle \right)
\]
basis of Slater determinants

\[ \int d\mathbf{x} \prod_{n=1}^{N} \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N) \Phi_{\beta_1 \cdots \beta_N}(x_1, \ldots, x_N) = \text{det} \left( \langle \varphi_{\alpha_n} | \varphi_{\beta_m} \rangle \right) \]

Slater determinants of ortho-normal orbitals \( \varphi_{\alpha}(\mathbf{x}) \) 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 \( \{ \varphi_{\alpha}(\mathbf{x}) | \alpha \in \{1, \ldots, K\} \} \)

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

\[ \left\{ \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N) \mid \alpha_1 < \alpha_2 < \cdots < \alpha_N \in \{1, \ldots, K\} \right\} \]

are an ortho-normal basis of the \( N \)-electron Hilbert space
reduced density-matrices: \( p=1 \)

Laplace expansion

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

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

for ortho-normal orbitals

\[
\Gamma^{(1)}(x'; x) = \sum_n \varphi_{\alpha_n}(x') \varphi_{\alpha_n}(x) \quad \text{and} \quad n(x) = \sum_n |\varphi_n(x)|^2
\]
red\textit{uced} density-matrices

expansion of determinant in product of determinants

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

\textit{$p$-electron} Slater det \hspace{1em} \textit{$(N-p)$-electron} Slater det

express \textit{$p$-body} density matrix in terms of $p$-electron Slater determinants:

\[ \Gamma^{(1)}(x'; x) = \sum_n \varphi_{\alpha_n}(x') \varphi_{\alpha_n}(x) \quad \text{and} \quad n(x) = \sum_n |\varphi_{\alpha_n}(x)|^2 \]

\[ \Gamma^{(2)}(x'_1 x'_2; x_1, x_2) = \sum_{n < m} \Phi_{\alpha_n, \alpha_m}(x'_1, x'_2) \Phi_{\alpha_n, \alpha_m}(x_1, x_2) \]

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

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

\[ = \sum_{n,m} \left( |\varphi_{\alpha_n}(x_1)|^2 |\varphi_{\alpha_m}(x_2)|^2 - \overline{\varphi_{\alpha_n}(x_1) \varphi_{\alpha_m}(x_1)} \overline{\varphi_{\alpha_m}(x_2) \varphi_{\alpha_n}(x_2)} \right) \]
pair correlation function for Slater determinant \( \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N) \)

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

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

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

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

\[= -9 \frac{(\sin(k_F r) - k_F r \cos(k_F r))^2}{(k_F r)^6}
\]

exchange hole
for electrons of same spin
The exchange hole is given by the equation:

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

(110) plane of Si, electron at bond center

\( g_{xc}^{\text{VMC}}(\vec{r}) \)

\( g_{c}^{\text{VMC}}(\vec{r}) \)

Slater determinants

Hartree-Fock method:
know how to represent 2-body density matrix derived from Slater determinant

\[ \Gamma^{(2)}(x'_1 x'_2; x_1, x_2) = \sum_{n<m} \Phi_{\alpha_n,\alpha_m}(x'_1, x'_2) \Phi_{\alpha_n,\alpha_m}(x_1, x_2) \]

minimize (à 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 \( \Phi_{\alpha\beta}(x_1, x_2) = \frac{1}{\sqrt{2}} (\varphi_{\alpha}(x_1)\varphi_{\beta}(x_2) - \varphi_{\beta}(x_1)\varphi_{\alpha}(x_2)) \)

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

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 \( \{A, B\} := AB + BA \)
second quantization: motivation

specify \( N \)-electron states using operators

\( N=0: \quad |0\rangle \quad \text{(vacuum state)} \)

normalization:  \( \langle 0 | 0 \rangle = 1 \)

\( N=1: \quad |\alpha\rangle = c_\alpha^\dagger |0\rangle \quad \text{(creation operator adds one electron)} \)

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

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

\( N=2: \quad |\alpha, \beta\rangle = c_\beta^\dagger c_\alpha^\dagger |0\rangle \)

antisymmetry:  \[ c_\alpha^\dagger c_\beta^\dagger = - c_\beta^\dagger c_\alpha^\dagger \]
second quantization: formalism

vacuum state $|0\rangle$

and

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

defined by:

\[
\begin{align*}
c_\alpha |0\rangle &= 0 \\
\langle 0 |0\rangle &= 1 \\
\{c_\alpha, c_\beta\} &= 0 = \{c_\alpha^\dagger, c_\beta^\dagger\} \\
\{c_\alpha, c_\beta^\dagger\} &= \langle \alpha |\beta \rangle
\end{align*}
\]
second quantization: field operators

creation/annihilation operators in real-space basis

\[ \hat{\Psi}^\dagger(x) \] with \( x = (r, \sigma) \) creates electron of spin \( \sigma \) at position \( r \)

then

\[ c_\alpha^\dagger = \int dx \, \varphi_\alpha(x) \hat{\Psi}^\dagger(x) \]

put electron at \( x \) with amplitude \( \varphi_\alpha(x) \)

\( \{\varphi_\alpha_n(x)\} \) 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

\[ \{\hat{\Psi}(x), \hat{\Psi}(x')\} = 0 = \{\hat{\Psi}^\dagger(x), \hat{\Psi}^\dagger(x')\} \]

\[ \{\hat{\Psi}(x), \hat{\Psi}^\dagger(x')\} = \delta(x - x') \]
second quantization: Slater determinants

\[ \Phi_{\alpha_1 \alpha_2 \ldots \alpha_N}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \langle 0 | \hat{\psi}(x_1) \hat{\psi}(x_2) \ldots \hat{\psi}(x_N) \ c_{\alpha_N}^\dagger \ldots c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger | 0 \rangle \]

proof by induction

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

\( N=1: \quad \langle 0 | \hat{\psi}(x_1) \ c_{\alpha_1}^\dagger | 0 \rangle = \langle 0 | \varphi_{\alpha_1}(x_1) - c_{\alpha_1}^\dagger \hat{\psi}(x_1) | 0 \rangle = \varphi_{\alpha_1}(x_1) \)

using \[ \{ \hat{\psi}(x), c_{\alpha}^\dagger \} = \int dx' \varphi_{\alpha}(x') \{ \hat{\psi}(x), \hat{\psi}^\dagger(x') \} = \varphi_{\alpha}(x) \]

\( N=2: \quad \langle 0 | \hat{\psi}(x_1) \hat{\psi}(x_2) \ c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger | 0 \rangle \)

\[ = \langle 0 | \hat{\psi}(x_1) (\varphi_{\alpha_2}(x_2) - c_{\alpha_2}^\dagger \hat{\psi}(x_2)) \ c_{\alpha_1}^\dagger | 0 \rangle \]

\[ = \langle 0 | \hat{\psi}(x_1) c_{\alpha_1}^\dagger | 0 \rangle \varphi_{\alpha_2}(x_2) - \langle 0 | \hat{\psi}(x_1) c_{\alpha_2}^\dagger \hat{\psi}(x_2) c_{\alpha_1}^\dagger | 0 \rangle \]

\[ = \varphi_{\alpha_1}(x_1) \varphi_{\alpha_2}(x_2) - \varphi_{\alpha_2}(x_1) \varphi_{\alpha_1}(x_2) \]
second quantization: Slater determinants

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

$$
\langle 0 | \hat{\Psi}(x_1) \ldots \hat{\Psi}(x_{N-1}) \hat{\Psi}(x_N) \ c_{\alpha_N} \ c_{\alpha_{N-1}} \ldots \ c_{\alpha_1} | 0 \rangle = 
$$

$$
+ \langle 0 | \hat{\Psi}(x_1) \ldots \hat{\Psi}(x_{N-1}) \ c_{\alpha_{N-1}} \ldots \ c_{\alpha_1} | 0 \rangle \phi_{\alpha_N}(x_N) \\
- \langle 0 | \hat{\Psi}(x_1) \ldots \hat{\Psi}(x_{N-1}) \ \prod_{n \neq N-1} c_{\alpha_n}^\dagger | 0 \rangle \phi_{\alpha_{N-1}}(x_N) \\
\vdots \\
(-1)^N \langle 0 | \hat{\Psi}(x_1) \ldots \hat{\Psi}(x_{N-1}) \ c_{\alpha_N}^\dagger \ldots \ c_{\alpha_2}^\dagger | 0 \rangle \phi_{\alpha_1}(x_N)
$$

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

$$
= 
\begin{vmatrix}
\phi_{\alpha_1}(x_1) & \phi_{\alpha_2}(x_1) & \ldots & \phi_{\alpha_N}(x_1) \\
\phi_{\alpha_1}(x_2) & \phi_{\alpha_2}(x_2) & \ldots & \phi_{\alpha_N}(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_{\alpha_1}(x_N) & \phi_{\alpha_2}(x_N) & \ldots & \phi_{\alpha_N}(x_N)
\end{vmatrix}
$$
second quantization: Dirac notation

Product state $c_{\alpha N}^\dagger \cdots c_{\alpha 2}^\dagger c_{\alpha 1}^\dagger |0\rangle$

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

\[
\int dx_1 \cdots dx_N \Phi_{\beta_1 \cdots \beta_N}(x_1, \cdots, x_N) M(x_1, \cdots, x_N) \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \cdots, x_N) = \left\langle 0 \left| c_{\beta_1} \cdots c_{\beta_N} \hat{M} c_{\alpha_N}^\dagger \cdots c_{\alpha_1}^\dagger \right| 0 \right\rangle
\]

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

|0⟩⟨0| = 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 \( \hat{M}_0(x_1, \ldots x_N) = 1 \) independent of particle coordinates

second quantized form for operating on \( N \)-electron states:

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

\[
= \frac{1}{N!} \int dx_2 \cdots x_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_2) \hat{\psi}(x_2) \cdots \hat{\psi}(x_N)
\]

\[
= \frac{1}{N!} \int dx_2 \cdots x_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_2) 1 \hat{\psi}(x_2) \cdots \hat{\psi}(x_N)
\]

\[
\vdots
\]

\[
= \frac{1}{N!} 1 \cdot 2 \cdots N = 1
\]

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 \( M(x_1, \ldots, x_N) = \sum_j M_1(x_j) \)

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

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

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

\[
= \int dx \ \hat{\psi}^\dagger(x) M_1(x) \hat{\psi}(x) \quad \text{result independent of } N
\]

expand in complete orthonormal set of orbitals

\[
\hat{M}_1 = \sum_{n,m} \int dx \ \varphi_{\alpha_n}(x) M(x) \varphi_{\alpha_m}(x) c_{\alpha_n}^\dagger c_{\alpha_m} = \sum_{n,m} \langle \alpha_n | M_1 | \alpha_m \rangle c_{\alpha_n}^\dagger c_{\alpha_m}
\]
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

\[ \hat{M}_2 = \frac{1}{2} \sum_{n,n',m,m'} \int dx \, dx' \varphi_{\alpha_n'}(x') \varphi_{\alpha_n}(x) M_2(x, x') \varphi_{\alpha_m}(x) \varphi_{\alpha_{m'}}(x') c_{\alpha_n'}^\dagger c_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}} \]

\[ = \frac{1}{2} \sum_{n,n',m,m'} \langle \alpha_n \alpha_{n'} | M_2 | \alpha_m \alpha_{m'} \rangle c_{\alpha_n'}^\dagger c_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}} \]
electron-hole transformation

consider spin-orbital $\varphi_a(x)$

\begin{align*}
|0\rangle & \quad \text{vacuum state} \\
{c}_\alpha^{\dagger}|0\rangle & \quad \text{single-electron state} \\
{c}_\alpha^{\dagger}|0\rangle & \\
{c}_\alpha^{\dagger}{c}_\alpha^{\dagger}|0\rangle & \quad \text{two-electron state} \\
= |\text{full}\rangle & \quad \text{orbital full}
\end{align*}

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

\textbf{idea:} $|\text{full}\rangle$ looks like vacuum state if we rename operators: $h_{\alpha\sigma} = c_{\alpha\sigma}^{\dagger}$
isomorphism

vacuum state $|0\rangle$

and

set of operators $c_\alpha$ related to single-electron states $\varphi_\alpha(x)$
defined by:

\[
\begin{align*}
  c_\alpha |0\rangle &= 0 & \{c_\alpha, c_\beta\} &= 0 = \{c_\alpha^\dagger, c_\beta^\dagger\} \\
  \langle 0|0 \rangle &= 1 & \{c_\alpha, c_\beta^\dagger\} &= \langle \alpha|\beta \rangle
\end{align*}
\]

algebra unchanged if we choose hole operators such that

\[
\{h_\alpha, h_\beta^\dagger\} = \{c_\alpha^\dagger, c_\beta^\dagger\} = \langle \bar{\beta}|\bar{\alpha} \rangle = \langle \alpha|\beta \rangle
\]
e.g. complex conjugate orbitals: $h_\delta = c_\delta^\dagger$ with $\varphi_\delta(x) = \overline{\varphi_\delta(x)}$
examples

atomic shells

\[ |\text{full shell}\rangle = d_{-2\downarrow}^\dagger d_{-1\downarrow}^\dagger \cdots d_{2\downarrow}^\dagger d_{-2\uparrow}^\dagger d_{-1\uparrow}^\dagger \cdots d_{2\uparrow}^\dagger |0\rangle = \prod_{\sigma} \prod_{m=2}^{-2} d_{m\sigma}^\dagger |0\rangle \]

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

\[ h_{m\sigma}^\dagger = d_{-m,-\sigma} \]

electron band

\[ |\text{full band}\rangle = \prod_{\sigma} \prod_{k} b_{k\sigma}^\dagger |0\rangle \]

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

\[ h_{k\sigma}^\dagger = b_{-k,-\sigma} \]
Hubbard model

two sites

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

\[ N=1: \text{basis} \quad \{ c_{1\uparrow}^\dagger |0\rangle, c_{2\uparrow}^\dagger |0\rangle \} \]

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

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

two sites

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

\( N=2: N_{\uparrow} = 1 = N_{\downarrow} \)

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

ground state

\[ \epsilon_{gs} = \frac{U - \sqrt{U^2 + 16t^2}}{2} \]

\[ \tan \theta = 4t/U \]

\[ |gs\rangle = \frac{1}{\sqrt{2}} \left( \cos \frac{\theta}{2} c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger + \cos \frac{\theta}{2} c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger + \sin \frac{\theta}{2} c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger + \sin \frac{\theta}{2} c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle \]

cannot be factorized for \( U>0 \); approaches maximally entangled state for \( \Theta \to 0 \)
two sites

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

\(N=2: \; N_{\uparrow} = 1 = N_{\downarrow}\)

\[
|gs\rangle = \frac{1}{\sqrt{2}} \left( \cos \frac{\Theta}{2} \; c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger + \cos \frac{\Theta}{2} \; c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger + \sin \frac{\Theta}{2} \; c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger + \sin \frac{\Theta}{2} \; c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle
\]

\[
\rightarrow \frac{1}{\sqrt{2}} \left( c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger + c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger \right)
\]

\(\tan \theta = 4t/U\)

strongly correlated limit \(\Theta \rightarrow 0\)

cannot be factorized in Hilbert space

factorized Fock-space wave-function:

\[
|\text{VB}\rangle = \left( 1 + c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger \right) \left( 1 + c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle
\]

\[
= |0\rangle + \left( c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger + c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle + c_{2\downarrow}^\dagger c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger c_{1\uparrow}^\dagger |0\rangle
\]

\(N=0\) \(N_{\uparrow}=1=N_{\downarrow}\) \(N=4\)
Hubbard model

\[
H = -t \sum_{ij,\sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}
\]

generalize product wave-function to more sites?

\[
|\text{VB}?\rangle = \prod_{\langle ij \rangle} \left( 1 + c_{j\downarrow}^\dagger c_{i\uparrow}^\dagger + c_{i\downarrow}^\dagger c_{j\uparrow}^\dagger \right) |0\rangle
\]

product over distinct bonds to avoid double occupancies

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

two sites

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

spectrum \( N_{\uparrow} = 1 = N_{\downarrow} \)
Hubbard model

two sites

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

\( N=2: \) \( N_\uparrow = 1 = N_\downarrow \)

\( U < 0 \)

\[ \tan \theta = 4t/U \]

\[ |gs\rangle = \frac{1}{\sqrt{2}} \left( \cos \frac{\theta}{2} c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger + \cos \frac{\theta}{2} c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger + \sin \frac{\theta}{2} c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger + \sin \frac{\theta}{2} c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle \]

\[ \rightarrow \frac{1}{\sqrt{2}} \left( c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger + c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger \right) \]

local pairing limit \( \Theta \rightarrow \pi \)

factorized Fock-space wave-function:

\[ |\text{pair}\rangle = \frac{1}{2} \left( 1 + c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger \right) \left( 1 + c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger \right) |0\rangle \]

readily generalizes:

\[ |\text{pair}\rangle = \prod_i \frac{1}{\sqrt{2}} \left( 1 + c_{i\downarrow}^\dagger c_{i\uparrow}^\dagger \right) |0\rangle \]
BCS model

\[ H_{\text{BCS}} = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k,k'} V_{k,k'} c_{-k'\downarrow}^\dagger c_{k'\uparrow}^\dagger c_{k\uparrow} c_{-k\downarrow} \]

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

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

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

note: here \(k = -k\)
Hubbard model

two sites

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

\( N = 2: N_{\uparrow} = 1 = N_{\downarrow} \)

\[ \langle 0 | \begin{pmatrix} c_{0\uparrow} c_{\pi\downarrow} \\ c_{\pi\uparrow} c_{0\downarrow} \\ c_{0\uparrow} c_{0\downarrow} \\ c_{\pi\uparrow} c_{\pi\downarrow} \end{pmatrix} \begin{pmatrix} c_{0\downarrow}^\dagger c_{\pi\uparrow}^\dagger \\ c_{0\uparrow}^\dagger c_{\pi\uparrow}^\dagger \\ c_{0\downarrow}^\dagger c_{0\uparrow}^\dagger \\ c_{\pi\downarrow}^\dagger c_{\pi\uparrow}^\dagger \end{pmatrix} H \begin{pmatrix} c_{0\downarrow}^\dagger c_{\pi\uparrow}^\dagger \\ c_{0\uparrow}^\dagger c_{\pi\uparrow}^\dagger \\ c_{0\downarrow}^\dagger c_{0\uparrow}^\dagger \\ c_{\pi\downarrow}^\dagger c_{\pi\uparrow}^\dagger \end{pmatrix} | 0 \rangle = \begin{pmatrix} \varepsilon_0 + \varepsilon_\pi & 0 & 0 & 0 \\ 0 & \varepsilon_0 + \varepsilon_\pi & 0 & 0 \\ 0 & 0 & 2\varepsilon_0 & -I \\ 0 & 0 & -I & 2\varepsilon_\pi \end{pmatrix} \]

ground state

\[ \varepsilon_{gs} = \frac{\varepsilon_0 + \varepsilon_\pi}{2} - \sqrt{I^2 + (\varepsilon_\pi - \varepsilon_0)^2} \quad \tan \theta = (\varepsilon_\pi - \varepsilon_0)/I \]

\[ |gs\rangle = \left( \cos \frac{\Theta}{2} c_{0\downarrow}^\dagger c_{0\uparrow}^\dagger + \sin \frac{\Theta}{2} c_{\pi\downarrow}^\dagger c_{\pi\uparrow}^\dagger \right) |0\rangle \]

factorized Fock-space wave-function:

\[ |BCS\rangle = \prod_{k \in \{0, \pi\}} \frac{1}{\sqrt{1 + \cos^2 \Theta_k/2}} \left( 1 + \cos \frac{\Theta_k}{2} c_{-k\downarrow}^\dagger c_{k\uparrow}^\dagger \right) |0\rangle \]
summary

for quantum particles
indistinguishability is the norm

spin-statistics connection
exotic statistics

(reduced density matrices
pair correlations

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

(anti)symmetrization is hard
Slater determinants to the rescue

\[
c_\alpha |0\rangle = 0 \quad \{c_\alpha, c_\beta\} = 0 = \{c_\alpha^\dagger, c_\beta^\dagger\}
\langle 0 | 0 \rangle = 1 \quad \{c_\alpha, c_\beta^\dagger\} = \langle \alpha | \beta \rangle
\]

second quantization:
keeping track of signs

\[
H = -t \sum_{ij, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}
\]

second quantization:
operators and states in Fock-space

\[
|\text{BCS}\rangle = \prod_{k \in \{0, \pi\}} \frac{1}{\sqrt{1 + \cos^2 \Theta_k/2}} \left(1 + \frac{\cos \Theta_k/2}{c_{k\downarrow}^\dagger c_{k\uparrow}}\right) |0\rangle
\]