Mean-Field Theory: HF and BCS

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

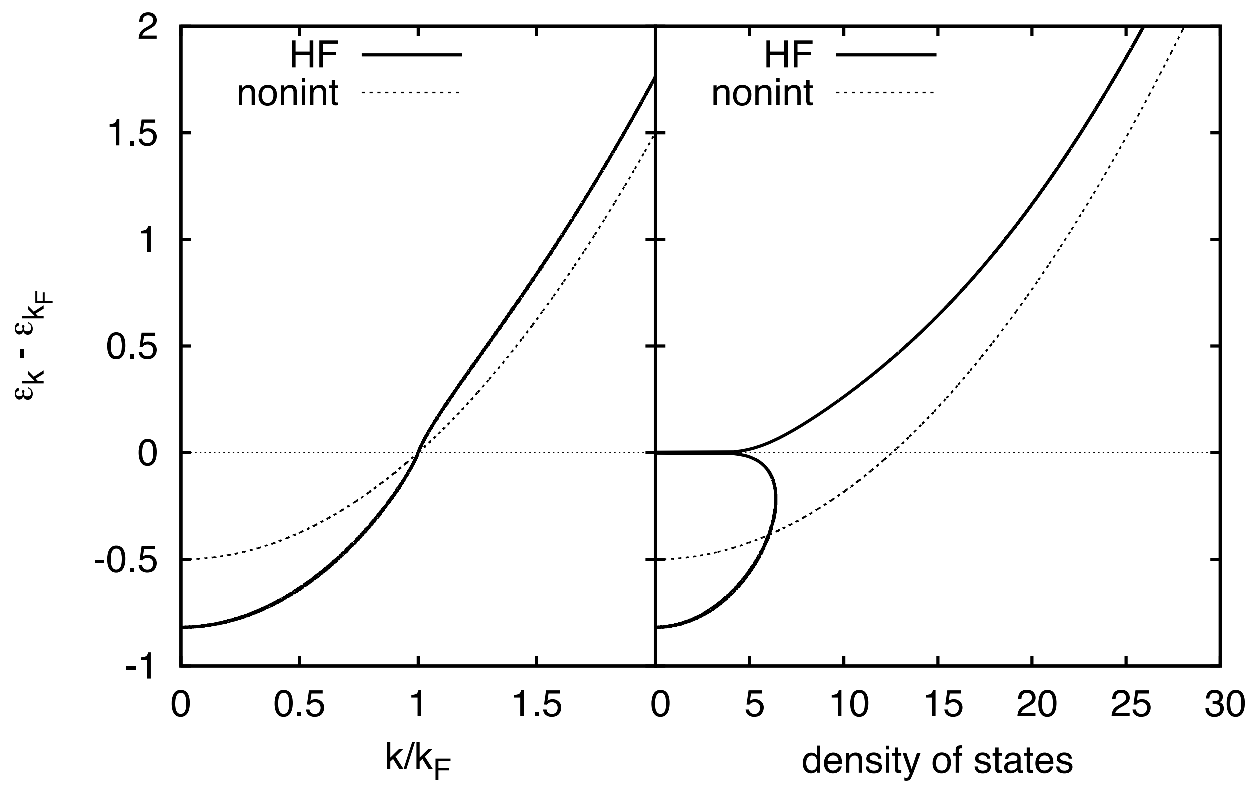
Slater determinant

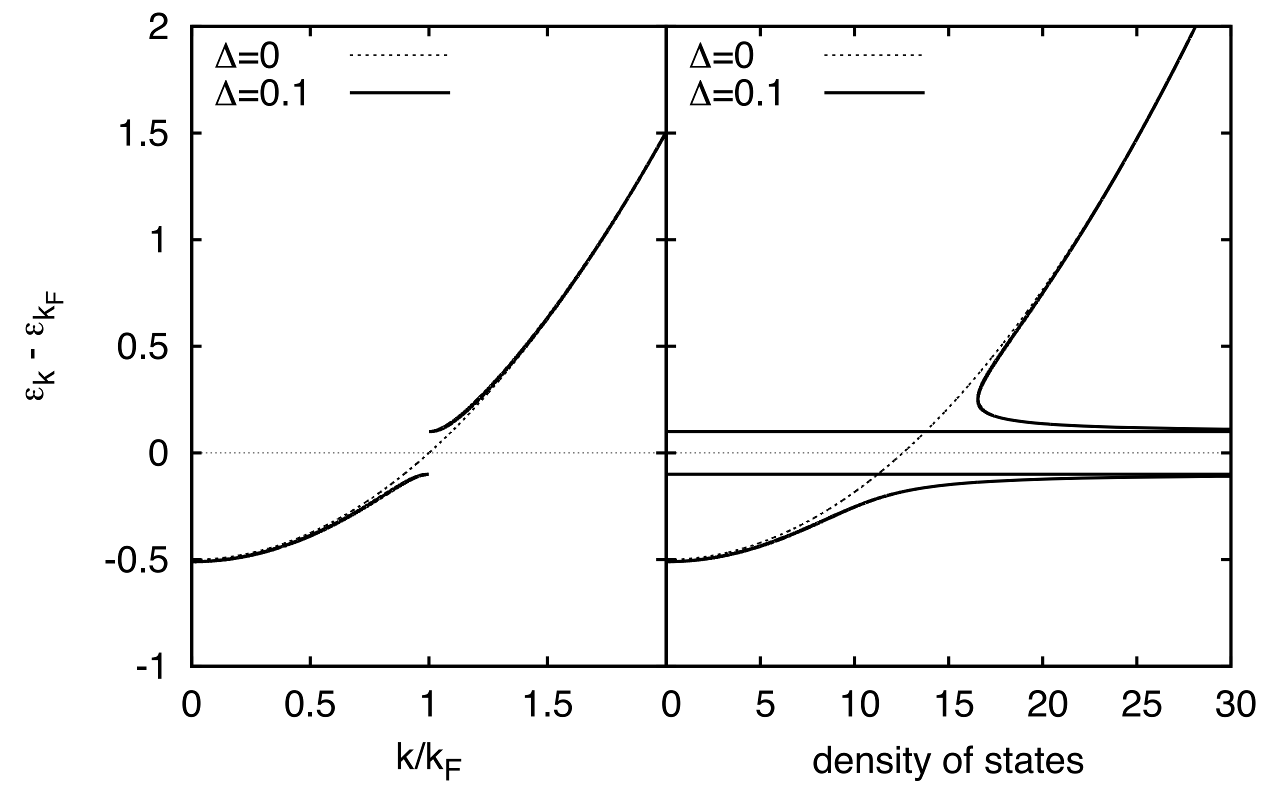
$$c_\alpha|0\rangle = 0 \qquad \left\{c_\alpha, c_\beta\right\} = 0 = \left\{c_\alpha^\dagger, c_\beta^\dagger\right\}$$

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

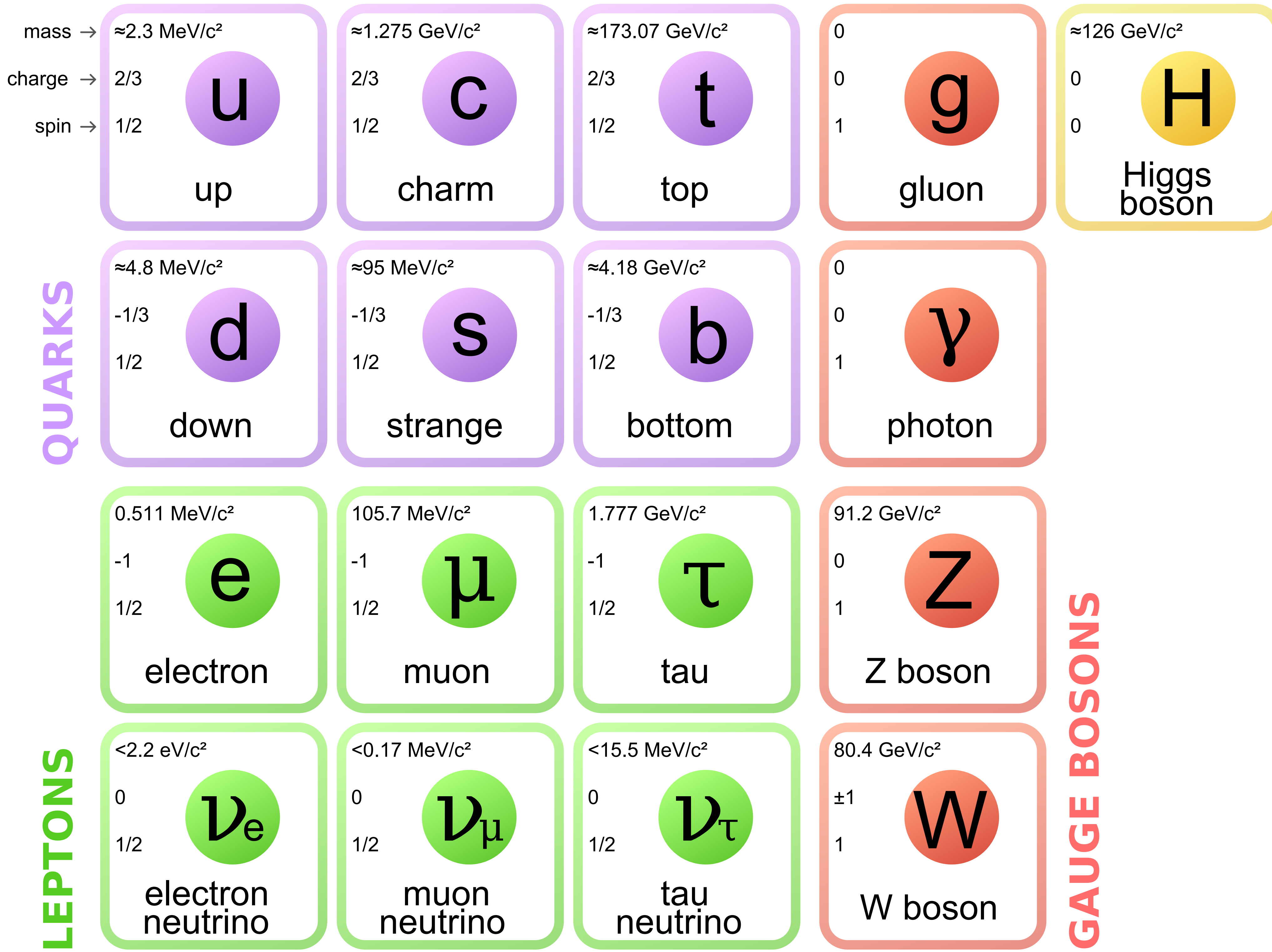
$$|\Phi_{\alpha_N\cdots\alpha_1}\rangle = c_{\alpha_N}^\dagger \cdots c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger |0\rangle$$

product state in Fock space





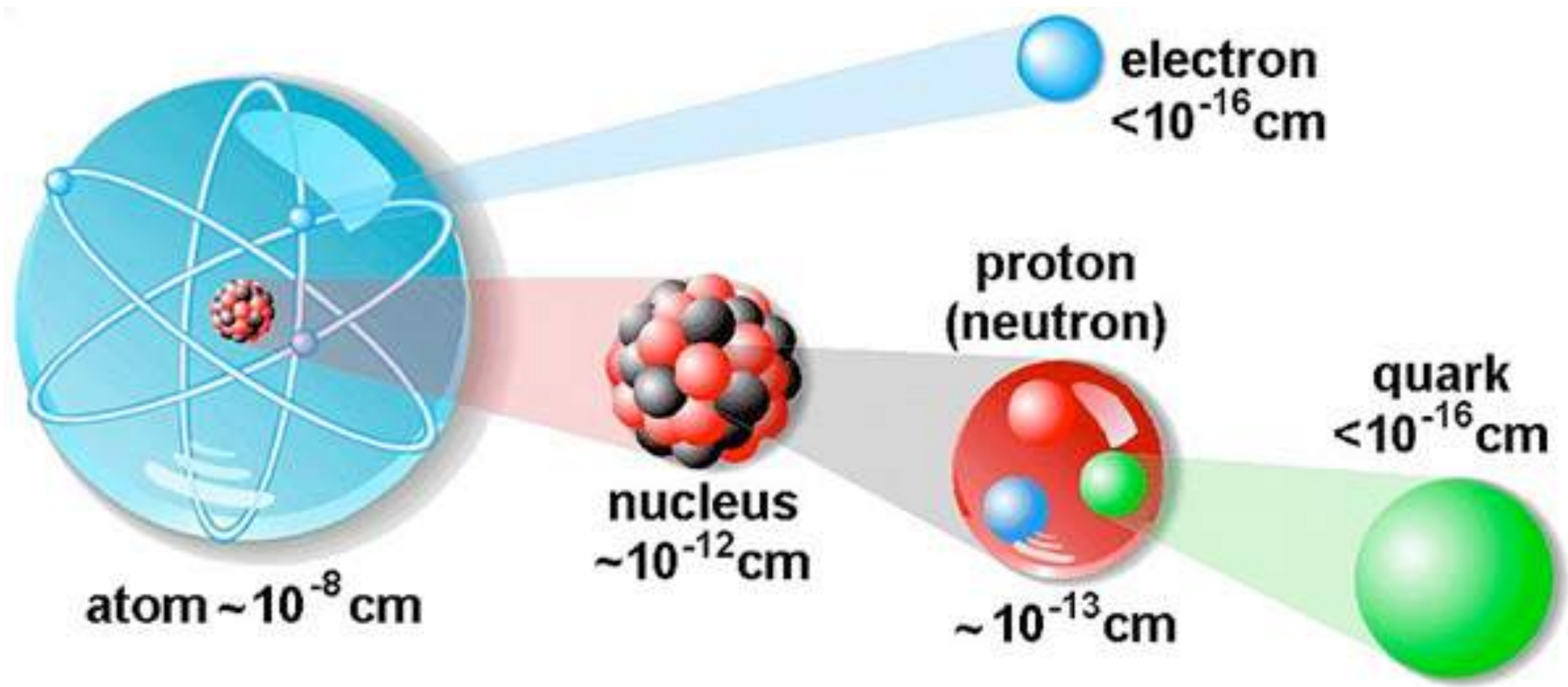
Standard Model: Elementary Particles



en.wikipedia.org/wiki/Standard_Model

indistinguishable particles

notion of elementary particle change over time/length/energy-scale



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

what does indistinguishable mean?

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...

indistinguishability and statistics

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

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

introduces **labeling** of particles

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

probability density is an observable

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 permutation)

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

Do we need the wave-function?

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

expectation value

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

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

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

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

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

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

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

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

representability problem:

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

antisymmetric wave-functions

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

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

computationally hard!

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

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:

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

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 orthonormal orbitals

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

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:

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

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

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

in particular

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

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

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:

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

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

creators/annihilators operate in Fock space
transform like orbitals!

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

then $c^\dagger_\alpha = \int dx\, \varphi_\alpha(x) \hat{\Psi}^\dagger(x)$

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

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

proof by induction

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

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: $\left\langle 0 \,\middle|\, \hat{\Psi}(x_1)\hat{\Psi}(x_2)\; c^\dagger_{\alpha_2} c^\dagger_{\alpha_1} \,\middle|\, 0 \right\rangle$

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

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

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

second quantization: Slater determinants

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

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

$$\begin{aligned}
&+ && \left\langle 0 \left| \hat\Psi(x_1)\ldots\hat\Psi(x_{N-1})\, c^\dagger_{\alpha_{N-1}} \ldots c^\dagger_{\alpha_1} \right| 0 \right\rangle && \varphi_{\alpha_N}(x_N) \\
&- && \left\langle 0 \left| \hat\Psi(x_1)\ldots\hat\Psi(x_{N-1})\, \textstyle\prod_{n\neq N-1} c^\dagger_{\alpha_n} \right| 0 \right\rangle && \varphi_{\alpha_{N-1}}(x_N) \\
&\vdots && && \\
&(-1)^N && \left\langle 0 \left| \hat\Psi(x_1)\ldots\hat\Psi(x_{N-1})\, c^\dagger_{\alpha_N} \ldots c^\dagger_{\alpha_2} \right| 0 \right\rangle && \varphi_{\alpha_1}(x_N)
\end{aligned}$$

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 $\Phi_{\alpha_1 \alpha_2 \dots \alpha_N}(x_1, x_2, \dots, x_N)$

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

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

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

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

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

$|0\rangle\langle 0| = \mathbb{1}$ 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 $M_0(x_1,...x_N)$=1 independent of particle coordinates

second quantized form for operating on N-electron states:

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

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

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

only(!) when operating on N-electron state

$$\vdots$$

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

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

result independent of N

second quantization: one-body operators

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

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

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

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

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

result independent of N

expand in complete orthonormal set of orbitals

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

transforms as 1-body operator

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

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

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

expectation values

$$\langle\Psi|M^{(1)}|\Psi\rangle = \sum_{n,m} M^{(1)}_{nm} \underbrace{\langle\Psi|c_n^\dagger c_m|\Psi\rangle}_{=:\Gamma^{(1)}_{nm}} = \mathrm{Tr}\,\boldsymbol{\Gamma}^{(1)}\boldsymbol{M}^{(1)}$$

$$\langle\Psi|M^{(2)}|\Psi\rangle = \sum_{n'>n,\, m'>m} \breve{M}^{(2)}_{nn',\,mm'} \underbrace{\langle\Psi|c_{n'}^\dagger c_n^\dagger c_m c_{m'}|\Psi\rangle}_{=:\breve{\Gamma}^{(2)}_{nn',\,mm'}} = \mathrm{Tr}\,\breve{\boldsymbol{\Gamma}}^{(2)}\breve{\boldsymbol{M}}^{(2)}$$

Slater determinant

$$|\Phi\rangle = c^\dagger_{\alpha_N}\cdots c^\dagger_{\alpha_1}|0\rangle \qquad \boldsymbol{P} = \sum_n |\alpha_n\rangle\langle\alpha_n|$$

1-DM: projector on occupied subspace

$$\Gamma^{(1)}_{nm} = \langle\varphi_m|\boldsymbol{P}|\varphi_n\rangle$$

$$\Gamma^{(p)}_{n_1\cdots n_p,m_1\cdots m_p} = \langle\Phi|c^\dagger_{n_p}\cdots c^\dagger_{n_1} c_{m_1}\cdots c_{m_p}|\Phi\rangle = \det\begin{pmatrix} \Gamma^{(1)}_{n_1 m_1} & \cdots & \Gamma^{(1)}_{n_1 m_p} \\ \vdots & \ddots & \vdots \\ \Gamma^{(1)}_{n_p m_1} & \cdots & \Gamma^{(1)}_{n_p m_p} \end{pmatrix}$$

many-body problem

$$H|\Psi\rangle = E|\Psi\rangle$$

introduce (orthonormal) orbital basis $\{|\varphi_n\rangle \mid n = 1, \ldots, K\}$

induces an orthonormal basis in N-electron space $\left\{|\Phi_{n_1 \cdots n_N}\rangle \mid n_1 < \cdots < n_N\right\}$

CI expansion

$$|\Psi\rangle = \sum_{n_1<\cdots<n_N} a_{n_1,\ldots,n_N} |\Phi_{n_1,\ldots,n_N}\rangle = \sum_{\boldsymbol{n}_i} a_{\boldsymbol{n}_i} |\Phi_{\boldsymbol{n}_i}\rangle$$

matrix eigenvalue problem

$$\begin{pmatrix} \langle\Phi_{\boldsymbol{n}_1}|H|\Phi_{\boldsymbol{n}_1}\rangle & \langle\Phi_{\boldsymbol{n}_1}|H|\Phi_{\boldsymbol{n}_2}\rangle & \cdots \\ \langle\Phi_{\boldsymbol{n}_2}|H|\Phi_{\boldsymbol{n}_1}\rangle & \langle\Phi_{\boldsymbol{n}_2}|H|\Phi_{\boldsymbol{n}_2}\rangle & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_{\boldsymbol{n}_1} \\ a_{\boldsymbol{n}_2} \\ \vdots \end{pmatrix} = E \begin{pmatrix} a_{\boldsymbol{n}_1} \\ a_{\boldsymbol{n}_2} \\ \vdots \end{pmatrix}$$

dimension of Hilbert space

number of ways to pick N different indices out of K

$$K \cdot (K-1) \cdot (K-2) \cdots (K-(N-1))$$

pick one ordering of the set of indices: $1/N!$

$$\dim \mathcal{H}_K^{(N)} = \frac{K!}{N!(K-N)!} = \binom{K}{N}$$

```
> bc
bc 1.06
Copyright 1991-1994, 1997, 1998, 2000 Free Software Foundation, Inc.
This is free software with ABSOLUTELY NO WARRANTY.
For details type `warranty'.
define f(n) { if (n==0) return 1 else return n*f(n-1) }
define b(k,n) { return f(k)/f(n)/f(k-n) }
b(100,25)
242519269720337121015504
b(100,25)*8/1024/1024/1024 # memory in GB
1806909365358480
```

non-interacting electrons

$$\hat{H} = \sum_{n,m} H_{nm}\, c_n^\dagger c_m$$

apply to single Slater determinant: linear combination of single-excitations

choose orbitals that diagonalize **single-electron matrix *H***

$$\hat{H} = \sum_{n,m} \varepsilon_n \delta_{n,m}\, c_n^\dagger c_m = \sum_n \varepsilon_n\, c_n^\dagger c_n$$

N-electron eigenstates $\quad |\Phi_{\boldsymbol{n}}\rangle = c_{n_N}^\dagger \cdots c_{n_1}^\dagger |0\rangle$

$$\sum_n \varepsilon_n c_n^\dagger c_n\, c_{n_N}^\dagger \cdots c_{n_1}^\dagger |0\rangle = \left(\sum_{i=1}^{N} \varepsilon_{n_i}\right) c_{n_N}^\dagger \cdots c_{n_1}^\dagger |0\rangle$$

Hartree-Fock

variational principle on manifold of Slater determinants

$$E_{\mathrm{HF}} = \min_{\Phi} \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

unitary transformations among Slater determinants

$$\hat{U}(\lambda) = e^{i\lambda\hat{M}} \quad \text{with} \quad \hat{M} = \sum_{\alpha,\beta} M_{\alpha\beta}\, c_\alpha^\dagger c_\beta \quad \text{hermitian}$$

energy expectation value

$$E(\lambda) = \langle \Phi | e^{i\lambda\hat{M}}\, \hat{H}\, e^{-i\lambda\hat{M}} | \Phi \rangle = \langle \Phi | \hat{H} | \Phi \rangle + i\lambda \langle \Phi | [\hat{H},\, \hat{M}] | \Phi \rangle + \frac{(i\lambda)^2}{2} \langle \Phi | \big[[\hat{H},\, \hat{M}],\, \hat{M} \big] | \Phi \rangle + \cdots$$

variational equation

$$\langle \Phi^{\mathrm{HF}} | [\hat{H},\, \hat{M}] | \Phi^{\mathrm{HF}} \rangle = 0$$

unitary transformations on Slater manifold

$$\hat{U}(\lambda) = e^{i\lambda\hat{M}} \quad \text{with} \quad \hat{M} = \sum_{\alpha,\beta} M_{\alpha\beta}\, c_\alpha^\dagger c_\beta \quad \text{hermitian}$$

$$e^{i\lambda\hat{M}}\, c_{\alpha_N}^\dagger \cdots c_{\alpha_1}|0\rangle = \underbrace{e^{i\lambda\hat{M}} c_{\alpha_N}^\dagger e^{-i\lambda\hat{M}}}_{\sum_\beta (e^{i\lambda \boldsymbol{M}})_{\alpha_N\beta}\, c_\beta}\; e^{i\lambda\hat{M}} \cdots e^{-i\lambda\hat{M}} e^{i\lambda\hat{M}} c_{\alpha_1}^\dagger e^{-i\lambda\hat{M}}\; \underbrace{e^{i\lambda\hat{M}}|0\rangle}_{=|0\rangle}$$

$$\frac{d}{d\lambda}\bigg|_{\lambda=0} e^{i\lambda\hat{M}}\, c_\gamma^\dagger\, e^{-i\lambda\hat{M}} = \qquad e^{i\lambda\hat{M}}\; i\,[\hat{M},\, c_\alpha^\dagger]\, e^{-i\lambda\hat{M}}\bigg|_{\lambda=0} \qquad = i\sum_\alpha c_\alpha^\dagger\, M_{\alpha\gamma}$$

$$\frac{d^2}{d\lambda^2}\bigg|_{\lambda=0} e^{i\lambda\hat{M}}\, c_\gamma^\dagger\, e^{-i\lambda\hat{M}} = \frac{d}{d\lambda}\bigg|_{\lambda=0} e^{i\lambda\hat{M}} \left(i\sum_{\alpha'} c_{\alpha'}^\dagger\, M_{\alpha'\gamma}\right) e^{-i\lambda\hat{M}} \quad = i^2 \sum_\alpha c_\alpha^\dagger \underbrace{\sum_{\alpha'} M_{\alpha\alpha'} M_{\alpha'\gamma}}_{(\boldsymbol{M}^2)_{\alpha\gamma}}$$

$$\vdots$$

$$\frac{d^n}{d\lambda^n}\bigg|_{\lambda=0} e^{i\lambda\hat{M}}\, c_\gamma^\dagger\, e^{-i\lambda\hat{M}} = \qquad i^n \sum_\alpha c_\alpha^\dagger\, (\boldsymbol{M}^n)_{\alpha\gamma}$$

$$[c_\alpha^\dagger c_\beta,\, c_\gamma^\dagger] = c_\alpha^\dagger \{c_\beta,\, c_\gamma^\dagger\} - \{c_\alpha^\dagger,\, c_\gamma^\dagger\} c_\beta = c_\alpha^\dagger\, \delta_{\beta,\gamma}$$

HF variational condition

$$\langle \Phi^{\text{HF}} | [\hat{H},\, \hat{M}] | \Phi^{\text{HF}} \rangle = 0 \;\leadsto\; \langle \Phi^{\text{HF}} | [\hat{H},\, c_n^\dagger c_m + c_m^\dagger c_n] | \Phi^{\text{HF}} \rangle = 0 \quad \forall\, n \geq m$$

orthonormal basis $\quad |\Phi^{\text{HF}}\rangle = c_N^\dagger \cdots c_1^\dagger |0\rangle$

$$c_n^\dagger c_m |\Phi^{\text{HF}}\rangle = \begin{cases} \delta_{n,m} |\Phi^{\text{HF}}\rangle & \text{if } n,\, m \in \{1, \ldots, N\} \\ 0 & \text{if } m \quad \notin \{1, \ldots, N\} \end{cases}$$

simplifies variational condition to (Brillouin theorem)

$$\langle \Phi^{\text{HF}} | c_m^\dagger c_n \hat{H} | \Phi^{\text{HF}} \rangle = 0 \quad \forall\, m \in \{1, \ldots, N\},\, n \notin \{1, \ldots, N\}$$

applying Hamiltonian does not generate singly excited determinants

analogy to non-interacting problem

$$\hat{H} = \sum_{n,m} c_n^\dagger \, T_{nm} \, c_m + \sum_{n>n',m>m'} c_n^\dagger c_{n'}^\dagger \left(U_{nn',mm'} - U_{nn',m'm}\right) c_{m'} c_m$$

Brillouin condition

$$\underbrace{\left(T_{nm} + \sum_{m'\leq N} \left(U_{nm',mm'} - U_{nm',m'm}\right)\right)}_{=:F_{nm}} c_n^\dagger c_m |\Phi^{\mathrm{HF}}\rangle = 0 \quad \forall n > N \geq m$$

same condition as for non-interacting Hamiltonian F_{nm} (Fock-matrix)

depends on Φ^{HF} ⇒ self-consistent problem

$$\varepsilon_m^{\mathrm{HF}} = \left(T_{mm} + \sum_{m'\leq N} \underbrace{\left(U_{mm',mm'} - U_{mm',m'm}\right)}_{=:\Delta_{mm'}}\right) = \left(T_{mm} + \sum_{m'\leq N} \Delta_{mm'}\right)$$

quasi-particle picture

total energy

$$\langle \Phi^{\mathrm{HF}} | \hat{H} | \Phi^{\mathrm{HF}} \rangle = \sum_{m \le N} \left(T_{mm} + \sum_{m' < m} \Delta_{mm'} \right) = \sum_{m \le N} \left(T_{mm} + \frac{1}{2} \sum_{m' \le N} \Delta_{mm'} \right) = \sum_{m \le N} \left(\varepsilon_m^{\mathrm{HF}} - \frac{1}{2} \sum_{m' \le N} \Delta_{mm'} \right)$$

remove electron from eigenstate of F_{mn} (Koopmans' theorem)

$$\langle \Phi^{\mathrm{HF}} | c_a^\dagger \, \hat{H} \, c_a | \Phi^{\mathrm{HF}} \rangle - \langle \Phi^{\mathrm{HF}} | \hat{H} | \Phi^{\mathrm{HF}} \rangle = - \left(T_{aa} + \frac{1}{2} \sum_{m' \le N} \Delta_{am'} \right) - \frac{1}{2} \sum_{m \ne a \le N} \Delta_{ma} = -\varepsilon_a^{\mathrm{HF}}$$

electron-hole excitation ($b > N \geq a$)

$$\varepsilon_{a \to b}^{\mathrm{HF}} = \langle \Phi_{a \to b}^{\mathrm{HF}} | \hat{H} | \Phi_{a \to b}^{\mathrm{HF}} \rangle - \langle \Phi^{\mathrm{HF}} | \hat{H} | \Phi^{\mathrm{HF}} \rangle = \varepsilon_b^{\mathrm{HF}} - \varepsilon_a^{\mathrm{HF}} - \Delta_{ab}$$

electron-hole attraction

$$\Delta_{ab} = \frac{1}{2} (\Delta_{ab} + \Delta_{ba}) = \frac{1}{2} \left\langle \varphi_a \varphi_b - \varphi_b \varphi_a \left| \frac{1}{r - r'} \right| \varphi_a \varphi_b - \varphi_b \varphi_a \right\rangle > 0$$

The Sveriges Riksbank Prize in Economic Sciences in Memory of Alfred Nobel 1975

Leonid Vitaliyevich Kantorovich, Tjalling C. Koopmans

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The Sveriges Riksbank Prize in Economic Sciences in Memory of Alfred Nobel 1975

Leonid Vitaliyevich Kantorovich
Prize share: 1/2

Tjalling C. Koopmans
Prize share: 1/2

The Sveriges Riksbank Prize in Economic Sciences in Memory of Alfred Nobel 1975 was awarded jointly to Leonid Vitaliyevich Kantorovich and Tjalling C. Koopmans *"for their contributions to the theory of optimum allocation of resources"*

homogeneous electron gas

$$\hat{H} = \sum_{\sigma} \int d\boldsymbol{k}\, \frac{|\boldsymbol{k}^2|}{2}\, c^{\dagger}_{\boldsymbol{k},\sigma} c_{\boldsymbol{k},\sigma} + \frac{1}{2(2\pi)^3} \sum_{\sigma,\sigma'} \int d\boldsymbol{k} \int d\boldsymbol{k}' \int' d\boldsymbol{q}\, \frac{4\pi}{|\boldsymbol{q}|^2}\, c^{\dagger}_{\boldsymbol{k}-\boldsymbol{q},\sigma} c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q},\sigma'} c_{\boldsymbol{k}',\sigma'} c_{\boldsymbol{k},\sigma}$$

Slater determinant of plane waves

$$|\Phi^{\mathrm{HF}}\rangle = \prod_{|\boldsymbol{k}|<k_F} c^{\dagger}_{\boldsymbol{k}\sigma} |0\rangle$$

no single-excitations (Brillouin condition)

density of electrons of spin σ

$$n_\sigma(\boldsymbol{r}) = \langle \Phi^{\mathrm{HF}} | \hat{\Psi}^{\dagger}_{\sigma}(\boldsymbol{r}) \hat{\Psi}_{\sigma}(\boldsymbol{r}) | \Phi^{\mathrm{HF}} \rangle = \int_{|\boldsymbol{k}|<k_F} d\boldsymbol{k}\, \left| \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{(2\pi)^{3/2}} \right|^2 = \frac{k_F^3}{6\pi^2}$$

$$\{\hat{\Psi}^{\dagger}_{\sigma}(\boldsymbol{r}),\, c_{\boldsymbol{k},\sigma}\} = \int d\boldsymbol{r}'\, \frac{e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}}{(2\pi)^{3/2}}\, \{\hat{\Psi}^{\dagger}_{\sigma}(\boldsymbol{r}),\, \hat{\Psi}_{\sigma}(\boldsymbol{r}')\} = \frac{e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}}{(2\pi)^{3/2}}$$

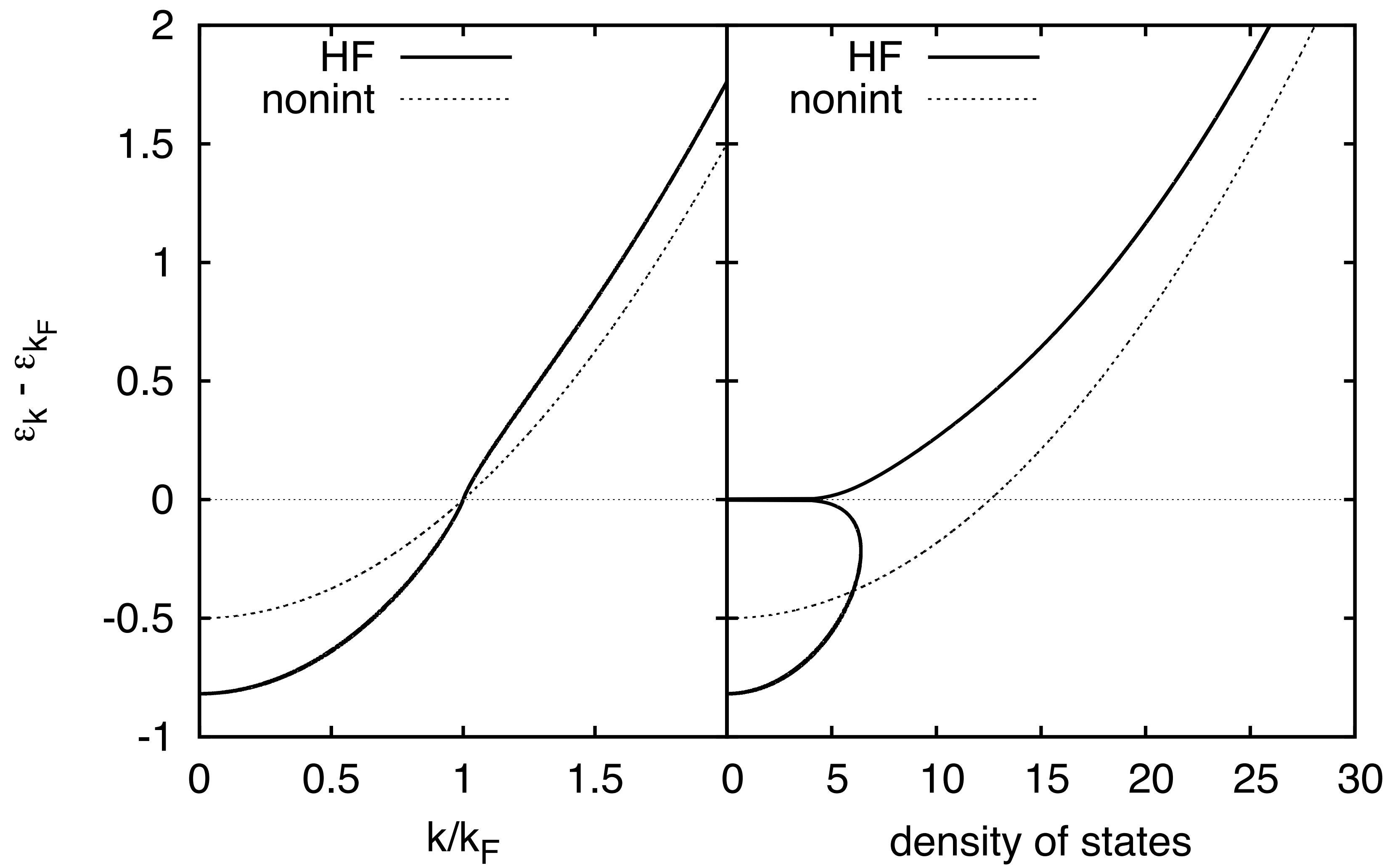
dispersion & DOS

quasiparticle energies

$$\varepsilon^{\mathrm{HF}}_{k,\sigma} = \frac{|\boldsymbol{k}|^2}{2} - \frac{1}{4\pi^2}\int_{|\boldsymbol{k}'|<k_F} d\boldsymbol{k}'\,\frac{1}{|\boldsymbol{k}-\boldsymbol{k}'|^2} = \frac{k^2}{2} - \frac{k_F}{\pi}\left(1 + \frac{k_F^2 - k^2}{2k_F k}\ln\left|\frac{k_F + k}{k_F - k}\right|\right)$$

quasiparticle density-of-states

$$D^{\mathrm{HF}}_{\sigma}(\varepsilon) = 4\pi k^2 \left(\frac{d\varepsilon^{\mathrm{HF}}_{k,\sigma}}{dk}\right)^{-1} = 4\pi k^2\left(k - \frac{k_F}{\pi k}\left(1 - \frac{k_F^2 + k^2}{2k_F k}\ln\left|\frac{k_F + k}{k_F - k}\right|\right)\right)^{-1}$$



exchange hole

diagonal of two-body density matrix

$$\langle \Phi_{k_F} | \hat{\Psi}^\dagger_{\sigma'}(\boldsymbol{r}') \hat{\Psi}^\dagger_{\sigma}(\boldsymbol{r}) \hat{\Psi}_{\sigma}(\boldsymbol{r}) \hat{\Psi}_{\sigma'}(\boldsymbol{r}') | \Phi_{k_F} \rangle = \det \begin{pmatrix} \Gamma^{(1)}_{\sigma\sigma}(\boldsymbol{r}, \boldsymbol{r}) & \Gamma^{(1)}_{\sigma\sigma'}(\boldsymbol{r}, \boldsymbol{r}') \\ \Gamma^{(1)}_{\sigma'\sigma}(\boldsymbol{r}', \boldsymbol{r}) & \Gamma^{(1)}_{\sigma'\sigma'}(\boldsymbol{r}', \boldsymbol{r}') \end{pmatrix}$$

one-body density matrix for like spins

$$\Gamma_{\sigma\sigma}(\boldsymbol{r}, \boldsymbol{r}') = \int_{|\boldsymbol{k}|<k_F} d\boldsymbol{k}\, \frac{e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{(2\pi)^3} = 3n_\sigma\, \frac{\sin x - x\cos x}{x^3}$$

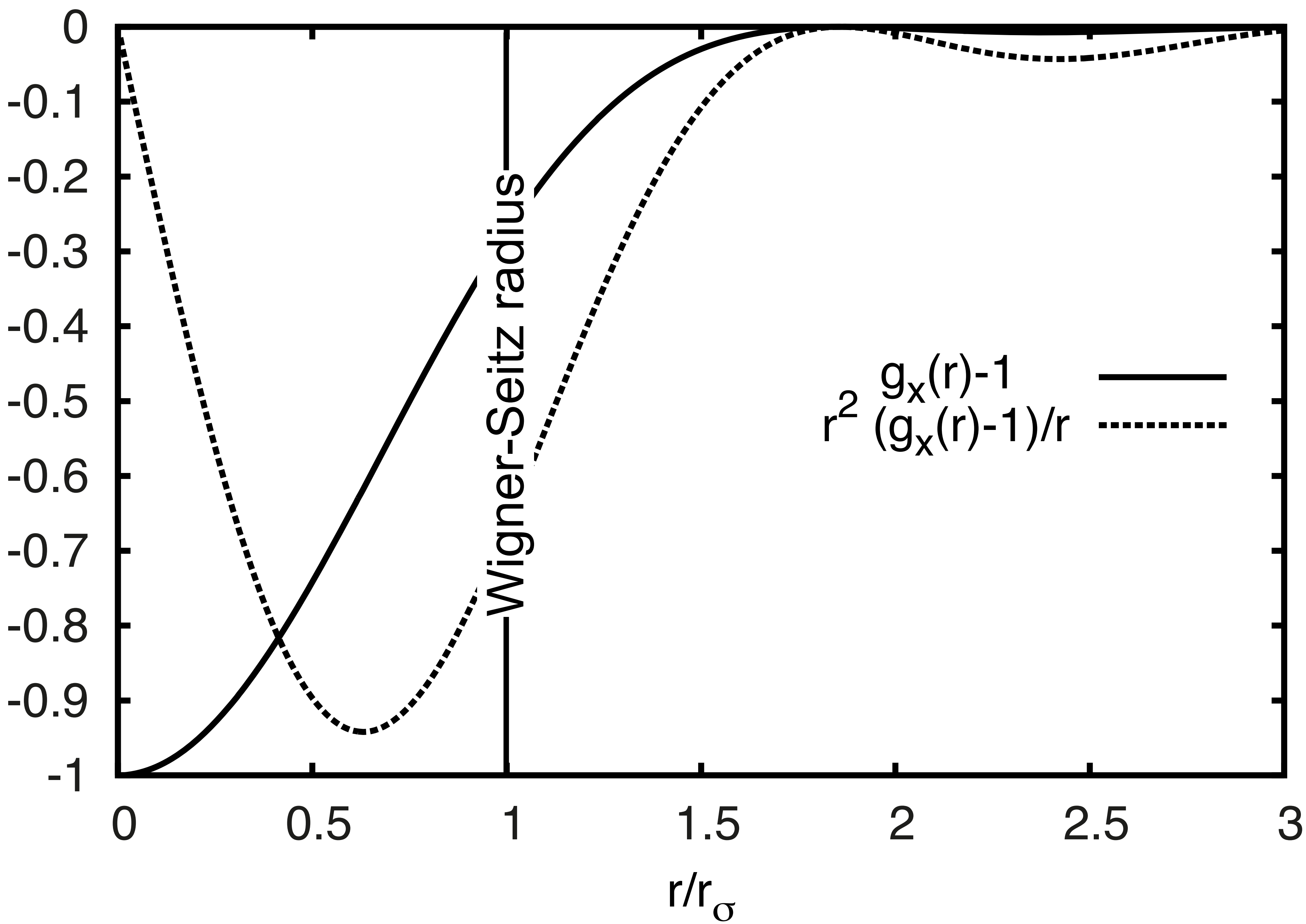
exchange hole

$$g_x(r, 0) - 1 = \frac{\langle \Phi_{k_F} | \hat{\Psi}^\dagger_{\sigma'}(\boldsymbol{r}') \hat{\Psi}^\dagger_{\sigma}(\boldsymbol{r}) \hat{\Psi}_{\sigma}(\boldsymbol{r}) \hat{\Psi}_{\sigma'}(\boldsymbol{r}')}{n_\sigma(\boldsymbol{r}) n_\sigma(\boldsymbol{r}')}$$

$$= -9 \left(\frac{\sin k_F r - k_F r \cos k_F r}{(k_F r)^3} \right)^2$$

exchange hole

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



exchange energy

correction to Hartree energy due to antisymmetry

$$E_x = \frac{1}{2}\int d\boldsymbol{r}\, n_\sigma \int d\boldsymbol{r}'\, n_\sigma \frac{g_x(r,r')-1}{|\boldsymbol{r}-\boldsymbol{r}'|} = \frac{1}{2}\underbrace{\int d\boldsymbol{r}\, n_\sigma}_{=N} \int d\tilde{\boldsymbol{r}}\, n_\sigma \frac{g_x(\tilde{r},0)-1}{\tilde{r}}$$

exchange energy per electron of spin σ

$$\varepsilon_x^\sigma = \frac{4\pi n_\sigma}{2}\int_0^\infty dr\, r^2\, \frac{g(r,0)-1}{r} = -\frac{9\cdot 4\pi n_\sigma}{2k_F^2}\underbrace{\int_0^\infty dx\, \frac{(\sin x - x\cos x)^2}{x^5}}_{=1/4} = -\frac{3k_F}{4\pi}$$

HF state as vacuum

$$|\Phi^{\mathrm{HF}}\rangle = \prod_{|\boldsymbol{k}|<k_F} c^\dagger_{\boldsymbol{k}\sigma}|0\rangle$$

$$c^\dagger_{\boldsymbol{k}\sigma}|\Phi_{k_F}\rangle = 0 \;\; \text{for } |\boldsymbol{k}| < k_F$$

$$c_{\boldsymbol{k}\sigma}|\Phi_{k_F}\rangle = 0 \;\; \text{otherwise.}$$

HF ground state acts as vacuum state for transformed operators

$$\tilde{c}_{\boldsymbol{k}\sigma} = \Theta(k_F - |\boldsymbol{k}|)\, c^\dagger_{\boldsymbol{k}\sigma} + \Theta(|\boldsymbol{k}| - k_F)\, c_{\boldsymbol{k}\sigma} = \begin{cases} c^\dagger_{\boldsymbol{k}\sigma} & \text{for } |\boldsymbol{k}| < k_F \\ c_{\boldsymbol{k}\sigma} & \text{for } |\boldsymbol{k}| > k_F \end{cases}$$

$$\tilde{c}_{\boldsymbol{k}\sigma}|\Phi^{\mathrm{HF}}\rangle = 0 \qquad \left\{\tilde{c}_{\boldsymbol{k}\sigma}, \tilde{c}_{\boldsymbol{k}'\sigma'}\right\} = 0 = \left\{\tilde{c}^\dagger_{\boldsymbol{k}\sigma}, \tilde{c}^\dagger_{\boldsymbol{k}'\sigma'}\right\}$$

$$\langle\Phi^{\mathrm{HF}}|\Phi^{\mathrm{HF}}\rangle = 1 \qquad \left\{\tilde{c}_{\boldsymbol{k}\sigma}, \tilde{c}^\dagger_{\boldsymbol{k}'\sigma'}\right\} = \delta(\boldsymbol{k} - \boldsymbol{k}')\,\delta_{\sigma,\sigma'}$$

note: vacuum state no longer invariant under basis transformations!

BCS theory

BCS Hamiltonian

$$\hat{H}_{\mathrm{BCS}} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} \, c^\dagger_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} - \sum_{\boldsymbol{k}\boldsymbol{k}'} G_{\boldsymbol{k}\boldsymbol{k}'} \, c^\dagger_{\boldsymbol{k}\uparrow} c^\dagger_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow}$$

Bogoliubov-Valatin operators mix creators & annihilators

$$b_{\boldsymbol{k}\uparrow} = u_k \, c_{\boldsymbol{k}\uparrow} - v_k \, c^\dagger_{-\boldsymbol{k}\downarrow}$$

$$b_{\boldsymbol{k}\downarrow} = u_k \, c_{\boldsymbol{k}\downarrow} + v_k \, c^\dagger_{-\boldsymbol{k}\uparrow}$$

canonical anticommutation relations

$$\{b_{\boldsymbol{k}\sigma},\, b_{\boldsymbol{k}'\sigma'}\} = 0 = \{b^\dagger_{\boldsymbol{k}\sigma},\, b^\dagger_{\boldsymbol{k}'\sigma'}\} \quad \text{and} \quad \{b_{\boldsymbol{k}\sigma},\, b_{\boldsymbol{k}'\sigma'}\} = \delta(\boldsymbol{k} - \boldsymbol{k}')\, \delta_{\sigma,\sigma'}$$

fulfilled for $u_k^2 + v_k^2 = 1$

corresponding vacuum state?

BCS state

obvious candidate (product state in Fock-space)

$$|\mathrm{BCS}\rangle \propto \prod_{\boldsymbol{k}\sigma} b_{\boldsymbol{k}\sigma}|0\rangle$$

need only consider groups of operators with fixed $\pm\boldsymbol{k}$

$$b_{-\boldsymbol{k}\uparrow}b_{\boldsymbol{k}\downarrow}b_{\boldsymbol{k}\uparrow}b_{-\boldsymbol{k}\downarrow}|0\rangle = v_k(u_k + v_k\, c^\dagger_{-\boldsymbol{k}\uparrow}c^\dagger_{\boldsymbol{k}\downarrow})\, v_k(u_k + v_k\, c^\dagger_{\boldsymbol{k}\uparrow}c^\dagger_{-\boldsymbol{k}\downarrow})\, |0\rangle$$

normalizable?

$$\langle 0|(u_k+v_k c_{-\boldsymbol{k}\downarrow}c_{\boldsymbol{k}\uparrow})(u_k+v_k c^\dagger_{\boldsymbol{k}\downarrow}c^\dagger_{-\boldsymbol{k}\uparrow})(u_k+v_k c^\dagger_{-\boldsymbol{k}\uparrow}c^\dagger_{\boldsymbol{k}\downarrow})(u_k+v_k c^\dagger_{\boldsymbol{k}\uparrow}c^\dagger_{-\boldsymbol{k}\downarrow})|0\rangle = u_k^4+2u_k^2v_k^2+v_k^4$$

(normalized) vacuum

$$|\mathrm{BCS}\rangle = \prod_{\boldsymbol{k}} \frac{1}{v_k} b_{\boldsymbol{k}\sigma}|0\rangle = \prod_{\boldsymbol{k}}(u_k + v_k\, c^\dagger_{\boldsymbol{k}\uparrow}c^\dagger_{-\boldsymbol{k}\downarrow})\, |0\rangle$$

contributions in all sectors with even number of electrons

electronic properties

$$c_{\boldsymbol{k}\uparrow} = u_k b_{\boldsymbol{k}\uparrow} + v_k b^{\dagger}_{-\boldsymbol{k}\downarrow}$$
$$c_{\boldsymbol{k}\downarrow} = u_k b_{\boldsymbol{k}\downarrow} - v_k b^{\dagger}_{-\boldsymbol{k}\uparrow}$$

momentum distribution

$$\langle \mathrm{BCS}|\, c^{\dagger}_{\boldsymbol{k}\uparrow}\, c_{\boldsymbol{k}\uparrow}\, |\mathrm{BCS}\rangle = \langle \mathrm{BCS}|(u_k b^{\dagger}_{\boldsymbol{k}\uparrow} + v_k b_{-\boldsymbol{k}\downarrow})(u_k b_{\boldsymbol{k}\uparrow} + v_k b^{\dagger}_{-\boldsymbol{k}\downarrow})|\mathrm{BCS}\rangle = v_k^2$$

BCS wave function has amplitude in all even-*N* Hilbert spaces

pairing density

$$\langle \mathrm{BCS}| c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} |\mathrm{BCS}\rangle = \langle \mathrm{BCS}|(u_k b^{\dagger}_{\boldsymbol{k}\uparrow} + v_k b_{-\boldsymbol{k}\downarrow})(u_k b^{\dagger}_{-\boldsymbol{k}\downarrow} - v_k b_{\boldsymbol{k},\uparrow})|\mathrm{BCS}\rangle = u_k v_k$$

minimize energy expectation value

energy expectation value

fix average particle number via chemical potential

$$\langle \mathrm{BCS}|\hat{H} - \mu\hat{N}|\mathrm{BCS}\rangle = \sum_{\boldsymbol{k}\sigma}(\varepsilon_{\boldsymbol{k}} - \mu)\, v_k^2 - \sum_{\boldsymbol{k},\boldsymbol{k}'} G_{\boldsymbol{k}\boldsymbol{k}'}\, u_k v_k u_{k'} v_{k'}$$

variational equations

$$4(\varepsilon_{\boldsymbol{k}} - \mu)\, v_k = 2\sum_{\boldsymbol{k}'} G_{\boldsymbol{k}\boldsymbol{k}'} \left(u_k - \frac{v_k}{u_k} v_k\right) u_{k'} v_{k'}$$

$$N = \sum_{\boldsymbol{k}} 2v_{\boldsymbol{k}}^2$$

solve (numerically) for v_k and μ

simplified model

assume constant attraction only for electrons close to Fermi level

$$\Delta := \sum_{\boldsymbol{k}'} G_{\boldsymbol{k}\boldsymbol{k}'}\, u_{k'} v_{k'} = G \sum_{\boldsymbol{k}:\text{close to FS}} u_k v_k$$

momentum distribution

$$v_k^2 = \frac{1}{2}\left(1 - \frac{\varepsilon_{\boldsymbol{k}} - \mu}{\sqrt{(\varepsilon_{\boldsymbol{k}} - \mu)^2 + \Delta^2}}\right)$$

gap equation

$$1 = \frac{G}{2} \sum_{\boldsymbol{k}} \frac{1}{\sqrt{(\varepsilon_k - \mu)^2 + \Delta^2}}$$

electron density

$$1 = \frac{1}{N} \sum_{\boldsymbol{k}} \left(1 - \frac{\varepsilon_{\boldsymbol{k}} - \mu}{\sqrt{(\varepsilon_{\boldsymbol{k}} - \mu)^2 + \Delta^2}}\right)$$

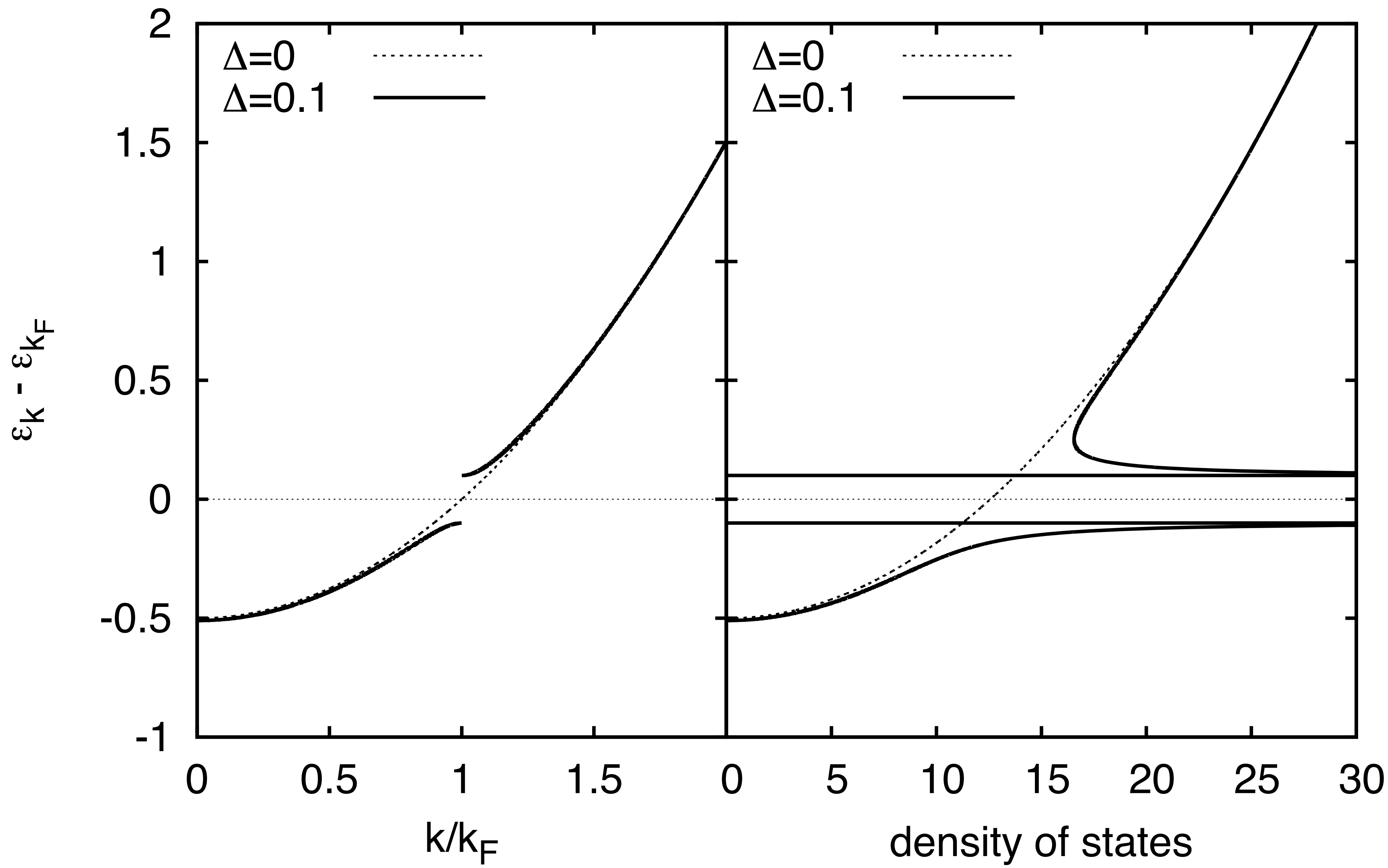
solve for Δ and μ

quasi electrons

(unrelaxed) quasi-electron state $\quad |\boldsymbol{k}\uparrow\rangle = \frac{1}{u_k} c^\dagger_{\boldsymbol{k}\uparrow}|\mathrm{BCS}\rangle = b^\dagger_{\boldsymbol{k}\uparrow}|\mathrm{BCS}\rangle$

quasi-particle energy

$$\langle \boldsymbol{k}\uparrow|\hat{H}-\mu\hat{N}|\boldsymbol{k}\uparrow\rangle - \langle \mathrm{BCS}|\hat{H}-\mu\hat{N}|\mathrm{BCS}\rangle = \mathrm{sgn}(\varepsilon_{\boldsymbol{k}}-\mu)\,\sqrt{(\varepsilon_{\boldsymbol{k}}-\mu)^2+\Delta^2}$$



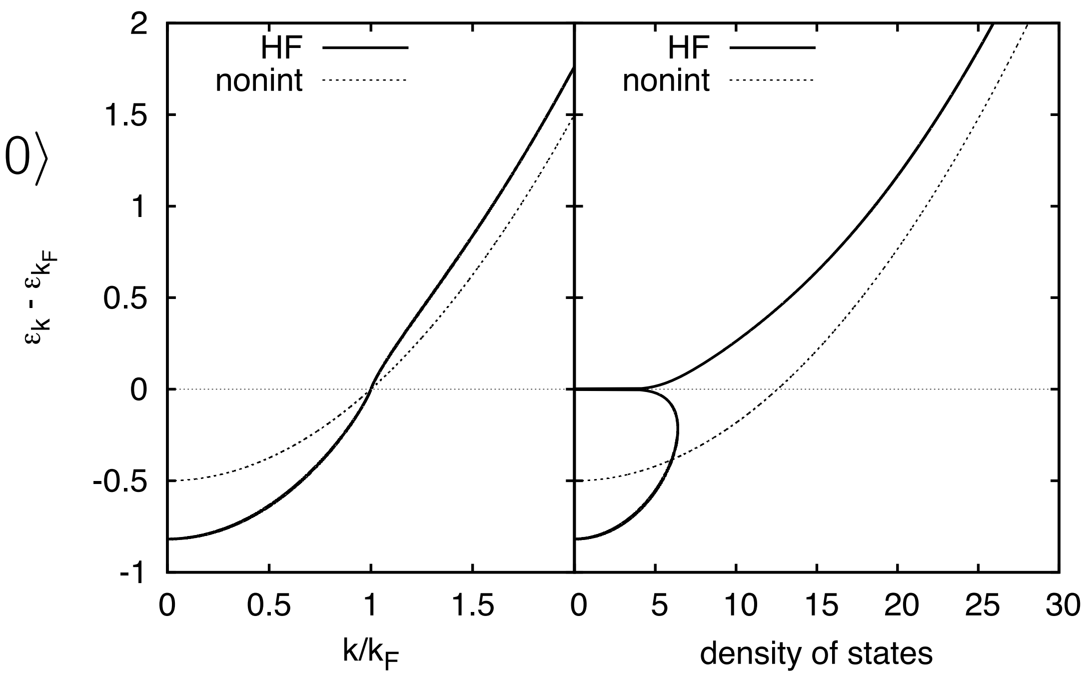
summary

indistinguishable electrons

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

(anti)symmetrization is hard
Slater determinants to the rescue

$$|\Phi^{\mathrm{HF}}\rangle = \prod_{|\boldsymbol{k}|<k_F} c^\dagger_{\boldsymbol{k}\sigma}|0\rangle$$



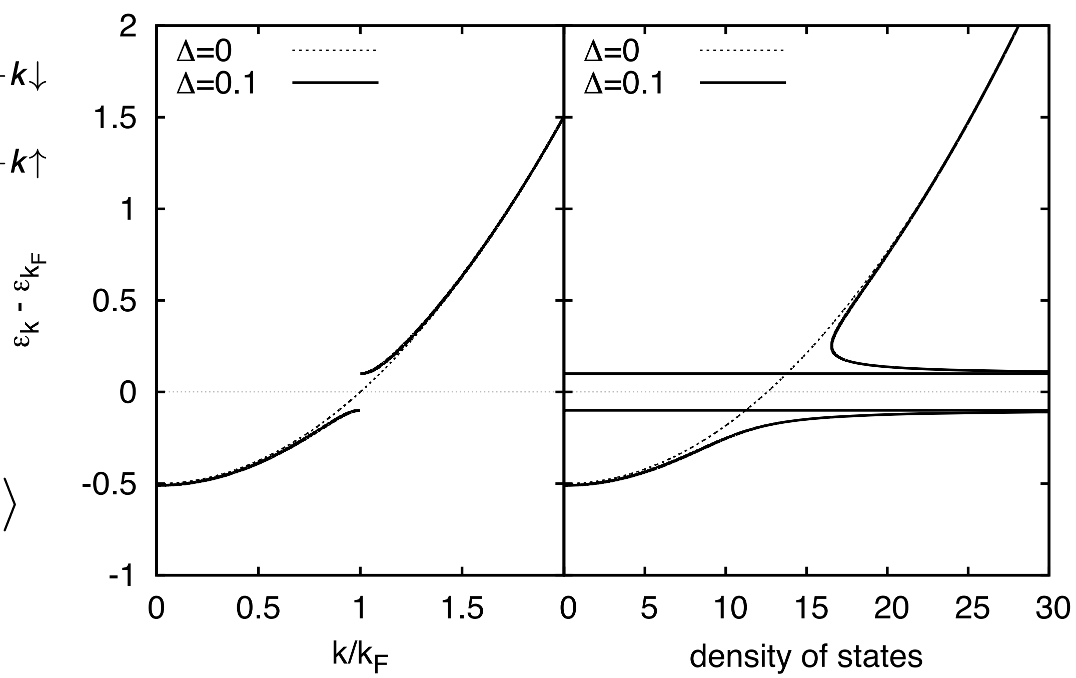
$$c_\alpha|0\rangle = 0 \qquad \{c_\alpha, c_\beta\} = 0 = \{c^\dagger_\alpha, c^\dagger_\beta\}$$

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

$$b_{\boldsymbol{k}\uparrow} = u_k c_{\boldsymbol{k}\uparrow} - v_k c^\dagger_{-\boldsymbol{k}\downarrow}$$

$$b_{\boldsymbol{k}\downarrow} = u_k c_{\boldsymbol{k}\downarrow} + v_k c^\dagger_{-\boldsymbol{k}\uparrow}$$

$$|\mathrm{BCS}\rangle \propto \prod_{\boldsymbol{k}\sigma} b_{\boldsymbol{k}\sigma}|0\rangle$$



second quantization:
keeping track of signs
Dirac states

extends to Fock space

$$\hat{H} = \sum_{n,m} c^\dagger_n\, T_{nm}\, c_m + \sum_{nn',mm'} c^\dagger_n c^\dagger_{n'}\, U_{nn',mm'}\, c_{m'} c_m$$