Mean-Field Theory: HF and BCS

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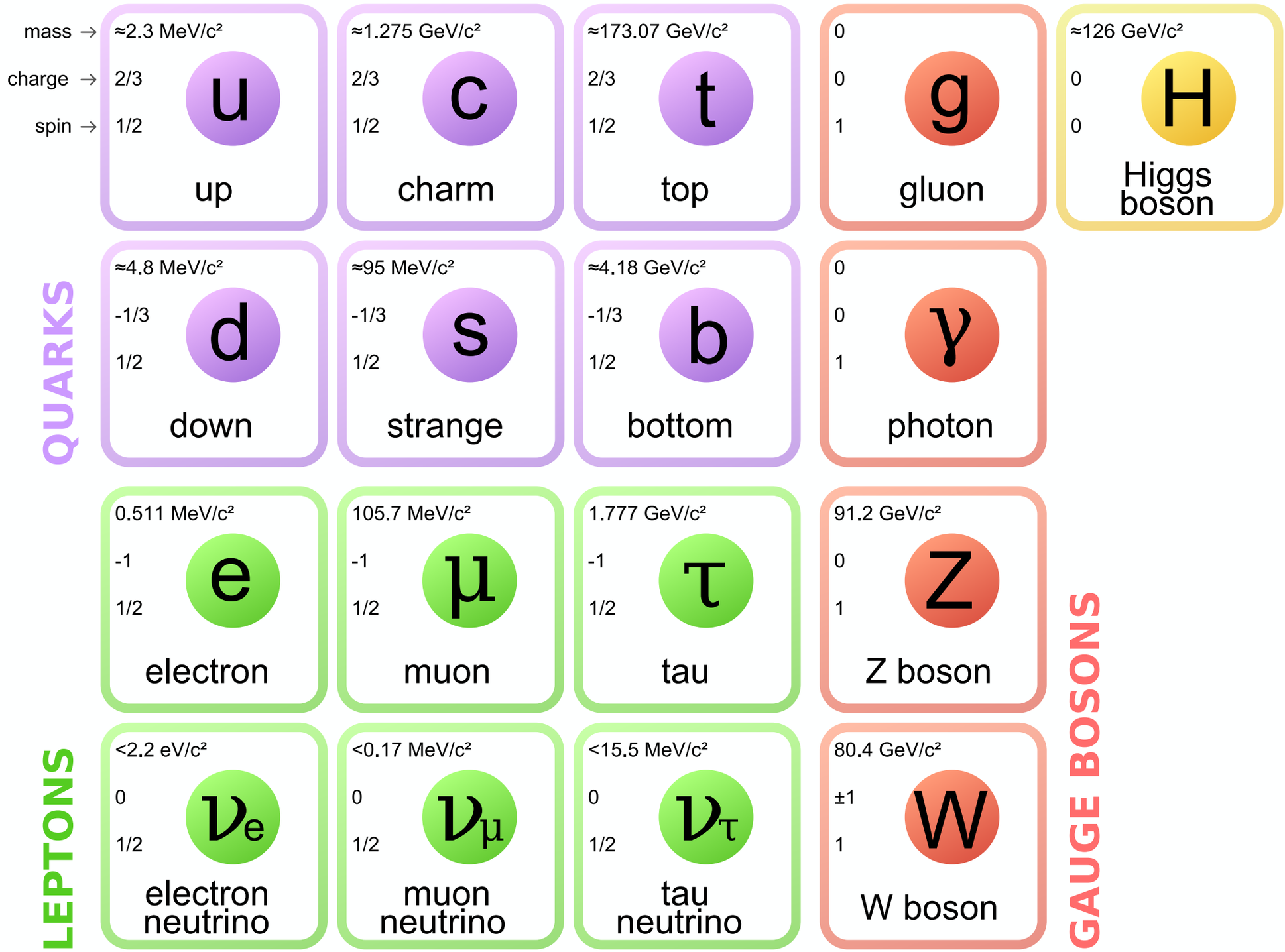
Martin Schoeller
IDENTICAL
Portraits of Twins
teNeues Verlag, 2012

Identical Twins

Diane Arbus:
Identical Twins,
Roselle, NJ, 1967

Standard Model: Elementary Particles



en.wikipedia.org/wiki/Standard_Model

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

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

spin-statistics connection

bosons (integer spin): symmetric wave-function

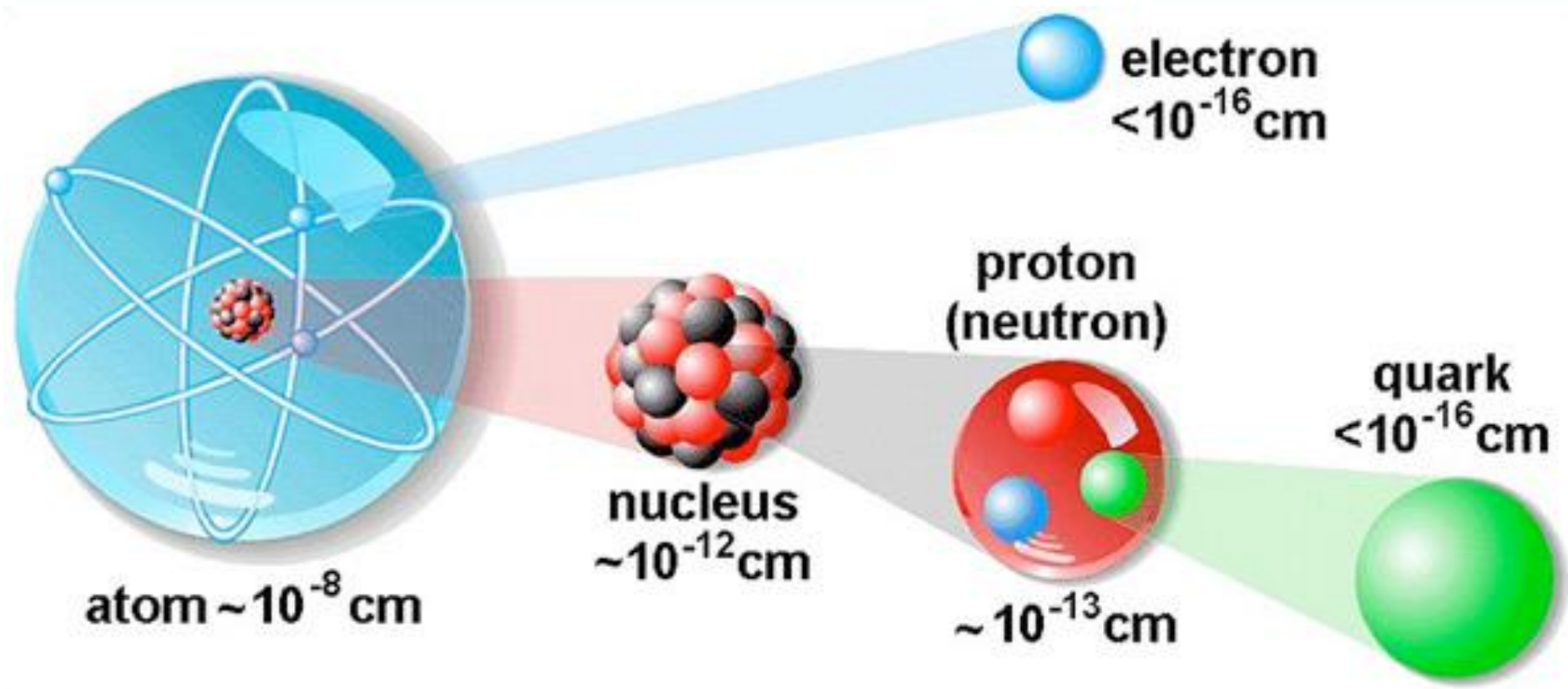
fermions (half-integer spin): anti-symmetric wave-function

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.

indistinguishable particles

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



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

The Theory of Everything

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Contributed by David Pines, November 18, 1999

We discuss recent developments in our understanding of matter, broadly construed, and their implications for contemporary research in fundamental physics.

The Theory of Everything is a term for the ultimate theory of the universe—a set of equations capable of describing all phenomena that have been observed, or that will ever be observed (1). It is the modern incarnation of the reductionist ideal of the ancient Greeks, an approach to the natural world that has been fabulously successful in bettering the lot of mankind and continues in many people's minds to be the central paradigm of physics. A special case of this idea, and also a beautiful instance of it, is the equation of conventional nonrelativistic quantum mechanics, which describes the everyday world of human beings—air, water, rocks, fire, people, and so forth. The details of this equation are less important than the fact that it can be written down simply and is completely specified by a handful of known quantities: the charge and mass of the electron, the charges and masses of the atomic nuclei, and Planck's constant. For experts we write

$$i\hbar\,\frac{\partial}{\partial t}\,|\Psi> \;=\; \mathcal{H}|\Psi> \qquad [1]$$

where

$$\mathcal{H} = -\sum_{j}^{N_e}\frac{\hbar^2}{2m}\nabla_j^2 - \sum_{\alpha}^{N_i}\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 - \sum_{j}^{N_e}\sum_{\alpha}^{N_i}\frac{Z_\alpha e^2}{|\vec{r}_j-\vec{R}_\alpha|} + \sum_{j\ll k}^{N_e}\frac{e^2}{|\vec{r}_j-\vec{r}_k|} + \sum_{\alpha\ll\beta}^{N_j}\frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha-\vec{r}_\beta|}. \qquad [2]$$

we have learned why atoms have the size they do, why chemical bonds have the length and strength they do, why solid matter has the elastic properties it does, why some things are transparent while others reflect or absorb light (6). With a little more experimental input for guidance it is even possible to predict atomic conformations of small molecules, simple chemical reaction rates, structural phase transitions, ferromagnetism, and sometimes even superconducting transition temperatures (7). But the schemes for approximating are not first-principles deductions but are rather art keyed to experiment, and thus tend to be the least reliable precisely when reliability is most needed, i.e., when experimental information is scarce, the physical behavior has no precedent, and the key questions have not yet been identified. There are many notorious failures of alleged *ab initio* computation methods, including the phase diagram of liquid ^{3}He and the entire phenomenonology of high-temperature superconductors (8–10). Predicting protein functionality or the behavior of the human brain from these equations is patently absurd. So the triumph of the reductionism of the Greeks is a pyrrhic victory: We have succeeded in reducing all of ordinary physical behavior to a simple, correct Theory of Everything only to discover that it has revealed exactly nothing about many things of great importance.

In light of this fact it strikes a thinking person as odd that the parameters e, $\hbar$, and m appearing in these equations may be measured accurately in laboratory experiments involving large numbers of particles. The electron charge, for example, may be accurately measured by passing current through an electrochemical cell, plating out metal atoms, and measuring the mass deposited, the separation of the atoms in the crystal being known from x-ray diffraction (11). Simple electrical measurements performed on superconducting rings determine to high accuracy the quantity the quantum of magnetic flux $hc/2e$ (11). A version

Theory of Almost Everything

given Hamiltonian

$$H = -\frac{1}{2}\sum_{j=1}^{N_e}\nabla_j^2 + \sum_{j<k}^{N_e}\frac{1}{|r_j - r_k|} - \sum_{j=1}^{N_e}\sum_{\alpha=1}^{N_i}\frac{Z_\alpha}{|r_j - R_\alpha|} + \sum_{\alpha<\beta}^{N_i}\frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}$$

solve eigenvalue problem

$$H\Psi(x_1, \ldots, x_N) = E\,\Psi(x_1, \ldots, x_N)$$

3*N*-dimensional pde

electrons indistinguishable

how possible?

no observable $M(x_1,\ldots,x_N)$ can distinguish them
i.e. M symmetric under exchange of coordinates

eigenfunction needs to be antisymmetrized

still eigenfunction?

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

N! terms

antisymmetrization

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

$N!$ terms — hard problem in general
easy $O(N^3)$ for product wavefunctions

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

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

basis of Slater determinants

complete set of single-electron orbitals

$$\sum_n \overline{\varphi_n(x')}\,\varphi_n(x) = \delta(x'-x)$$

expand *N*-electron function in 1st variable

$$a(x_1,\ldots,x_N) = \sum_{n_1}\int dx_1'\ \underbrace{a(x_1',\ldots,x_N)\,\overline{\varphi_{n_1}(x_1')}}_{=:a_{n_1}(x_2,\ldots,x_N)}\ \varphi_{n_1}(x_1)$$

and repeat to obtain expansion in product states

antisymmetric: states with $n_i{=}n_j$ vanish, $n_i{\leftrightarrow}n_j$ only differ by sign

basis of Slater determinants

$$\left\{\Phi_{n_1,\ldots,n_N}(x_1,\ldots,x_N)\,\middle|\ n_1<n_2<\cdots<n_N\right\}$$

second quantization: motivation

labeling of coordinates of identical particles is artificial
get rid of coordinates?

Dirac formalism
separate coordinates from states

$$\varphi(x) = \langle x|\varphi\rangle$$

absorb coordinates in operators

$$\int dx\, \overline{\varphi_n(x)} M(x) \varphi_m(x) = \int dx\, \langle \varphi_n|x\rangle M(x) \langle x|\varphi_m\rangle =: \langle \varphi_n|\hat{M}|\varphi_m\rangle$$

coordinate-free formalism

second quantization: coordinates

vacuum state $|0\rangle$

and

set of operators operators $\hat{\Psi}(x)$

defined by:

$$\hat{\psi}(x)|0\rangle = 0 \qquad \{\hat{\psi}(x), \hat{\psi}(x')\} = 0 = \{\hat{\psi}^\dagger(x), \hat{\psi}^\dagger(x')\}$$

$$\langle 0|0\rangle = 1 \qquad \{\hat{\psi}(x), \hat{\psi}^\dagger(x')\} = \delta(x-x')$$

anticommutator: $\{A, B\} := AB + BA$

second quantization: states

creation operator $\quad c_\alpha^\dagger := \int dx\, \varphi_\alpha(x)\, \hat{\psi}^\dagger(x)$

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

$$\{c_\alpha,\ c_\beta^\dagger\} = \int dx'\, \overline{\varphi_\alpha(x')}\, \{\hat{\psi}(x'),\ c_\beta^\dagger\} = \int dx'\, \overline{\varphi_\alpha(x')}\varphi_\beta(x') = \langle\alpha|\beta\rangle$$

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

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

orbital basis transforms

creation operators transform as the orbitals they represent

$$|\beta_i\rangle = U|\alpha_i\rangle = \sum_j |\beta_j\rangle\langle\alpha_j|\alpha_i\rangle = \sum_\mu |\alpha_\mu\rangle \underbrace{\langle\alpha_\mu|U|\alpha_i\rangle}_{=:U_{\mu i}} \quad \rightsquigarrow \quad c^\dagger_{\beta_i} = \sum_\mu c^\dagger_{\alpha_\mu} U_{\mu i}$$

operators transform like vectors?

write transformation matrix $\boldsymbol{U} = e^{\boldsymbol{M}}$

$$c^\dagger_{\beta_i} = e^{\boldsymbol{c}^\dagger \boldsymbol{M} \boldsymbol{c}}\, c^\dagger_{\alpha_\mu}\, e^{-\boldsymbol{c}^\dagger \boldsymbol{M} \boldsymbol{c}} \qquad c_{\beta_i} = e^{-\boldsymbol{c}^\dagger \boldsymbol{M}^\dagger \boldsymbol{c}}\, c_{\alpha_\mu}\, e^{\boldsymbol{c}^\dagger \boldsymbol{M}^\dagger \boldsymbol{c}}$$

when ***M*** anti-hermitian (***U*** unitary) annihilators transform like creators

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

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

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

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

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

separate coordinates from orbitals

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

analogous to Dirac notation

$$\varphi_\alpha(x) = \langle x|\alpha\rangle$$

product states $\prod_{n=1}^{N} c^\dagger_{\alpha_n}|0\rangle$ are many-body generalization of Dirac states

evaluate matrix elements …

second quantization: expectation values

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

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

$$= \int d\boldsymbol{x} \, \frac{1}{\sqrt{N!}} \langle 0 | \prod c_{\beta_i} \prod \hat{\psi}^\dagger(x_n) | 0 \rangle \, M(\boldsymbol{x}) \, \frac{1}{\sqrt{N!}} \langle 0 | \prod \hat{\psi}(x_n) \prod c^\dagger_{\alpha_j} | 0 \rangle$$

$$= \langle 0 | \prod c_{\beta_i} \underbrace{\frac{1}{N!} \int d\boldsymbol{x} \, \prod \hat{\psi}^\dagger(x_n) \, M(\boldsymbol{x}) \, \prod \hat{\psi}(x_n)}_{=: \hat{M}} \prod c^\dagger_{\alpha_j} | 0 \rangle$$

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

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

only valid for *N*-electron states!

second quantization: zero-body operator

zero-body operator $M(x_1,\ldots x_N) = 1$ 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 $\hat{N} := \int dx\, \hat{\psi}^\dagger(x)\hat{\psi}(x)$ with $\left[\hat{N},\, c_\alpha^\dagger\right] = c_\alpha^\dagger$

$$\rightsquigarrow \hat{N}c_\alpha^\dagger = c_\alpha^\dagger\left(\hat{N}+1\right) \quad \rightsquigarrow \hat{N}c_\alpha = c_\alpha\left(\hat{N}-1\right)$$

result independent of N

overlap of Slater determinants

$$\int dx\, \overline{\Phi_{\alpha_n}(x)}\,\Phi_{\beta_m}(x) = \langle 0|c_{\alpha_1}\cdots c_{\alpha_N}\; c_{\beta_N}^\dagger\cdots c_{\beta_1}^\dagger|0\rangle$$

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

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

transforms as 1-body operator

second quantization: two-body operators

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

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

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

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

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

result independent of N

expand in complete orthonormal set of orbitals

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

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

2-body matrix

$$\hat{M}_2 = \frac{1}{2} \sum_{n,n',m,m'} \underbrace{\langle \alpha_n \alpha_{n'} | M_2 | \alpha_m \alpha_{m'} \rangle}_{=: M_{nn',mm'}} c^\dagger_{\alpha_{n'}} c^\dagger_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}}$$

4-index tensor

no contribution for
$n=n'$ or $m=m'$
sign-change for
$n \leftrightarrow n'$ or $m \leftrightarrow m'$

no self-interaction

exchange terms

collect terms with same operator content

$$\hat{M}_2 = \sum_{n<n',m<m'} \left(\underbrace{M_{nn',mm'} - M_{nn',m'm}}_{=: \breve{M}_{nn',mm'}} \right) c^\dagger_{\alpha_{n'}} c^\dagger_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}}$$

two-body matrix
of dim $N_{orb}(N_{orb}-1)/2$

together with N_{orb}^2 hopping terms
completely specifies Hamiltonian

variational principle and Schrödinger equation

energy expectation value $E[\psi] = \dfrac{\langle\psi|H|\psi\rangle}{\langle\Psi|\Psi\rangle}$

variation

$$E[\Psi+\delta\Psi] = E[\Psi] + \frac{\langle\delta\Psi|H|\Psi\rangle + \langle\Psi|H|\delta\Psi\rangle}{\langle\Psi|\Psi\rangle} - \langle\Psi|H|\Psi\rangle \frac{\langle\delta\Psi|\Psi\rangle + \langle\Psi|\delta\Psi\rangle}{\langle\Psi|\Psi\rangle^2} + \mathcal{O}^2$$

variational equation: $0 = \dfrac{\delta E[\Psi]}{\delta\Psi} = \dfrac{H|\Psi\rangle - \overbrace{\langle\Psi|H|\Psi\rangle}^{=E[\Psi]}\ |\Psi\rangle}{\langle\Psi|\Psi\rangle} + \text{H.c.}$

equivalent to eigenvalue equation

$$H|\Psi_n\rangle = E_n|\Psi_n\rangle$$

variational principle

expand $|\Psi\rangle \neq 0$ in eigenfunctions

$$E[\Psi] = \frac{\sum \langle\Psi|\Psi_m\rangle\langle\Psi_m|H|\Psi_n\rangle\langle\Psi_n|\Psi\rangle}{\sum \langle\Psi|\Psi_m\rangle\langle\Psi_m|\Psi_n\rangle\langle\Psi_n|\Psi\rangle} = \frac{\sum E_n \left|\langle\Psi_n|\Psi\rangle\right|^2}{\sum \left|\langle\Psi_n|\Psi\rangle\right|^2} \geq \frac{\sum E_0 \left|\langle\Psi_n|\Psi\rangle\right|^2}{\sum \left|\langle\Psi_n|\Psi\rangle\right|^2} = E_0$$

assume eigenvalues sorted $E_0 \leq E_1 \leq \ldots$

$$E[\Psi_{\perp_n}] \geq E_n \quad \text{if } \langle\Psi_i|\Psi_{\perp_n}\rangle = 0 \text{ for } i = 0, \ldots, n{-}1.$$

variational principle for excited states

in practice only useful when orthogonality to (unknown) states ensured, e.g., by symmetry

expand in Slater basis

rewrite $H|\Psi_n\rangle = E_n|\Psi_n\rangle$

choose (orthonormal) orbital basis $\{ \varphi_k \,|\, k \}$ and corresponding basis of Slater determinants $\{ \phi_{k1,\ldots,kN} \,|\, k_1 < \ldots < k_N \}$

$$|\Psi\rangle = \sum_{k_1<\cdots<k_N} a_{k_1,\ldots,k_N} \, |\Phi_{k_1,\ldots,k_N}\rangle = \sum_i a_i \, |\Phi_i\rangle = |\boldsymbol{\Phi}\rangle \, \boldsymbol{a}$$

expand Schrödinger equation in Slater basis

$$E \, \langle \Phi_i|\Psi\rangle = \langle \Phi_i|H|\Psi\rangle = \sum_j \langle \Phi_i|H|\Phi_j\rangle\langle \Phi_j|\Psi\rangle$$

matrix eigenvalue problem

$$\boldsymbol{H}\boldsymbol{a} = \langle \boldsymbol{\Phi}|\hat{H}|\boldsymbol{\Phi}\rangle \boldsymbol{a} = \begin{pmatrix} \langle \Phi_1|\hat{H}|\Phi_1\rangle & \langle \Phi_1|\hat{H}|\Phi_2\rangle & \cdots \\ \langle \Phi_2|\hat{H}|\Phi_1\rangle & \langle \Phi_2|\hat{H}|\Phi_2\rangle & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix} = E\boldsymbol{a}$$

variational principle

restrict to finite Slater basis $|\tilde{\mathbf{\Phi}}\rangle := \left(|\Phi_1\rangle, \ldots, |\Phi_{\tilde{L}}\rangle\right)$

$$\langle\tilde{\mathbf{\Phi}}|\hat{H}|\tilde{\mathbf{\Phi}}\rangle\tilde{\boldsymbol{a}}_n = \tilde{\boldsymbol{H}}\tilde{\boldsymbol{a}}_n = \tilde{E}_n\tilde{\boldsymbol{a}}_n \quad \rightsquigarrow \quad |\tilde{\Psi}_n\rangle := |\tilde{\mathbf{\Phi}}\rangle\,\tilde{\boldsymbol{a}}_n$$

solve with LAPACK

variational principle: $E_n \leq \tilde{E}_n$ for $n \in \{0, \ldots, \tilde{L}-1\}$

n

construct $|\tilde{\Psi}\rangle = \sum_{i=0} c_i\,|\tilde{\Psi}_i\rangle \neq 0$ with $\langle\Psi_i|\tilde{\Psi}\rangle = 0$ for $i=0, \ldots, n-1$

$$\rightsquigarrow\ \tilde{E}_n\ \geq\ E[\tilde{\Psi}]\ \geq\ E_n$$

art: systematically increase basis to achieve convergence

nesting of eigenvalues

consider problem with basis size L as exact problem

variational principle for $-H$: $-E_{L-i} \leq -\tilde{E}_{\tilde{L}-i}$ for $i \in \{1, \ldots, \tilde{L}\}$

$$E_n \leq \tilde{E}_n \leq E_{n+(L-\tilde{L})} \quad \text{for } n \in \{0, \ldots, \tilde{L}-1\}$$

many-body problem

dimension of Hilbert space

ways of putting N electrons in K orbitals: $K\,(K–1)\,(K–2)\cdots(K–(N–1)) = K!/(K–N)!$

order in which electrons are put does not matter: $N!$

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

use symmetry to reduce dimension
e.g., spin conserved

$$\dim \mathcal{H}_{2K}^{(N_\uparrow,N_\downarrow)} = \binom{K}{N_\uparrow} \times \binom{K}{N_\downarrow}$$

```
>>> def binom(K,N):
...   if N==0:
...     return 1
...   else:
...     return (K-N+1)*binom(K,N-1)/N
...
>>> binom(24,12)**2
7312459672336
>>> binom(24,12)**2*8/2**30
54482
```

M	$N_\uparrow$	$N_\downarrow$	dimension of Hilbert space
2	1	1	4
4	2	2	36
6	3	3	400
8	4	4	4 900
10	5	5	63 504
12	6	6	853 776
14	7	7	11 778 624
16	8	8	165 636 900
18	9	9	2 363 904 400
20	10	10	34 134 779 536
22	11	11	497 634 306 624
24	12	12	7 312 459 672 336

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

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

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

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

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

$$\vdots$$

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

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

HF variational condition

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

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

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

simplifies variational condition to (Brillouin theorem)

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

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

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

$$=: F_{nm}$$

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

depends on Φ^{HF} $\Rightarrow$ 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)

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

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

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

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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

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

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

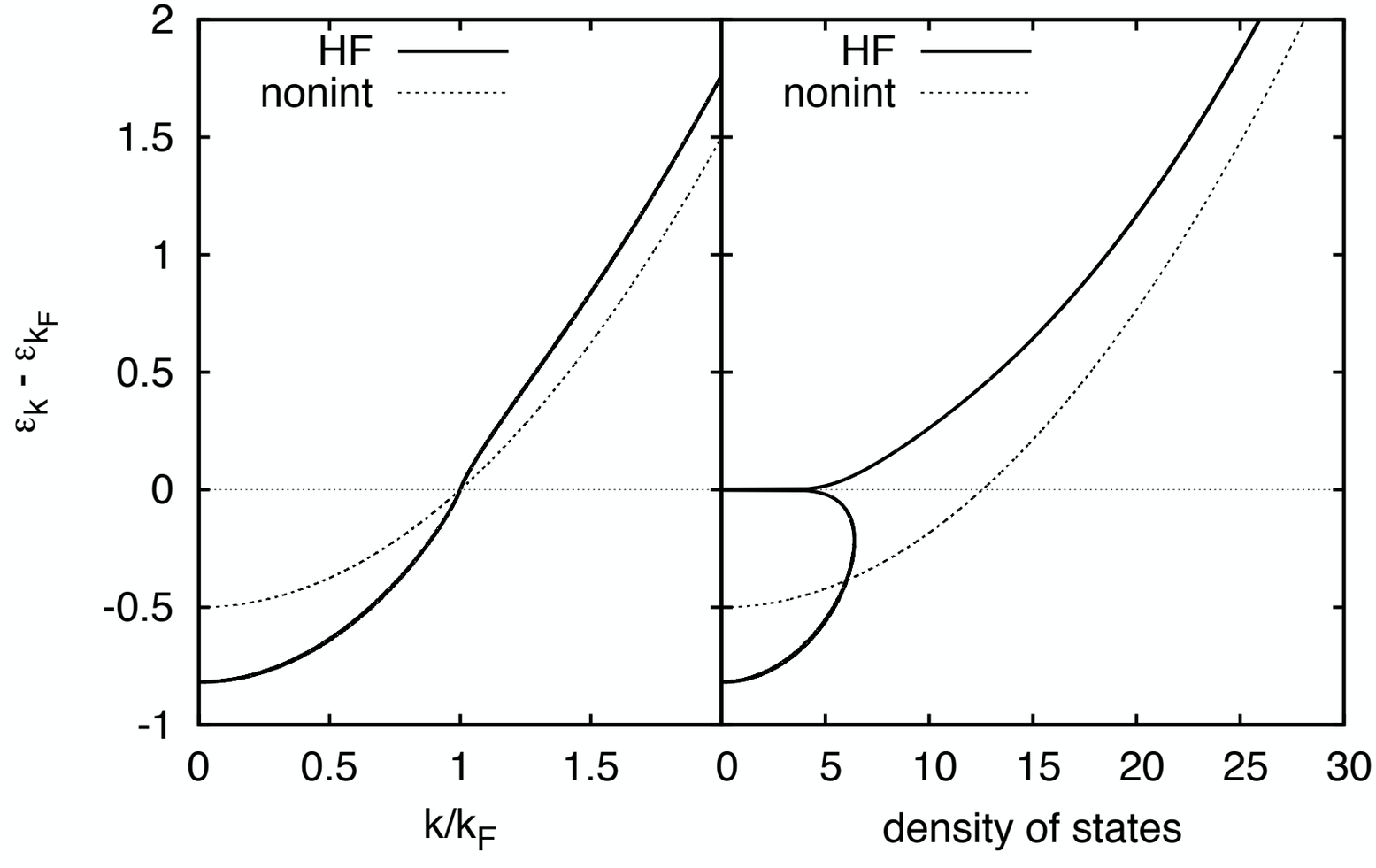
dispersion & DOS

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

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

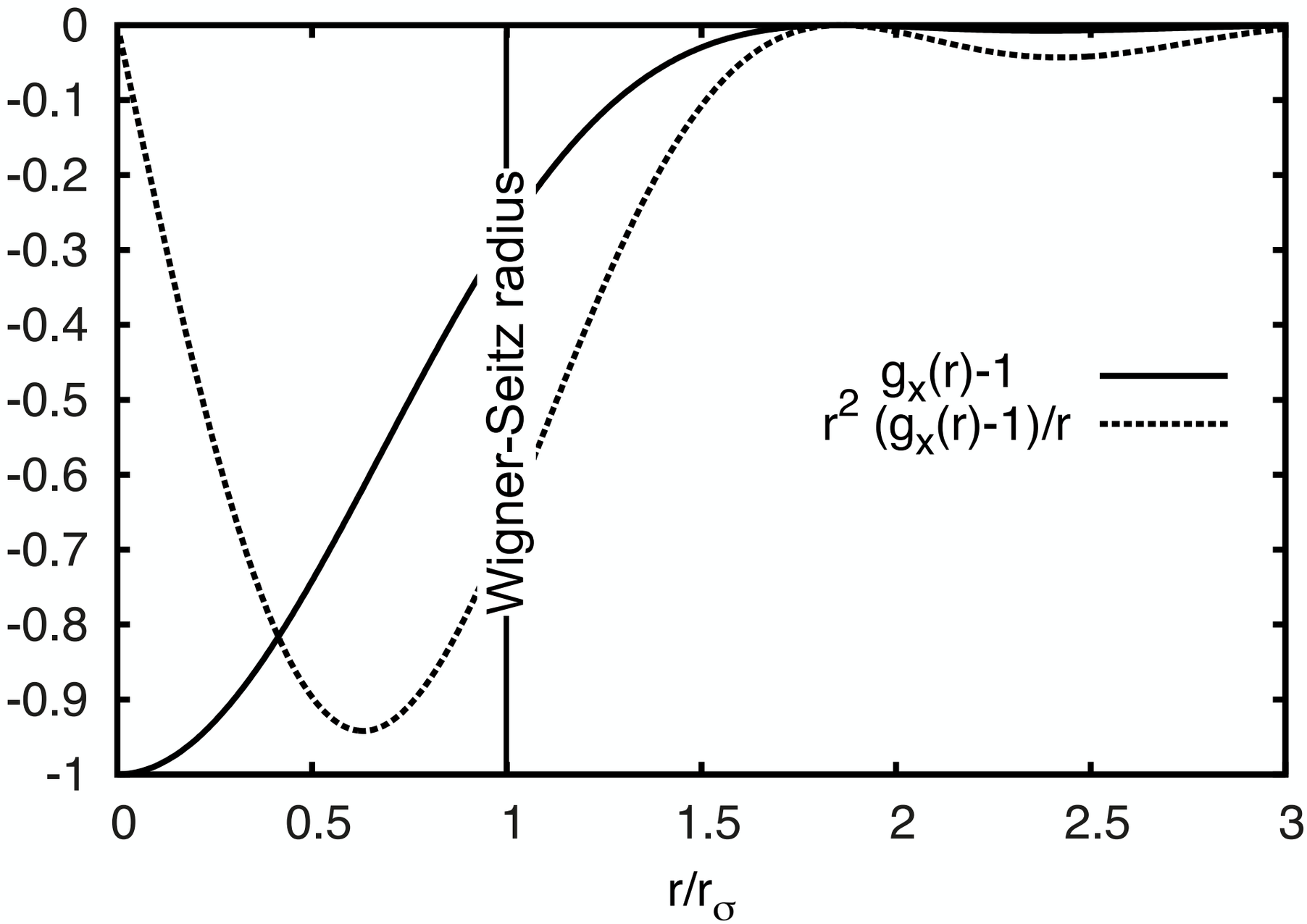
exchange hole

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

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

exchange hole

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



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

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

$$c^\dagger_{\boldsymbol{k}\sigma}|\Phi_{k_F}\rangle = 0 \quad \text{for } |\boldsymbol{k}| < k_F$$
$$c_{\boldsymbol{k}\sigma}|\Phi_{k_F}\rangle = 0 \quad \text{otherwise.}$$

HF ground state acts as vacuum state for transformed operators

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

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

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

note: vacuum state no longer invariant under basis transformations!

BCS theory

BCS Hamiltonian

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

Bogoliubov-Valatin operators mix creators & annihilators

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

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

canonical anticommutation relations

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

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

corresponding vacuum state?

BCS state

obvious candidate (product state in Fock-space)

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

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

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

normalizable?

$$\langle 0|(\overline{u}_k + \overline{v}_k c_{-k\downarrow} c_{k\uparrow})(\overline{u}_k + \overline{v}_k c_{k\downarrow} c_{-k\uparrow})(u_k + v_k c^\dagger_{-k\uparrow} c^\dagger_{k\downarrow})(u_k + v_k c^\dagger_{k\uparrow} c^\dagger_{-k\downarrow})|0\rangle = \left(|u_k|^2 + |v_k|^2\right)^2$$

(normalized) vacuum

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

contributions in all sectors with even number of electrons

electronic properties

$$c_{\boldsymbol{k}\uparrow} = \overline{u}_k b_{\boldsymbol{k}\uparrow} + v_k b^\dagger_{-\boldsymbol{k}\downarrow}$$
$$c_{\boldsymbol{k}\downarrow} = \overline{u}_k b_{\boldsymbol{k}\downarrow} - v_k b^\dagger_{-\boldsymbol{k}\uparrow}$$

momentum distribution

$$\langle \mathrm{BCS}|\, c^\dagger_{\boldsymbol{k}\uparrow} c_{\boldsymbol{k}\uparrow} |\mathrm{BCS}\rangle = \langle \mathrm{BCS}|(u_k b^\dagger_{\boldsymbol{k}\uparrow} + \overline{v}_k b_{-\boldsymbol{k}\downarrow})(\overline{u}_k b_{\boldsymbol{k}\uparrow} + v_k b^\dagger_{-\boldsymbol{k}\downarrow})|\mathrm{BCS}\rangle = |v_k|^2$$

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

pairing density

$$\langle \mathrm{BCS}|c^\dagger_{\boldsymbol{k}\uparrow} c^\dagger_{-\boldsymbol{k}\downarrow}|\mathrm{BCS}\rangle = \langle \mathrm{BCS}|(u_k b^\dagger_{\boldsymbol{k}\uparrow} + \overline{v}_k b_{-\boldsymbol{k}\downarrow})(u_k b^\dagger_{-\boldsymbol{k}\downarrow} - \overline{v}_k b_{\boldsymbol{k},\uparrow})|\mathrm{BCS}\rangle = u_k \overline{v}_k$$

minimize energy expectation value

energy expectation value

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

optimize phase

$$u_k = |u_k|\,e^{i\alpha_k} \text{ and } v_k = |v_k|\,e^{i(\alpha_k+\varphi_k)} \rightsquigarrow \Re\overline{v}_k u_k v_{k'}\overline{u}_{k'} = \left|v_k u_k v_{k'} u_{k'}\right| \cos(\varphi_{k'}-\varphi_k)$$

for attractive interaction energy minimized for *phase coherent* Cooper pairs:

$$\left|\mathrm{BCS}(\varphi)\right\rangle = \prod_{\boldsymbol{k}} \left(|u_k| + |v_k| e^{i\varphi} c^\dagger_{\boldsymbol{k}\uparrow} c^\dagger_{-\boldsymbol{k}\downarrow}\right)\left|0\right\rangle$$

gap equation

writing $|u_k| = \sin\Theta_k$ and $|v_k| = \cos\Theta_k$

$$\left\langle \mathrm{BCS}(\varphi)\middle|\hat{H}-\mu\hat{N}\middle|\mathrm{BCS}(\varphi)\right\rangle = \sum_{k\sigma}(\varepsilon_k-\mu)\,\frac{1+\cos 2\Theta_k}{2} - \sum_{k,k'} G_{kk'}\,\frac{\sin 2\Theta_k}{2}\,\frac{\sin 2\Theta_{k'}}{2}$$

variational equations

$$\tan 2\Theta_k = -\frac{\sum_{k'} G_{kk'}\sin(2\Theta_{k'})/2}{\varepsilon_k-\mu} =: \frac{\Delta_k}{\mu-\varepsilon_k}$$

momentum distribution $\qquad (\cos x)^2 = \dfrac{1}{1+(\tan x)^2}$

$$\langle n_{k\sigma}\rangle = |v_k|^2 = \frac{1+\cos 2\Theta_k}{2} = \frac{1}{2}\left(1 - \frac{\varepsilon_k-\mu}{\sqrt{(\varepsilon_k-\mu)^2+\Delta_k^2}}\right)$$

gap equations

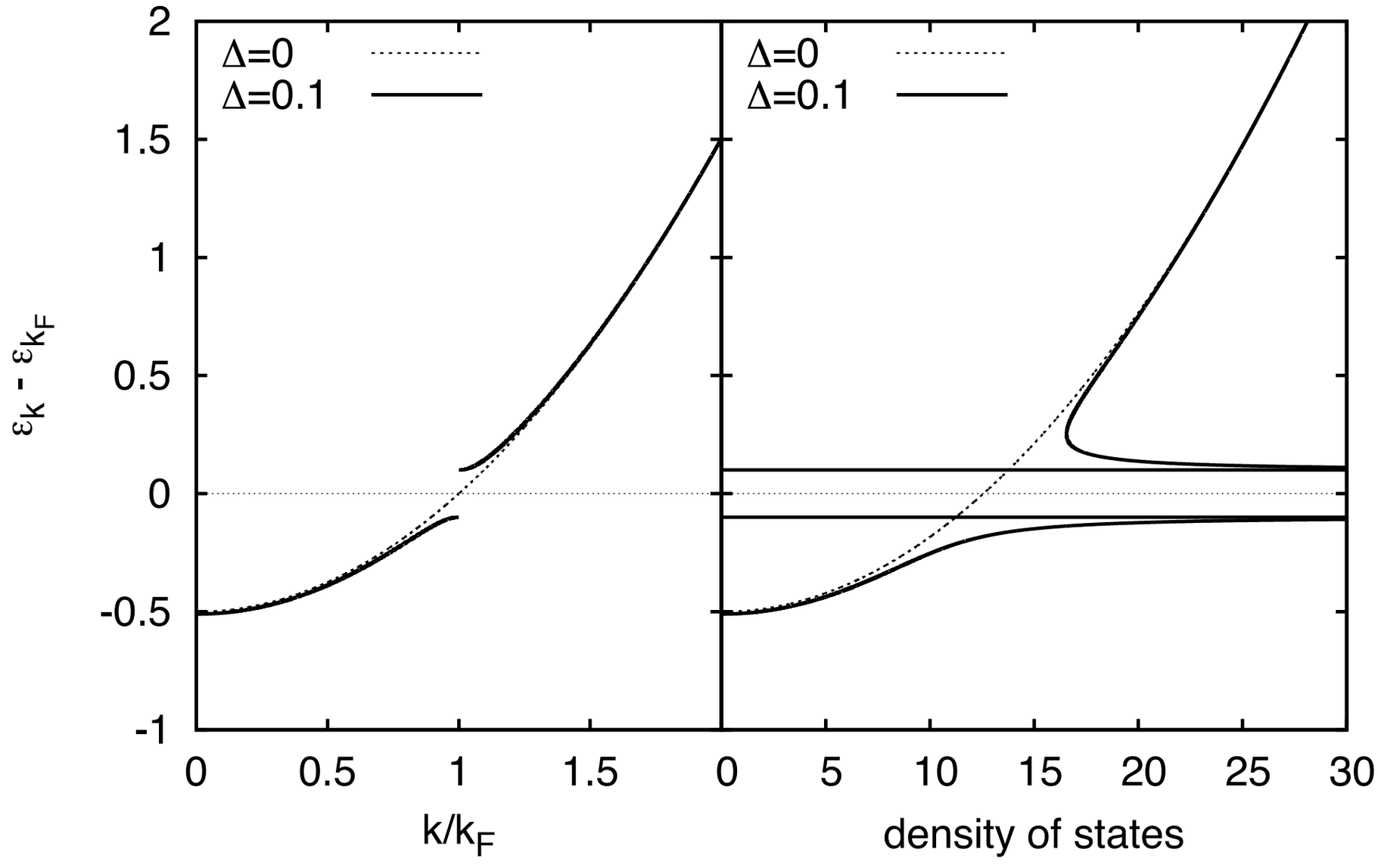
$$\Delta_k = \sum_{k'} G_{kk'}\sin(2\Theta_{k'})/2 = \frac{1}{2}\sum_{k'}\frac{G_{kk'}\Delta_{k'}}{\sqrt{(\varepsilon_{k'}-\mu)^2+\Delta_{k'}^2}}$$

quasi electrons

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

quasi-particle energy

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



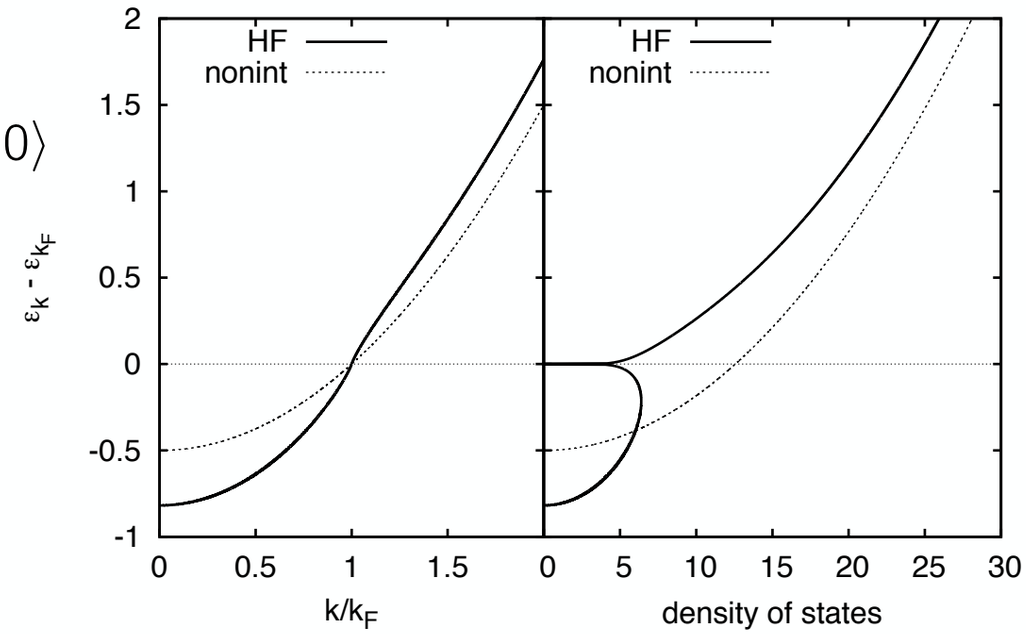
summary

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

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



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

second quantization:
separate coordinates
from state

extends to Fock space

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

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

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