2 Mean-Field Theory: Hartree-Fock and BCS

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Contents

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1 Many-electron states

One of the deepest mysteries of physics is that all the different objects that surround us are built from a small set of indistinguishable particles. The very existence of such elementary particles that have all their properties in common is a direct consequence of quantum physics. Classical objects can always be distinguished by their location in space. This lead Leibniz to formulate his Principle of the Identity of Indiscernibles [1]. For quantum objects, however, the uncertainty principle makes the distinction of particles by their position impossible. Indistinguishability of quantum objects then means that there is no measurement that would let us tell them apart, i.e., all expectation values $\langle\varPsi|M|\varPsi\rangle$ must remain the same when we change the labeling of the distinct but indistinguishable the particles.

The consequences for observables are straightforward: An observable $M(x)$ acting on a single-particle degree of freedom x must operate on all indistinguishable particles in the same way, i.e., $\sum_i M(x_i)$. A two-body observable $M(x,x')$ must operate on all pairs in the same way, $\sum_{i,j} M(x_i,x_j)$ with $M(x,x')=M(x',x)$. We can thus write any observable in the form

$$\begin{aligned} M(\mathbf{x}) &= M^{(0)} + \sum_i M^{(1)}(x_i) + \frac{1}{2!}\sum_{i\neq j} M^{(2)}(x_i,x_j) + \frac{1}{3!}\sum_{i\neq j\neq k} M^{(3)}(x_i,x_j,x_k) + \cdots & (1)\\ &= M^{(0)} + \sum_i M^{(1)}(x_i) + \sum_{i<j} M^{(2)}(x_i,x_j) + \sum_{i<j<k} M^{(3)}(x_i,x_j,x_k) + \cdots\,, & (2)\end{aligned}$$

where the summations can be restricted since the operators must be symmetric in their arguments, e.g. $M^{(2)}(x_i,x_j)=M^{(2)}(x_j,x_i)$, while for two or more identical coordinates the operator is really one of lower order: $M^{(2)}(x_i,x_i)$, e.g., only acts on a single coordinate and should be included in $M^{(1)}$.

For the many-body wave functions $\varPsi(x_1,x_2,\cdots)$ the situation is slightly more complex. Since the probability density $|\varPsi(x_1,x_2,\cdots)|^2$ is an observable, they should transform as one-dimensional (irreducible) representations, i.e., either be symmetric or antisymmetric under particle permutations. Which of the two options applies to a given elementary particle is determined by the spin-statistics theorem [2,3]: The wave functions of particles with integer spin are symmetric, those of particles with half-integer spin change sign wen arguments are exchanged. From an arbitrary N-particle wave function we thus obtain a many-electron wavefunction by antisymmetrizing

$$\mathcal{S}_-\,\varPsi(x_1,\ldots,x_N) := \frac{1}{\sqrt{N!}}\sum_P (-1)^P \varPsi\left(x_{p(1)},\ldots,x_{p(N)}\right)\,, \tag{3}$$

where $(-1)^P$ is the parity of the permutation P that maps $n\to p(n)$. Since there are $N!$ different permutations, this can easily become an extremely costly operation. Remarkably, a product of N single-electron states φ_α can be antisymmetrized much more efficiently (in $\mathcal{O}(N^3)$ steps) by writing it in the form of a determinant

$$\Phi_{\alpha_1,\dots,\alpha_N}(x_1,\dots,x_N) := \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}. \tag{4}$$

For $N = 1$ the Slater determinant is simply the one-electron orbital $\Phi_\alpha(x) = \varphi_\alpha(x)$ and for $N = 2$ we get the familiar two-electron Slater determinant $\Phi_{\alpha,\alpha'}(x,x') = (\varphi_\alpha(x)\varphi_{\alpha'}(x') - \varphi_{\alpha'}(x)\varphi_\alpha(x'))/\sqrt{2}$.

Slater determinants are important because they can be used to build a basis of the many-electron Hilbert space. To see how, we consider a complete set of orthonormal single-electron states

$$\int\!dx\, \overline{\varphi_n(x)}\, \varphi_m(x) = \delta_{n,m} \text{ (orthonormal)} \qquad \sum_n \overline{\varphi_n(x)}\, \varphi_n(x') = \delta(x-x') \text{ (complete)}\,. \tag{5}$$

To expand an arbitrary N-particle function $a(x_1,\dots,x_N)$, we start by considering it as a function of x_1 with $x_2,\dots,x_N$ kept fixed. We can then expand it in the complete set $\{\varphi_n\}$ as

$$a(x_1,\dots,x_N) = \sum_{n_1} a_{n_1}(x_2,\dots,x_N)\, \varphi_{n_1}(x_1)$$

with expansion coefficients

$$a_{n_1}(x_2,\dots,x_N) = \int\!dx\; \overline{\varphi_{n_1}(x_1)}\, a(x_1,x_2,\dots,x_N)\,.$$

These, in turn, can be expanded as a functions of x_2

$$a_{n_1}(x_2,\dots,x_N) = \sum_{n_2} a_{n_1,n_2}(x_3,\dots,x_N)\, \varphi_{n_2}(x_2)\,.$$

Repeating this, we obtain the expansion of a in product states

$$a(x_1,\dots,x_N) = \sum_{n_1,\dots,n_N} a_{n_1,\dots,n_N}\, \varphi_{n_1}(x_1)\cdots\varphi_{n_N}(x_N)\,.$$

When the N-particle function Ψ is antisymmetric, the expansion coefficients will be antisymmetric under permutation of the indices $a_{n_{p(1)},\dots,n_{p(N)}} = (-1)^P a_{n_1,\dots,n_N}$. Fixing an order of the indices, e.g., $n_1 < n_2 < \ldots < n_N$, we thus get an expansion in Slater determinants

$$\Psi(x_1,\dots,x_N) = \sum_{n_1<\ldots<n_N} \sqrt{N!}\, a_{n_1,\dots,n_N}\, \Phi_{n_1,\dots,n_N}(x_1,\dots,x_N)\,.$$

Since we can write any antisymmetric function as such a configuration-interaction expansion, the set of Slater determinants

$$\Big\{\Phi_{n_1,\dots,n_N}(x_1,\dots,x_N)\,\Big|\; n_1 < n_2 < \cdots < n_N\Big\} \tag{6}$$

forms a basis of the N-electron Hilbert space. Since the overlap of two Slater determinants

$$\int d\boldsymbol{x}\ \overline{\Phi_{\alpha_1,\dots,\alpha_N}(\boldsymbol{x})}\,\Phi_{\beta_1,\dots,\beta_N}(\boldsymbol{x}) = \frac{1}{N!}\sum_{P,P'}(-1)^{P+P'}\prod_n\int dx_n\ \overline{\varphi_{\alpha_{p(n)}}(x_n)}\,\varphi_{\alpha_{p'(n)}}(x_n)$$
$$= \langle\Phi_{\alpha_1,\dots,\alpha_N}|\Phi_{\beta_1,\dots,\beta_N}\rangle = \begin{vmatrix} \langle\varphi_{\alpha_1}|\varphi_{\beta_1}\rangle & \cdots & \langle\varphi_{\alpha_1}|\varphi_{\beta_N}\rangle \\ \vdots & \ddots & \vdots \\ \langle\varphi_{\alpha_N}|\varphi_{\beta_1}\rangle & \cdots & \langle\varphi_{\alpha_N}|\varphi_{\beta_N}\rangle \end{vmatrix} \tag{7}$$

is the determinant of the overlap of the constituent orbitals, the Slater determinants (6) form a complete orthonormal basis of the N-electron Hilbert space when the orbitals $\varphi_n(x)$ are a complete orthonormal basis of the one-electron Hilbert space.

While we use a set of N one-electron orbitals $\varphi_n(x)$ to define an N-electron Slater determinant $\Phi_{\alpha_1,\dots,\alpha_N}(\boldsymbol{x})$ (4), this representation is not unique: Any unitary transformation among the N occupied orbitals will not change the determinant. Thus, strictly, a Slater determinant is not determined by the set of indices we usually give, but, up to a phase, by the N-dimensional subspace spanned by the orbitals $\varphi_1,\ \dots,\varphi_N$ in the single-electron Hilbert space. The projector to this space is the one-body density matrix

$$\Gamma^{(1)}(x,x') = N\int dx_2\cdots dx_N\ \overline{\Phi(x,x_2,\dots,x_N)}\,\Phi(x',x_2,\dots,x_N)\,. \tag{8}$$

To see this, we expand the Slater determinant along its first row

$$\Phi_{\alpha_1\cdots\alpha_N}(x_1,\dots,x_N) = \frac{1}{\sqrt{N}}\sum_{n=1}^{N}(-1)^{1+n}\,\varphi_{\alpha_n}(x_1)\,\Phi_{\alpha_{i\neq n}}(x_2,\dots,x_N)\,, \tag{9}$$

where $\Phi_{\alpha_{i\neq n}}(x_2,\dots,x_N)$ is the determinant with the first row and the n-th column removed, which can be written as $N-1$-electron Slater determinants with orbital α_n removed. Inserting this into (8) we find

$$\Gamma^{(1)}_{\Phi}(x,x') = \sum_{n=1}^{N}\overline{\varphi_{\alpha_n}(x)}\,\varphi_{\alpha_n}(x')\,, \tag{10}$$

which is the expansion of the one-body density matrix in eigenfunctions (natural orbitals) showing that its eigenvalues (natural occupation numbers) are one. Any many-electron wave function $\Psi(\boldsymbol{x})$ with the same one-body density matrix $\Gamma^{(1)}_{\Phi}$ equals $\Phi(\boldsymbol{x})$ up to a phase, i.e., $|\langle\Psi|\Phi\rangle| = 1$.

We can generalize this procedure and calculate higher order density matrices by introducing the generalized Laplace expansion

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

which is obtained by writing the permutation of all N indices as a permutation of $N-p$ indices and the remaining p indices separately summing over all distinct sets of p indices. This allows us to evaluate arbitrary matrix elements and higher order density matrices [4]. But as can be seen from the above expansion, the expressions very quickly get quite cumbersome. Fortunately there is a representation that is much better suited to handling antisymmetric wave functions. It is called second quantization.

2 Second quantization

While originally introduced for quantizing the electromagnetic field, we can use the formalism of second quantization just as a convenient way of handling antisymmetric wave functions [5,6]. The idea behind this approach is remarkably simple: When writing Slater determinants in the form (4) we are working in a real-space basis. It is, however, often better not to work in a specific basis but to consider abstract states: Instead of a wave function $\varphi_\alpha(x)$, we write a Dirac state $|\alpha\rangle$. Second quantization allows us to do the same for Slater determinants.

Let us consider a Slater determinant for two electrons, one in state $\varphi_\alpha(x)$, the other in state $\varphi_\beta(x)$. It is simply the antisymmetrized product of the two states

$$\Phi_{\alpha\beta}(x_1, x_2) = \frac{1}{\sqrt{2}} \big(\varphi_\alpha(x_1)\varphi_\beta(x_2) - \varphi_\beta(x_1)\varphi_\alpha(x_2)\big) . \tag{11}$$

This expression is quite cumbersome because we explicitly specify the coordinates. We can get rid of the coordinates by defining a two-particle Dirac state

$$|\alpha, \beta\rangle := \frac{1}{\sqrt{2}} \big(|\alpha\rangle|\beta\rangle - |\beta\rangle|\alpha\rangle\big) .$$

While the expression is already simpler, we still have to keep track of the order of the particles by specifying the position of the kets. The idea of second quantization is to specify the states using operators

$$c^\dagger_\beta c^\dagger_\alpha |0\rangle = |\alpha, \beta\rangle . \tag{12}$$

Now the order of the particles is specified by the order of the operators. To ensure the antisymmetry of the wave function the operators have to change sign when they are reordered

$$|\alpha, \beta\rangle = c^\dagger_\beta c^\dagger_\alpha |0\rangle = -c^\dagger_\alpha c^\dagger_\beta |0\rangle = -|\beta, \alpha\rangle . \tag{13}$$

Naturally, this also implies the Pauli principle for the special case $\beta = \alpha$.

2.1 Creation and annihilation operators

To arrive at the formalism of second quantization we postulate a set of operators that have certain reasonable properties. We then verify that we can use these operators to represent Slater determinants. But first we consider a few simple states to motivate what properties the new operators should have.

To be able to construct many-electron states we start from the simplest such state: $|0\rangle$ the *vacuum state* with no electron, which we assume to be normalized $\langle 0|0\rangle = 1$. Next we introduce for each single-electron state $|\alpha\rangle$ an operator $c^\dagger_\alpha$ such that $c^\dagger_\alpha|0\rangle = |\alpha\rangle$. These operators are called *creation operators* since they add an electron (in state α) to the state that they act on: in $c^\dagger_\alpha|0\rangle$ the creation operator adds an electron to the vacuum state ($N = 0$), resulting in a single-electron state. Applying another creation operator produces a two-electron state $c^\dagger_\beta c^\dagger_\alpha|0\rangle$. As we have seen above, to ensure the antisymmetry of the two electron state, the product of creation operators has to change sign when they are reordered: $c^\dagger_\alpha c^\dagger_\beta = -c^\dagger_\beta c^\dagger_\alpha$. This is more conveniently written as $\{c^\dagger_\alpha,\, c^\dagger_\beta\} = 0$ by introducing the *anti-commutator*

$$\{A,\, B\} := A\,B + B\,A\,. \tag{14}$$

As we have seen, the simplest state we can produce with the creation operators is the single-electron state $|\alpha\rangle = c^\dagger_\alpha|0\rangle$. When we want to calculate its norm, we have to consider the adjoint of $c^\dagger_\alpha|0\rangle$, formally obtaining $\langle\alpha|\alpha\rangle = \langle 0|c_\alpha c^\dagger_\alpha|0\rangle$, or, more generally, $\langle\alpha|\beta\rangle = \langle 0|c_\alpha c^\dagger_\beta|0\rangle$. This must mean that c_α, the adjoint of a creation operator, must remove an electron from the state, otherwise the overlap of $c_\alpha c^\dagger_\beta|0\rangle$ with the vacuum state $\langle 0|$ would vanish. We therefore call the adjoint of the creation operator an *annihilation operator*. We certainly cannot take an electron out of the vacuum state, so $c_\alpha|0\rangle = 0$. To obtain the correct overlap of one-electron states as $\langle\alpha|\beta\rangle = \langle 0|c_\alpha c^\dagger_\beta|0\rangle$ we postulate the anticommutation relation $\{c_\alpha, c^\dagger_\beta\} = \langle\alpha|\beta\rangle$. For completeness, taking the adjoint of the anticommutation relation for the creation operators, we obtain the corresponding anticommutator of the annihilators: $\{c_\alpha,\, c_\beta\} = 0$.

Thus, we define the vacuum state $|0\rangle$ and the set of operators c_α related to single-electron states $|\alpha\rangle$ with the properties

$$\boxed{\begin{array}{ll} c_\alpha|0\rangle = 0 & \{c_\alpha,\, c_\beta\} = 0 = \{c^\dagger_\alpha,\, c^\dagger_\beta\} \\ \langle 0|0\rangle = 1 & \{c_\alpha,\, c^\dagger_\beta\} = \langle\alpha|\beta\rangle \end{array}} \tag{15}$$

We note that the creators and annihilators are not ordinary operators in a Hilbert space, but transfer states from an N-electron to a $N \pm 1$-electron Hilbert space, i.e., they are operators defined on *Fock space*. It is also remarkable that the mixed anti-commutator is the only place where the orbitals that distinguish different operators enter. Moreover, despite being operators, the creators transform in the same way as the single-electron states they represent while the vacuum state is invariant:

$$|\tilde\alpha_i\rangle = \sum_\mu |\alpha_\mu\rangle\, U_{\mu i} \qquad \rightsquigarrow \qquad c^\dagger_{\tilde\alpha_i}|0\rangle = \sum_\mu c^\dagger_{\alpha_\mu}|0\rangle\, U_{\mu i} = \left(\sum_\mu c^\dagger_{\alpha_\mu} U_{\mu i}\right)|0\rangle. \tag{16}$$

A set of operators that allows us to make contact with the notation of first quantization are the *field operators* $\hat\Psi^\dagger(x)$, with $x = (r, \sigma)$, that create an electron of spin σ at position r, i.e., in state $|x\rangle = |r, \sigma\rangle$. Given a complete, orthonormal set of orbitals $\{\varphi_n\}$, we can expand $|x\rangle$

$$\hat\Psi^\dagger(x)|0\rangle = |x\rangle = \sum_n |\varphi_n\rangle\langle\varphi_n|x\rangle = \sum_n \langle\varphi_n|x\rangle\, c^\dagger_{\varphi_n}|0\rangle \tag{17}$$

from which we obtain

$$\hat\Psi^\dagger(x) = \sum_n \overline{\langle x|\varphi_n\rangle}\, c^\dagger_{\varphi_n} = \sum_n \overline{\varphi_n(x)}\, c^\dagger_{\varphi_n}. \tag{18}$$

The anticommutators then follow from (15) for an orthonormal and complete set, e.g.,

$$\{\hat\Psi(x),\, \hat\Psi^\dagger(x')\} = \sum_{n,m} \langle x|\varphi_n\rangle\, \underbrace{\{c_{\varphi_n},\, c^\dagger_{\varphi_m}\}}_{=\delta_{n,m}}\, \langle\varphi_m|x'\rangle = \sum_n \langle x|\varphi_n\rangle\langle\varphi_n|x'\rangle = \langle x|x'\rangle = \delta(x - x'),$$

resulting in the anticommutation relations for the field operators

$$\big\{\hat{\Psi}(x),\,\hat{\Psi}(x')\big\} = 0 = \big\{\hat{\Psi}^\dagger(x),\,\hat{\Psi}^\dagger(x')\big\} \quad\text{and}\quad \big\{\hat{\Psi}(x),\,\hat{\Psi}^\dagger(x')\big\} = \langle x|x'\rangle. \tag{19}$$

We can, of course, expand the field operators also in a non-orthogonal set of orbitals $\{|\chi_i\rangle\}$, as long as it is complete, $\sum_{i,j}|\chi_i\rangle(S^{-1})_{ij}\langle\chi_j| = \mathbb{1}$, where $S_{ij} = \langle\chi_i|\chi_j\rangle$ is the overlap matrix

$$\hat{\Psi}^\dagger(x) = \sum_{i,j} c_i^\dagger\,(S^{-1})_{ij}\,\langle\chi_j|x\rangle. \tag{20}$$

Conversely, given any single-electron wave functions in real space $\varphi(x)$, we can express the corresponding creation operator in terms of the field operators

$$c_\varphi^\dagger = \int dx\,\varphi(x)\,\hat{\Psi}^\dagger(x). \tag{21}$$

Its anticommutator with the field operators just gives back the single-electron wave function

$$\big\{\hat{\Psi}(x),\,c_\varphi^\dagger\big\} = \int dx'\,\varphi(x')\,\big\{\hat{\Psi}(x),\,\hat{\Psi}^\dagger(x')\big\} = \varphi(x)\,. \tag{22}$$

2.2 Representation of Slater determinants

We have now all the tools in place to write the Slater determinant (4) in second quantization, using the creation operators to specify the occupied orbitals and the field operators to define the coordinates for the real-space representation

$$\Phi_{\alpha_1\alpha_2\ldots\alpha_N}(x_1,x_2,\ldots,x_N) = \frac{1}{\sqrt{N!}}\Big\langle 0\,\Big|\,\hat{\Psi}(x_1)\hat{\Psi}(x_2)\ldots\hat{\Psi}(x_N)\,c_{\alpha_N}^\dagger\ldots c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger\,\Big|\,0\Big\rangle\,. \tag{23}$$

Not surprisingly, the proof is by induction. As a warm-up we consider the case of a single-electron wave function ($N=1$). Using the anticommutation relation (22), we see that

$$\Big\langle 0\,\Big|\,\hat{\Psi}(x_1)\,c_{\alpha_1}^\dagger\,\Big|\,0\Big\rangle = \Big\langle 0\,\Big|\,\varphi_{\alpha_1}(x_1) - c_{\alpha_1}^\dagger\hat{\Psi}(x_1)\,\Big|\,0\Big\rangle = \varphi_{\alpha_1}(x_1)\,. \tag{24}$$

For the two-electron state $N=2$, we anticommute $\hat{\Psi}(x_2)$ in two steps to the right

$$\begin{aligned}\Big\langle 0\,\Big|\,\hat{\Psi}(x_1)\hat{\Psi}(x_2)\,c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger\,\Big|\,0\Big\rangle &= \Big\langle 0\,\Big|\,\hat{\Psi}(x_1)\,\Big(\varphi_{\alpha_2}(x_2) - c_{\alpha_2}^\dagger\hat{\Psi}(x_2)\Big)\,c_{\alpha_1}^\dagger\,\Big|\,0\Big\rangle\\ &= \Big\langle 0\,\Big|\,\hat{\Psi}(x_1)c_{\alpha_1}^\dagger\,\Big|\,0\Big\rangle\,\varphi_{\alpha_2}(x_2) - \Big\langle 0\,\Big|\,\hat{\Psi}(x_1)c_{\alpha_2}^\dagger\hat{\Psi}(x_2)c_{\alpha_1}^\dagger\,\Big|\,0\Big\rangle\\ &= \varphi_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_2) - \varphi_{\alpha_2}(x_1)\varphi_{\alpha_1}(x_2)\,. \end{aligned}\tag{25}$$

We see how anticommuting automatically produces the appropriate signs for the antisymmetric wave function. Dividing by $\sqrt{2}$, we obtain the desired two-electron Slater determinant.

The general case of an N-electron state works just the same. Anti-commuting $\hat{\Psi}(x_N)$ all the way to the right produces $N-1$ terms with alternating sign

$$\begin{array}{lll} \multicolumn{3}{l}{\left\langle 0 \middle| \hat{\Psi}(x_1)\dots\hat{\Psi}(x_{N-1})\hat{\Psi}(x_N)\, c^\dagger_{\alpha_N} c^\dagger_{\alpha_{N-1}} \cdots c^\dagger_{\alpha_1} \middle| 0 \right\rangle \;=} \\ + & \left\langle 0 \middle| \hat{\Psi}(x_1)\dots\hat{\Psi}(x_{N-1})\, c^\dagger_{\alpha_{N-1}} \cdots c^\dagger_{\alpha_1} \middle| 0 \right\rangle & \varphi_{\alpha_N}(x_N) \\ - & \left\langle 0 \middle| \hat{\Psi}(x_1)\dots\hat{\Psi}(x_{N-1})\, \prod_{n\neq N-1} c^\dagger_{\alpha_n} \middle| 0 \right\rangle & \varphi_{\alpha_{N-1}}(x_N) \\ \vdots & & \\ (-1)^N & \left\langle 0 \middle| \hat{\Psi}(x_1)\dots\hat{\Psi}(x_{N-1})\, c^\dagger_{\alpha_N} \;\dots\; c^\dagger_{\alpha_2} \middle| 0 \right\rangle & \varphi_{\alpha_1}(x_N)\,. \end{array}$$

Using (23) for the $N-1$-electron states, this is nothing but the Laplace expansion of

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

along the Nth row. Dividing by $\sqrt{N!}$ we see that we have shown (23) for N-electron states, completing the proof by induction.

Thus, as we can write the representation of a single-electron state $|\varphi\rangle$ in real-space as the matrix element $\langle x|\varphi\rangle = \varphi(x)$, we can obtain the representation of the N-electron $\prod c^\dagger_{\alpha_n}|0\rangle$ as the matrix element with the field operators $\langle 0|\prod \hat{\Psi}(x_n)$. Thus, we can rewrite the basis (6) for the N-electron states in a form independent of the real-space representation

$$\left\{ c^\dagger_{n_N}\cdots c^\dagger_{n_1}|0\rangle \;\middle|\; n_1 < \cdots < n_N \right\}, \tag{26}$$

which allows us to write any N-electron state as

$$|\Psi\rangle = \sum_{n_1<\cdots<n_N} a_{n_1,\dots,n_N}\, c^\dagger_{n_N}\cdots c^\dagger_{n_1}|0\rangle. \tag{27}$$

From this we see that, for an orthonormal basis, the expectation value of the *occupation number operator* $\hat{n}_i = c^\dagger_i c_i$ is the probability that state φ_{n_i} is occupied

$$\langle\Psi|\hat{n}_i|\Psi\rangle = \sum_{n_i\in\{n1<\cdots<n_N\}} |a_{n_1,\dots,n_N}|^2, \tag{28}$$

since only determinants that contain φ_{n_i} contribute. The sum of all these operators $\hat{N} = \sum_i \hat{n}_i$ is the number operator, since now each determinant contributes N times

$$\langle\Psi|\sum_i \hat{n}_i|\Psi\rangle = \sum_i \sum_{n_i\in\{n1<\cdots<n_N\}} |a_{n_1,\dots,n_N}|^2 = N\,. \tag{29}$$

For the special case of the field operators we obtain the density operator $\hat{n}(x) = \hat{\Psi}^\dagger(x)\hat{\Psi}(x)$ and $\hat{N} = \int dx\, \hat{\Psi}^\dagger(x)\hat{\Psi}(x)$.

2.3 Representation of n-body operators

Having established the relation between product states and Slater determinants, it is straightforward to express the matrix elements of a general n-body operator (2)

$$M(\mathbf{x}) = M^{(0)} + \sum_i M^{(1)}(x_i) + \sum_{i<j} M^{(2)}(x_i, x_j) + \sum_{i<j<k} M^{(3)}(x_i, x_j, x_k) + \cdots \tag{30}$$

with N-electron Slater determinants:

$$\begin{aligned}
&\int dx_1 \cdots dx_N \, \overline{\Phi_{\beta_1 \cdots \beta_N}(x_1, \cdots, x_N)} \, M(x_1, \ldots, x_N) \, \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \cdots, x_N) \\
=&\int dx_1 \cdots dx_N \, \langle 0 | c_{\beta_1} \cdots c_{\beta_N} \hat{\Psi}^\dagger(x_N) \cdots \hat{\Psi}^\dagger(x_1) | 0 \rangle M(x_1, \ldots, x_N) \langle 0 | \hat{\Psi}(x_1) \cdots \hat{\Psi}(x_N) c^\dagger_{\alpha_N} \cdots c^\dagger_{\alpha_1} | 0 \rangle \\
&= \left\langle 0 \, \middle| \, c_{\beta_1} \cdots c_{\beta_N} \, \hat{M} \, c^\dagger_{\alpha_N} \cdots c^\dagger_{\alpha_1} \, \middle| \, 0 \right\rangle
\end{aligned}$$

with the representation of the n-body operator in terms of field operators

$$\hat{M} = \frac{1}{N!} \int dx_1 \cdots x_N \, \hat{\Psi}^\dagger(x_N) \cdots \hat{\Psi}^\dagger(x_1) \, M(x_1, \cdots, x_N) \, \hat{\Psi}(x_1) \cdots \hat{\Psi}(x_N) \, . \tag{31}$$

Note that this particular form of the operator is only valid when applied to N-electron states, since we have used that the N annihilation operators bring us to the zero-electron space, where $|0\rangle\langle 0| = \mathbb{1}$. Keeping this in mind, we can work entirely in terms of our algebra (15).

To see what (31) means we look at its parts (30). We start with the simplest case, the zero-body operator, which, up to a trivial prefactor, is $M^{(0)}(x_1, \cdots, x_N) = 1$. Operating on an N-electron wave function, it gives

$$\begin{aligned}
\hat{M}^{(0)} &= \frac{1}{N!} \int dx_1 dx_2 \cdots x_N \, \hat{\Psi}^\dagger(x_N) \cdots \hat{\Psi}^\dagger(x_2) \hat{\Psi}^\dagger(x_1) \, \hat{\Psi}(x_1) \hat{\Psi}(x_2) \cdots \hat{\Psi}(x_N) \\
&= \frac{1}{N!} \int \quad dx_2 \cdots x_N \, \hat{\Psi}^\dagger(x_N) \cdots \hat{\Psi}^\dagger(x_2) \qquad \hat{N} \qquad \hat{\Psi}(x_2) \cdots \hat{\Psi}(x_N) \\
&= \frac{1}{N!} \int \quad dx_2 \cdots x_N \, \hat{\Psi}^\dagger(x_N) \cdots \hat{\Psi}^\dagger(x_2) \qquad 1 \qquad \hat{\Psi}(x_2) \cdots \hat{\Psi}(x_N) \\
&\;\vdots \\
&= \frac{1}{N!} \, 1 \cdot 2 \, \cdots \, N = 1 \, ,
\end{aligned} \tag{32}$$

where we have used that

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

is the number operator and that applying n annihilation operators $\hat{\Psi}(x_j)$ to an N-electron state gives a state with $N - n$ electrons. We note that we obtain a form of $\hat{M}^{(0)} = 1$ that, contrary to (31), no longer depend on the number of electrons in the wave function that it is applied to.

2.3.1 One-body operators

Next we consider one-body operators $M(x_1,\dots,x_N)=\sum_j M^{(1)}(x_j)$

$$
\begin{aligned}
\hat{M}^{(1)} &= \frac{1}{N!}\int dx_1\cdots dx_N\,\hat{\Psi}^\dagger(x_N)\cdots\hat{\Psi}^\dagger(x_1)\sum_j M^{(1)}(x_j)\,\hat{\Psi}(x_1)\cdots\hat{\Psi}(x_N)\\
&= \frac{1}{N!}\sum_j\int dx_j\,\hat{\Psi}^\dagger(x_j)\,M^{(1)}(x_j)\,(N-1)!\,\hat{\Psi}(x_j)\\
&= \frac{1}{N}\sum_j\int dx_j\,\hat{\Psi}^\dagger(x_j)\,M^{(1)}(x_j)\,\hat{\Psi}(x_j)\\
&= \int dx\;\;\hat{\Psi}^\dagger(x)\;M^{(1)}(x)\;\hat{\Psi}(x)
\end{aligned}
$$

Here we have first anticommuted $\hat{\Psi}^\dagger(x_j)$ all the way to the left and $\hat{\Psi}(x_j)$ to the right. Since these take the same numbers of anticommutations, there is no sign involved. The operation leaves the integrals over the variables except x_i, a zero-body operator for $N-1$ electron states, operating on $\hat{\Psi}(x_j)|N\text{-electron state}\rangle$. Again we notice that we obtain an operator that no longer depends on the number of electrons, i.e., that is valid in the entire Fock space.

Expanding the field-operators in a complete orthonormal set $\hat{\Psi}(x)=\sum_n\varphi_n(x)\,c_n$ gives

$$
\hat{M}^{(1)}=\sum_{n,m}\int dx\,\overline{\varphi_n(x)}\,M(x)\,\varphi_m(x)\;c_n^\dagger c_m=\sum_{n,m}\langle\varphi_n|M^{(1)}|\varphi_m\rangle\;c_n^\dagger c_m=\sum_{n,m}c_n^\dagger\,M^{(1)}_{nm}\,c_m. \tag{33}
$$

The matrix elements $M^{(1)}_{nm}=\langle\varphi_n|M^{(1)}|\varphi_m\rangle$ transforms like a single-electron matrix $\boldsymbol{M}^{(1)}$: From (16) and writing the annihilation operators as a column vector $\boldsymbol{c}$ we see that

$$
\hat{M}^{(1)}=\boldsymbol{c}^\dagger\,\boldsymbol{M}^{(1)}\,\boldsymbol{c}\;=\boldsymbol{c}^\dagger\boldsymbol{U}^\dagger\;\boldsymbol{U}\boldsymbol{M}^{(1)}\boldsymbol{U}^\dagger\;\boldsymbol{U}\boldsymbol{c}=\tilde{\boldsymbol{c}}^\dagger\,\tilde{\boldsymbol{M}}^{(1)}\,\tilde{\boldsymbol{c}}\,. \tag{34}
$$

Once we have arrived at the representation in terms of orbitals, we can restrict the orbital basis to a non-complete set. This simply gives the operator in the variational (Fock) subspace spanned by the orbitals.

2.3.2 Two-body operators

For the two-body operators $M(x_1,\dots,x_N)=\sum_{i<j}M^{(2)}(x_i,x_j)$ we proceed in the familiar way, anti-commuting first the operators with the coordinates involved in $M^{(2)}$ all the way to the left and right, respectively. This time we are left with a zero-body operator for $N-2$ electrons:

$$
\begin{aligned}
\hat{M}^{(2)} &= \frac{1}{N!}\int dx_1\cdots dx_N\,\hat{\Psi}^\dagger(x_N)\cdots\hat{\Psi}^\dagger(x_1)\sum_{i<j}M^{(2)}(x_i,x_j)\,\hat{\Psi}(x_1)\cdots\hat{\Psi}(x_N)\\
&= \frac{1}{N!}\sum_{i<j}\int dx_i dx_j\,\hat{\Psi}^\dagger(x_j)\hat{\Psi}^\dagger(x_i)\,M^{(2)}(x_i,x_j)\,(N-2)!\,\hat{\Psi}(x_i)\hat{\Psi}(x_j)\\
&= \frac{1}{N(N-1)}\sum_{i<j}\int dx_i dx_j\,\hat{\Psi}^\dagger(x_j)\hat{\Psi}^\dagger(x_i)\,M^{(2)}(x_i,x_j)\,\hat{\Psi}(x_i)\hat{\Psi}(x_j)\\
&= \frac{1}{2}\int dx\,dx'\,\hat{\Psi}^\dagger(x')\,\hat{\Psi}^\dagger(x)\;M^{(2)}(x,x')\;\hat{\Psi}(x)\,\hat{\Psi}(x')
\end{aligned}
$$

Expanding in an orthonormal basis, we get

$$\begin{aligned}\hat{M}^{(2)} &= \frac{1}{2}\sum_{n,n',m,m'} \int dx dx'\, \overline{\varphi_{n'}(x')\varphi_n(x)}\, M^{(2)}(x,x')\, \varphi_m(x)\varphi_{m'}(x') \quad c^\dagger_{n'}c^\dagger_n c_m c_{m'} \\ &= \frac{1}{2}\sum_{n,n',m,m'} \langle \varphi_n\varphi_{n'}|M^{(2)}|\varphi_m\varphi_{m'}\rangle \quad c^\dagger_{n'}c^\dagger_n c_m c_{m'}\end{aligned} \tag{35}$$

where the exchange of the indices in the second line is a consequence of the way the Dirac state for two electrons is usually written: first index for the first coordinate, second index for the second, while taking the adjoint of the operators changes their order. $M_{nn',mm'} = \langle \varphi_n\varphi_{n'}|M^{(2)}|\varphi_m\varphi_{m'}\rangle$ transforms like a fourth-order tensor: Transforming to a different basis (16) gives

$$\tilde{M}^{(2)}_{\nu\nu',\mu\mu'} = \sum_{n,n',m,m'} U^\dagger_{\nu n}U^\dagger_{\nu' n'} M_{nn',mm'} U_{m\mu}U_{m'\mu'}\,. \tag{36}$$

Form the symmetry of the two-body operator $M^{(2)}(x,x') = M^{(2)}(x',x)$ follows $M_{nn',mm'} = M_{n'n,m'm}$. Moreover, $M_{nn,mm'}$ will not contribute to $\hat{M}^{(2)}$ since $c^\dagger_n c^\dagger_n = \{c^\dagger_n,\, c^\dagger_n\}/2 = 0$, and likewise for $M_{nn',mm}$.

Note that the representation (35) is not quite as efficient as it could be: The terms with n and n' and/or m and m' exchanged connect the same basis states. Collecting these terms by introducing an ordering of the operators and using the symmetry of the matrix elements we obtain

$$\hat{M}^{(2)} = \sum_{n'>n,m'>m} c^\dagger_{n'}c^\dagger_n \underbrace{\left(M^{(2)}_{nn',mm'} - M^{(2)}_{n'n,mm'}\right)}_{=:\breve{M}^{(2)}_{nn',mm'}} c_m c_{m'}\,. \tag{37}$$

Since the states $\{c^\dagger_{n'}c^\dagger_n|0\rangle \mid n'>n\}$ form a basis of the two-electron Hilbert space, considering nn' as the index of a basis state, the $\breve{M}^{(2)}_{nn',mm'}$ form a two-electron matrix $\breve{\boldsymbol{M}}^{(2)}$.

The procedure of rewriting operators in second quantization obviously generalizes to operators acting on more than two electrons in the natural way. We note that, while we started from a form of the operators (30) that was explicitly formulated in an N-electron Hilbert space, the results (32), (33), and (35) are of the same form no matter what value N takes. Thus these operators are valid not just on some N-electron Hilbert space, but on the entire Fock space. This is a particular strength of the second-quantized formulation.

2.4 Reduced density matrices and Wick's theorem

Introducing reduced density matrices it is straightforward to evaluate expectation values for general many-electron states. From the representation of single-electron operators (33) we find

$$\langle \varPsi|M^{(1)}|\varPsi\rangle = \sum_{n,m} M^{(1)}_{nm} \underbrace{\langle \varPsi|c^\dagger_n c_m|\varPsi\rangle}_{=:\varGamma^{(1)}_{nm}} = \mathrm{Tr}\,\boldsymbol{\varGamma}^{(1)}\boldsymbol{M}^{(1)}, \tag{38}$$

where the trace is over the one-electron basis and we use that observables are hermitian. For two-electron operators (37) we find

$$\langle\Psi|M^{(2)}|\Psi\rangle = \sum_{n'>n,\, m'>m} \breve{M}^{(2)}_{nn',\,mm'} \underbrace{\langle\Psi|c^\dagger_{n'}c^\dagger_{n}c_{m}c_{m'}|\Psi\rangle}_{=:\breve{\Gamma}^{(2)}_{nn',\,mm'}} = \mathrm{Tr}\,\breve{\boldsymbol{\Gamma}}^{(2)}\breve{\boldsymbol{M}}^{(2)}, \tag{39}$$

where now the trace in over the two-electron basis. In general, if we know the p-body density matrix $\breve{\boldsymbol{\Gamma}}^{(p)}$ for a given many-electron state $|\Psi\rangle$, we can calculate the expectation value of any operator of order up to p. We can obtain lower-order density matrices by taking partial traces over higher-order matrices, e.g.,

$$\sum_k \Gamma^{(2)}_{nk,\,mk} = \sum_k \langle\Psi|c^\dagger_n c^\dagger_k c_k c_m|\Psi\rangle = \langle\Psi|c^\dagger_n\,\hat{N}\,c_m|\Psi\rangle = (N-1)\,\Gamma^{(1)}_{nm}\,. \tag{40}$$

Note the similarity to (32). In terms of the two-electron matrix $\breve{\boldsymbol{\Gamma}}^{(2)}$ we trace (keeping track of the Fermion sign) over all two-electron states with orbital n or m occupied.

For Slater determinants $|\Phi\rangle = c^\dagger_{\alpha_N}\cdots c^\dagger_{\alpha_1}|0\rangle$ the density matrices have a particularly simple form. To see this we introduce the projection onto the space of occupied orbitals assuming, for simplicity, that the orbitals $|\alpha_n\rangle$ are orthonormal

$$P = \sum_n |\alpha_n\rangle\langle\alpha_n|\,. \tag{41}$$

We can then split any orbital into its components in the occupied and the virtual space: $|\varphi\rangle = P|\varphi\rangle + (\mathbb{1}-P)|\varphi\rangle$. Applying an annihilation operator to the Slater determinant we then find that only the component in the virtual space gives a zero contribution, similarly for a creation operator:

$$c_{|\varphi\rangle}|\Phi\rangle = c_{P|\varphi\rangle}|\Phi\rangle \qquad \text{and} \qquad c^\dagger_{|\varphi\rangle}|\Phi\rangle = c^\dagger_{(\mathbb{1}-P)|\varphi\rangle}|\Phi\rangle. \tag{42}$$

The one-body density matrix of a Slater determinant is thus given by

$$\begin{aligned}\Gamma^{(1)}_{nm} &= \langle\Phi|c^\dagger_n c_m|\Phi\rangle = \langle\Phi|c^\dagger_{P|\varphi_n\rangle}c_{P|\varphi_m\rangle}|\Phi\rangle = \langle P\varphi_m|P\varphi_n\rangle\langle\Phi|\Phi\rangle - \langle\Phi|c_{P|\varphi_m\rangle}c^\dagger_{P|\varphi_n\rangle}|\Phi\rangle\\ &= \langle\varphi_m|P|\varphi_n\rangle.\end{aligned} \tag{43}$$

As an operator in the one-electron Hilbert space $\mathcal{H}^{(1)}$, the one-body density matrix of a Slater determinant is thus the projector onto the occupied subspace. Up to a phase factor it defines the Slater determinant uniquely. All higher-order density matrices of a Slater determinant can thus be written in terms of the one-body density matrix. For the two-body density matrix we find, simply commuting $c^\dagger_{P|n_1\rangle}$ to the right (note the similarity to the derivation in Sec. 2.2)

$$\begin{aligned}\langle\Phi|c^\dagger_{n_2}c^\dagger_{n_1}c_{m_1}c_{m_2}|\Phi\rangle &= \langle\Phi|c^\dagger_{Pn_2}c^\dagger_{Pn_1}c_{Pm_1}c_{Pm_2}|\Phi\rangle\\ &= \langle Pm_1|Pn_1\rangle\langle\Phi|c^\dagger_{Pn_2}c_{Pm_2}|\Phi\rangle - \langle\Phi|c^\dagger_{Pn_2}c_{Pm_1}c^\dagger_{Pn_1}c_{Pm_2}|\Phi\rangle\\ &= \Gamma^{(1)}_{n_1m_1}\Gamma^{(1)}_{n_2m_2} - \langle Pm_2|Pn_1\rangle\langle\Phi|c^\dagger_{Pn_2}c_{Pm_1}|\Phi\rangle + \langle\Phi|c^\dagger_{Pn_2}c_{Pm_1}c_{Pm_2}c^\dagger_{Pn_1}|\Phi\rangle\\ &= \det\begin{pmatrix}\Gamma^{(1)}_{n_1m_1} & \Gamma^{(1)}_{n_1m_2}\\ \Gamma^{(1)}_{n_2m_1} & \Gamma^{(1)}_{n_2m_2}\end{pmatrix}.\end{aligned} \tag{44}$$

Using the same procedure together with the Laplace expansion we find the higher-order density matrices

$$\langle\varPhi|c^\dagger_{n_p}\cdots c^\dagger_{n_1}c_{m_1}\cdots c_{m_p}|\varPhi\rangle = \det\begin{pmatrix} \varGamma^{(1)}_{n_1m_1} & \cdots & \varGamma^{(1)}_{n_1m_p} \\ \vdots & \ddots & \vdots \\ \varGamma^{(1)}_{n_pm_1} & \cdots & \varGamma^{(1)}_{n_pm_p} \end{pmatrix}. \tag{45}$$

Matrix elements between different Slater determinants are not quite as simple, as the terms with the creation operator anticommuted to the right need no longer vanish. Still, we can express expectation values as determinants using (7)

$$\langle\varPhi_{\boldsymbol{\alpha}}|\varPhi_{\boldsymbol{\beta}}\rangle = \det\begin{pmatrix} \langle\alpha_1|\beta_1\rangle & \cdots & \langle\alpha_1|\beta_N\rangle \\ \vdots & \ddots & \vdots \\ \langle\alpha_N|\beta_1\rangle & \cdots & \langle\alpha_N|\beta_N\rangle \end{pmatrix}. \tag{46}$$

The overlap is non-zero if each vector in the occupied space of $|\varPhi_{\boldsymbol{\alpha}}\rangle$ has a component in the occupied space of $|\varPhi_{\boldsymbol{\beta}}\rangle$, i.e., $P_{\boldsymbol{\beta}}|\alpha_n\rangle \neq 0$, or, more symmetrically, $\dim(P_{\boldsymbol{\beta}}P_{\boldsymbol{\alpha}}\mathcal{H}^{(1)}) = N$. Note that the combination of the two projectors $P_{\boldsymbol{\alpha}}P_{\boldsymbol{\beta}}$ is, in general, no longer a projection.

To evaluate the matrix element for a one-electron operator we simply change the order of the operators to obtain an expression that is given by a determinant

$$\begin{aligned}
\langle\varPhi_{\boldsymbol{\alpha}}|c^\dagger_n c_m|\varPhi_{\boldsymbol{\beta}}\rangle &= \langle\varPhi_{\boldsymbol{\alpha}}|c^\dagger_{P_{\boldsymbol{\alpha}}n}c_{P_{\boldsymbol{\beta}}m}|\varPhi_{\boldsymbol{\beta}}\rangle \\
&= \langle\varphi_m|P_{\boldsymbol{\beta}}P_{\boldsymbol{\alpha}}|\varphi_n\rangle\langle\varPhi_{\boldsymbol{\alpha}}|\varPhi_{\boldsymbol{\beta}}\rangle - \langle\varPhi_{\boldsymbol{\alpha}}|c_{P_{\boldsymbol{\beta}}m}c^\dagger_{P_{\boldsymbol{\alpha}}n}|\varPhi_{\boldsymbol{\beta}}\rangle \\
&= \langle\varphi_m|P_{\boldsymbol{\beta}}P_{\boldsymbol{\alpha}}|\varphi_n\rangle\langle\varPhi_{\boldsymbol{\alpha}}|\varPhi_{\boldsymbol{\beta}}\rangle - \det\begin{pmatrix} \langle\alpha_1|\varphi_n\rangle & \langle\alpha_1|\beta_1\rangle & \cdots & \langle\alpha_1|\beta_N\rangle \\ \vdots & \vdots & & \vdots \\ \langle\alpha_N|\varphi_n\rangle & \langle\alpha_N|\beta_1\rangle & \cdots & \langle\alpha_N|\beta_N\rangle \\ \langle\varphi_m|P_{\boldsymbol{\beta}}P_{\boldsymbol{\alpha}}|\varphi_n\rangle & \langle\varphi_m|\beta_1\rangle & \cdots & \langle\varphi_m|\beta_N\rangle \end{pmatrix} \\
&= \langle\varphi_m|P_{\boldsymbol{\beta}}P_{\boldsymbol{\alpha}}|\varphi_n\rangle\langle\varPhi_{\boldsymbol{\alpha}}|\varPhi_{\boldsymbol{\beta}}\rangle - \langle\varPhi_{\boldsymbol{\alpha},P_{\boldsymbol{\beta}}\varphi_m}|\varPhi_{\boldsymbol{\beta},P_{\boldsymbol{\alpha}}\varphi_n}\rangle.
\end{aligned} \tag{47}$$

For $|\varPhi_{\boldsymbol{\alpha}}\rangle = |\varPhi_{\boldsymbol{\beta}}\rangle$ we recover (43). Higher-order expectation values are calculated in a similar way, moving the creation operators successively to the right, giving, e.g.,

$$\begin{aligned}
&\langle\varPhi_{\boldsymbol{\alpha}}|c^\dagger_{n_2}c^\dagger_{n_1}c_{m_1}c_{m_2}|\varPhi_{\boldsymbol{\beta}}\rangle = \langle\varPhi_{\boldsymbol{\alpha}}|c^\dagger_{P_{\boldsymbol{\alpha}}n_2}c^\dagger_{P_{\boldsymbol{\alpha}}n_1}c_{P_{\boldsymbol{\beta}}m_1}c_{P_{\boldsymbol{\beta}}m_2}|\varPhi_{\boldsymbol{\beta}}\rangle \\
&= \begin{vmatrix} \langle\varPhi_{\boldsymbol{\alpha}}|c^\dagger_{n_1}c_{m_1}|\varPhi_{\boldsymbol{\beta}}\rangle & \langle\varPhi_{\boldsymbol{\alpha}}|c^\dagger_{n_1}c_{m_2}|\varPhi_{\boldsymbol{\beta}}\rangle \\ \langle\varPhi_{\boldsymbol{\alpha}}|c^\dagger_{n_2}c_{m_1}|\varPhi_{\boldsymbol{\beta}}\rangle & \langle\varPhi_{\boldsymbol{\alpha}}|c^\dagger_{n_2}c_{m_2}|\varPhi_{\boldsymbol{\beta}}\rangle \end{vmatrix} - \begin{vmatrix} \varDelta_{n_1m_1} & \varDelta_{n_1m_2} \\ \varDelta_{n_2m_1} & \varDelta_{n_2m_2} \end{vmatrix} \\
&\quad + (1-\langle\varPhi_{\boldsymbol{\alpha}}|\varPhi_{\boldsymbol{\beta}}\rangle)\begin{vmatrix} \langle\varphi_{m_1}|P_{\boldsymbol{\beta}}P_{\boldsymbol{\alpha}}|\varphi_{n_1}\rangle & \langle\varphi_{m_2}|P_{\boldsymbol{\beta}}P_{\boldsymbol{\alpha}}|\varphi_{n_1}\rangle \\ \langle\varphi_{m_1}|P_{\boldsymbol{\beta}}P_{\boldsymbol{\alpha}}|\varphi_{n_2}\rangle & \langle\varphi_{m_2}|P_{\boldsymbol{\beta}}P_{\boldsymbol{\alpha}}|\varphi_{n_2}\rangle \end{vmatrix} + \langle\varPhi_{\boldsymbol{\alpha},P_{\boldsymbol{\beta}}\varphi_{m_1},P_{\boldsymbol{\beta}}\varphi_{m_2}}|\varPhi_{\boldsymbol{\beta},P_{\boldsymbol{\alpha}}\varphi_{n_1},P_{\boldsymbol{\alpha}}\varphi_{n_2}}\rangle,
\end{aligned}$$

where $\varDelta_{n,m} = \langle\varPhi_{\boldsymbol{\alpha}}|c^\dagger_n c_m|\varPhi_{\boldsymbol{\beta}}\rangle - \langle\varphi_m|P_{\boldsymbol{\beta}}P_{\boldsymbol{\alpha}}|\varphi_n\rangle$. For $|\varPhi_{\boldsymbol{\alpha}}\rangle = |\varPhi_{\boldsymbol{\beta}}\rangle$ this reduces to (44). While these expressions can be efficiently evaluated expanding the $N+p$-order determinant, the expressions quickly get quite involved.

The situation simplifies dramatically when we only consider operators c_n and $c^\dagger_n$ corresponding to an orthonormal basis $\{|\varphi_n\rangle\,|\,n\}$ of $\mathcal{H}^{(1)}$. The Slater determinants are then orthonormal and of the form $|\Phi_{\boldsymbol{n}}\rangle = |\Phi_{n_1,\dots,n_N}\rangle = c^\dagger_{n_N}\cdots c^\dagger_{n_1}|0\rangle$. Diagonal matrix elements are then

$$\begin{aligned}
\langle\Phi_{\boldsymbol{n}}|c^\dagger_n c_m|\Phi_{\boldsymbol{n}}\rangle &= \delta_{n,m}\delta_{n\in\{n_1,\dots,n_N\}}\\
\langle\Phi_{\boldsymbol{n}}|c^\dagger_n c^\dagger_{n'} c_{m'} c_m|\Phi_{\boldsymbol{n}}\rangle &= \left(\delta_{n,m}\delta_{m',m'} - \delta_{n,m'}\delta_{n',m}\right)\delta_{n,n',m,m'\in\{n_1,\dots,n_N\}}\\
\langle\Phi_{\boldsymbol{n}}|c^\dagger_{k_p}\cdots c^\dagger_{k_1} c_{m_1}\cdots c_{m_p}|\Phi_{\boldsymbol{n}}\rangle &= \det(\delta_{k_i,m_j})\,\delta_{k_1,\dots,k_p,m_1,\dots,m_p\in\{n_1,\dots,n_N\}}.
\end{aligned}$$

Off-diagonal matrix elements vanish unless the determinants differ in exactly the operators inside the matrix element:

$$\begin{aligned}
\langle\Phi_{\boldsymbol{n}}|c^\dagger_n c_m|\Phi_{\boldsymbol{m}}\rangle &= \pm\delta_{m=m_i}\delta_{n=n_j}\,\delta_{\{m_1,\dots,m_N\}\setminus\{m_i\}=\{n_1,\dots,n_N\}\setminus\{n_j\}}\\
\langle\Phi_{\boldsymbol{n}}|c^\dagger_n c^\dagger_{n'} c_{m'} c_m|\Phi_{\boldsymbol{m}}\rangle &= \pm\delta_{\{m,m'\}=\{m_i,m_{i'}\}}\delta_{\{n,n'\}=\{n_j,n_{j'}\}}\delta_{\{\boldsymbol{m}\}\setminus\{m_i,m_{i'}\}=\{\boldsymbol{n}\}\setminus\{n_j,n_{j'}\}}.
\end{aligned}$$

Thus, when we transform an operator $\hat{M}^{(p)}$ to the basis in which the Slater determinants are written, all matrix elements between determinants that differ by more than p operators vanish. These are the Slater-Condon rules.

3 Variational methods

The variational principle and the Schrödinger equation are equivalent. Consider the energy expectation value as a wave-function functional

$$E[\Psi] = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}\,. \tag{48}$$

Its variation is

$$E[\Psi+\delta\Psi] = E[\Psi] + \frac{\langle\delta\Psi|H|\Psi\rangle + \langle\Psi|H|\delta\Psi\rangle}{\langle\Psi|\Psi\rangle} - \langle\Psi|H|\Psi\rangle\,\frac{\langle\delta\Psi|\Psi\rangle + \langle\Psi|\delta\Psi\rangle}{\langle\Psi|\Psi\rangle^2} + \mathcal{O}^2. \tag{49}$$

The first-order term vanishes for

$$H|\Psi\rangle = E[\Psi]\,|\Psi\rangle\,, \tag{50}$$

which is the Schrödinger equation. The general approach to solving it for many-electron systems is configuration interaction (CI): We choose an orthonormal set of orbitals $\{\varphi_n\,|\,n\}$ from which we construct an orthonormal basis $\{\Phi_{n_1,\dots,n_N}\,|\,n_1<\cdots<n_N\}$ of N-electron Slater determinants. Expanding $|\Psi\rangle$ in this basis

$$|\Psi\rangle = \sum_{n_1<\cdots<n_N} a_{n_1,\dots,n_N}\,|\Phi_{n_1,\dots,n_N}\rangle = \sum_{\boldsymbol{n}_i} a_{\boldsymbol{n}_i}\,|\Phi_{\boldsymbol{n}_i}\rangle\,, \tag{51}$$

the Schrödinger equation (50) becomes a matrix eigenvalue problem

$$\begin{pmatrix}
\langle\Phi_{\boldsymbol{n}_1}|H|\Phi_{\boldsymbol{n}_1}\rangle & \langle\Phi_{\boldsymbol{n}_1}|H|\Phi_{\boldsymbol{n}_2}\rangle & \cdots\\
\langle\Phi_{\boldsymbol{n}_2}|H|\Phi_{\boldsymbol{n}_1}\rangle & \langle\Phi_{\boldsymbol{n}_2}|H|\Phi_{\boldsymbol{n}_2}\rangle & \cdots\\
\vdots & \vdots & \ddots
\end{pmatrix}
\begin{pmatrix} a_{\boldsymbol{n}_1}\\ a_{\boldsymbol{n}_2}\\ \vdots\end{pmatrix}
= E\begin{pmatrix} a_{\boldsymbol{n}_1}\\ a_{\boldsymbol{n}_2}\\ \vdots\end{pmatrix}. \tag{52}$$

Note that the indices $\boldsymbol{n}_i$ of the determinants are ordered sets of single-electron indices.
For a complete basis set the matrix dimension is, of course, infinite, but even for finite basis sets of K single-electron functions the dimension for an N-electron problem increase extremely rapidly. There are $K \cdot (K-1) \cdot (K-2) \cdots (K-(N-1))$ ways of picking N indices out of K. Since we only use one specific ordering of these indices, we still have to divide by $N!$ to obtain the number of such determinants:

$$\dim \mathcal{H}_K^{(N)} = \frac{K!}{N!(K-N)!} = \binom{K}{N}. \tag{53}$$

For $N = 25$ electrons and $K = 100$ orbitals the dimension already exceeds 10^{23}. And still, being a non-complete basis set, diagonalizing (52) still would only give a variational energy, meaning that, for example, the ground state of (52) is the state that minimizes the energy wave-function functional (48) on the $\binom{K}{N}$-dimensional subspace of the N-electron Hilbert space.

3.1 Non-interacting electrons

Even when considering a system of N non-interacting electrons we have to solve the large matrix eigenvalue problem (52). Writing the non-interacting Hamiltonian in the basis used for the CI expansion (51) we obtain

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

which, in general, has non-vanishing matrix elements between Slater determinants that differ in at most one operator. But we can simplify things drastically by realizing that we can choose any basis for the CI expansion. If we choose the eigenstates of the single-electron matrix H_{nm} as basis, second-quantized Hamiltonian is

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

In this basis all off-diagonal matrix elements vanish and the CI Hamiltonian (52) is diagonal. Thus all $\binom{K}{N}$ eigenstates are Slater determinants

$$|\Phi_{\boldsymbol{n}}\rangle = c_{n_N}^\dagger \cdots c_{n_1}^\dagger |0\rangle \qquad \text{with eigenenergy} \quad E_{\boldsymbol{n}} = \sum_i \varepsilon_{n_i}\,. \tag{54}$$

This shows that choosing an appropriate basis for a CI expansion is crucial. A good general strategy should thus be to solve the matrix problem (52) and at the same time look for the basis set (of given size) that minimizes the variational energy. This is the idea of the multi-configurational self-consistent field method (MCSCF) [7]. In the following we will restrict ourselves to the simplest case where the many-body basis consists of a single Slater determinant. This is the Hartree-Fock method.

3.2 Hartree-Fock theory

The idea of the Hartree-Fock approach is to find an approximation to the ground-state of the N-electron problem by minimizing the total-energy wave-function functional (48) allowing only N-electron Slater determinants as variational functions. Since expectation values of Slater determinants are determined by their one-body density matrix, remember (45), this means that we want to find the occupied subspace for which (48) is minimized.

To perform these variations we introduce unitary transformations in Fock-space (related to the Thouless representation of Slater determinants [8])

$$\hat{U}(\lambda) = e^{i\lambda\hat{M}} \qquad \text{with} \quad \hat{M} = \sum_{\alpha,\beta} M_{\alpha\beta}\, c^\dagger_\alpha c_\beta \quad \text{hermitian}\,. \tag{55}$$

To see that $\hat{U}$ is a transformation among Slater determinants, we apply it to a product state

$$e^{i\lambda\hat{M}}\, c^\dagger_{\alpha_N} \cdots c_{\alpha_1}|0\rangle = e^{i\lambda\hat{M}} c^\dagger_{\alpha_N} e^{-i\lambda\hat{M}}\; e^{i\lambda\hat{M}} \cdots e^{-i\lambda\hat{M}} e^{i\lambda\hat{M}} c^\dagger_{\alpha_1} e^{-i\lambda\hat{M}}\; e^{i\lambda\hat{M}}|0\rangle\,. \tag{56}$$

Since the annihilators produce zero when applied to the vacuum state, we have

$$e^{i\lambda\hat{M}}|0\rangle = |0\rangle\,. \tag{57}$$

To evaluate $e^{i\lambda\hat{M}}\, c^\dagger_\gamma\, e^{-i\lambda\hat{M}}$, we use that the commutator of the product of a creator and an annihilator with a creation operator is again a creation operator (see App. B)

$$[c^\dagger_\alpha c_\beta,\, c^\dagger_\gamma] = c^\dagger_\alpha \{c_\beta,\, c^\dagger_\gamma\} - \{c^\dagger_\alpha,\, c^\dagger_\gamma\} c_\beta = c^\dagger_\alpha\, \delta_{\beta,\gamma} \tag{58}$$

to calculate the coefficients of its power-series expansion in λ:

$$\begin{aligned}
\left.\frac{d}{d\lambda}\right|_{\lambda=0} e^{i\lambda\hat{M}}\, c^\dagger_\gamma\, e^{-i\lambda\hat{M}} &= \left. e^{i\lambda\hat{M}}\; i\,[\hat{M},\, c^\dagger_\alpha]\, e^{-i\lambda\hat{M}}\right|_{\lambda=0} &&= i\sum_\alpha c^\dagger_\alpha\, M_{\alpha\gamma}\\
\left.\frac{d^2}{d\lambda^2}\right|_{\lambda=0} e^{i\lambda\hat{M}}\, c^\dagger_\gamma\, e^{-i\lambda\hat{M}} &= \left.\frac{d}{d\lambda}\right|_{\lambda=0} e^{i\lambda\hat{M}} \left(i\sum_{\alpha'} c^\dagger_{\alpha'}\, M_{\alpha'\gamma}\right) e^{-i\lambda\hat{M}} &&= i^2 \sum_\alpha c^\dagger_\alpha \underbrace{\sum_{\alpha'} M_{\alpha\alpha'} M_{\alpha'\gamma}}_{(\boldsymbol{M}^2)_{\alpha\gamma}}\\
&\;\;\vdots\\
\left.\frac{d^n}{d\lambda^n}\right|_{\lambda=0} e^{i\lambda\hat{M}}\, c^\dagger_\gamma\, e^{-i\lambda\hat{M}} &= &&\;\; i^n \sum_\alpha c^\dagger_\alpha\, (\boldsymbol{M}^n)_{\alpha\gamma}
\end{aligned}$$

from which we find that

$$e^{i\lambda\hat{M}}\, c^\dagger_\gamma\, e^{-i\lambda\hat{M}} = \sum_\alpha \sum_{n=0}^{\infty} \frac{(i\lambda\boldsymbol{M})^n_{\alpha\gamma}}{n!} = \sum_\alpha c^\dagger_\alpha \left(e^{i\lambda\boldsymbol{M}}\right)_{\alpha\gamma} \tag{59}$$

the creation operators are transformed by the unitary matrix single-electron unitary $e^{i\lambda\boldsymbol{M}}$, i.e., $\hat{U}$ corresponds to a basis transformation in all operators, cf. (16). Thus, the right-hand-side of

(56) is again a Slater determinant formed from creation operators in the transformed basis. The annihilation operators transform accordingly as

$$e^{i\lambda\hat{M}}\, c_\gamma\, e^{-i\lambda\hat{M}} = \sum_\alpha \left(e^{i\lambda\boldsymbol{M}}\right)_{\gamma\alpha} c_\alpha\,. \tag{60}$$

Using this transformation, the variation of the energy expectation value can be written as

$$\begin{aligned} E(\lambda) &= \langle\Phi|e^{i\lambda\hat{M}}\,\hat{H}\,e^{-i\lambda\hat{M}}|\Phi\rangle \\ &= \langle\Phi|\hat{H}|\Phi\rangle + i\lambda\langle\Phi|[\hat{H},\,\hat{M}]|\Phi\rangle + \frac{(i\lambda)^2}{2}\langle\Phi|\big[[\hat{H},\,\hat{M}],\,\hat{M}\big]|\Phi\rangle + \cdots \end{aligned} \tag{61}$$

where each successive derivative in the power series expansion produces a commutator $[\,\cdot\,,\,\hat{M}]$ around those that were already present. The energy functional is stationary for Φ^{HF} when

$$\langle\Phi^{\mathrm{HF}}|[\hat{H},\,\hat{M}]|\Phi^{\mathrm{HF}}\rangle = 0 \tag{62}$$

for every hermitian single-electron operator $\hat{M}$. This condition is most easily understood when we work with orthonormal orbitals $\{|\varphi\rangle|\,n\}$ from which the Slater determinant can be constructed: $|\Phi^{\mathrm{HF}}\rangle = c_N^\dagger \cdots c_1^\dagger|0\rangle$. Then (62) is equivalent to

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

(actually $n \geq m$ suffices). Since

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

i.e., (62) is automatically fulfilled if both n and m are either occupied or unoccupied (virtual). This is not unexpected since transformations among the occupied or virtual orbitals, respectively, do not change the Slater determinant. The condition thus reduces to

$$\langle\Phi^{\mathrm{HF}}|c_m^\dagger c_n \hat{H}|\Phi^{\mathrm{HF}}\rangle = 0 \quad \forall\, m \in \{1,\ldots,N\},\, n \notin \{1,\ldots,N\}\,. \tag{63}$$

In other words, for the Hamiltonian there are no matrix elements between the stationary Slater determinant and determinants that differ from it in one orbital. The condition that for the Hartree-Fock determinant the Hamiltonian does not produce single excitations is called the Brillouin theorem.

Let us consider a Hamiltonian with one- and two-body terms

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

Then for each $n > N \geq m$ the singly-excited term

$$\left(T_{nm} + \sum_{m'\leq N}\left(U_{nm',mm'} - U_{nm',m'm}\right)\right) c_n^\dagger c_m|\Phi^{\mathrm{HF}}\rangle = 0$$

must vanish. This is the same condition as for a non-interacting Hamiltonian with matrix elements

$$F_{nm} = T_{nm} + \sum_{m'\leq N} \left(U_{nm',mm'} - U_{nm',m'm}\right). \tag{64}$$

$\boldsymbol{F}$ is called the Fock matrix. It depends, via the summation over occupied states, i.e., the density matrix, on the Slater determinant it is acting on. So we cannot simply diagonalize the single-electron matrix $\boldsymbol{F}$ since this will, in general, give a different determinant. Instead we need to find a Slater determinant for which $\boldsymbol{F}$ is diagonal (in fact, it is sufficient if it is block-diagonal in the occupied and virtual spaces). This is typically done by constructing a new Slater determinant from the N lowest eigenstates of $\boldsymbol{F}$ and iterating. Alternatively, we can use, e.g., steepest descent methods to minimize the expectation value directly or optimizing the one-body density matrix [9, 10]. At self-consistency the Fock matrix is diagonal with eigenvalues

$$\varepsilon_m^{\mathrm{HF}} = \left(T_{mm} + \sum_{m'\leq N} \underbrace{\left(U_{mm',mm'} - U_{mm',m'm}\right)}_{=:\varDelta_{mm'}}\right) = \left(T_{mm} + \sum_{m'\leq N} \varDelta_{mm'}\right) \tag{65}$$

and the Hartree-Fock energy is given by

$$\langle\varPhi^{\mathrm{HF}}|\hat{H}|\varPhi^{\mathrm{HF}}\rangle = \sum_{m\leq N}\left(T_{mm} + \sum_{m'<m} \varDelta_{mm'}\right) = \sum_{m\leq N}\left(T_{mm} + \frac{1}{2}\sum_{m'\leq N} \varDelta_{mm'}\right).$$

Removing an electron from the occupied orbital φ_a changes the energy expectation value by

$$\langle\varPhi^{\mathrm{HF}}_{a\,\mathrm{rem}}|\hat{H}|\varPhi^{\mathrm{HF}}_{a\,\mathrm{rem}}\rangle - \langle\varPhi^{\mathrm{HF}}|\hat{H}|\varPhi^{\mathrm{HF}}\rangle = -\left(T_{aa} + \frac{1}{2}\sum_{m'\leq N}\varDelta_{am'}\right) - \frac{1}{2}\sum_{m\neq a\leq N}\varDelta_{ma} = -\varepsilon_a^{\mathrm{HF}}. \tag{66}$$

When we assume that removing an electron does not change the orbitals much, which should be a good approximation in the limit of many electrons $N \gg 1$, this gives the ionization energy (Koopmans' theorem). Likewise, the energy expectation value of an excited Slater determinant $\varPhi^{\mathrm{HF}}_{a\to b}$ with an electron moved from orbital $a \leq N$ to orbital $b > N$ is

$$\varepsilon^{\mathrm{HF}}_{a\to b} = \langle\varPhi^{\mathrm{HF}}_{a\to b}|\hat{H}|\varPhi^{\mathrm{HF}}_{a\to b}\rangle - \langle\varPhi^{\mathrm{HF}}|\hat{H}|\varPhi^{\mathrm{HF}}\rangle = \varepsilon_b^{\mathrm{HF}} - \varepsilon_a^{\mathrm{HF}} - \varDelta_{ab} \tag{67}$$

It can be interpreted as the energy of a state with an electron-hole excitation, again neglecting relaxation effects. For the Coulomb interaction

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

so that the third term in (67) describes the attraction between the excited electron and the hole.

3.2.1 Homogeneous electron gas

Since the homogeneous electron gas is translation invariant it is natural to write the Hamiltonian (for states with homogeneous charge density) in the basis of plane waves $\langle r,\sigma|\boldsymbol{k},\sigma\rangle = \frac{1}{(2\pi)^{3/2}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$

$$\hat{H} = \sum_\sigma \int d\boldsymbol{k}\, \frac{|\boldsymbol{k}^2|}{2} c^\dagger_{\boldsymbol{k},\sigma} c_{\boldsymbol{k},\sigma} + \frac{1}{2(2\pi)^3} \sum_{\sigma,\sigma'} \int d\boldsymbol{k} \int d\boldsymbol{k}' \int' d\boldsymbol{q}\, \frac{4\pi}{|\boldsymbol{q}|^2} c^\dagger_{\boldsymbol{k}-\boldsymbol{q},\sigma} c^\dagger_{\boldsymbol{k}'+\boldsymbol{q},\sigma'} c_{\boldsymbol{k}',\sigma'} c_{\boldsymbol{k},\sigma}\,, \tag{68}$$

where the prime on the $\boldsymbol{q}$ integral means that $\boldsymbol{q} = 0$ is excluded since the homogeneous contribution to the Coulomb repulsion of the electrons is cancelled by its attraction with the homogeneous neutralizing background charge density. It seems reasonable to consider as an ansatz a Slater determinant $|\Phi_{k_F}\rangle$ of all plane wave states with momentum some Fermi momentum $|\boldsymbol{k}| < k_F$. The charge density for such a determinant follows, using the anticommutator of the field operator

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

from the diagonal of the density matrix

$$n_\sigma(\boldsymbol{r}) = \langle\Phi^{\mathrm{HF}}|\hat{\Psi}^\dagger_\sigma(\boldsymbol{r})\hat{\Psi}_\sigma(\boldsymbol{r})|\Phi^{\mathrm{HF}}\rangle = \int_{|\boldsymbol{k}|<k_F} d\boldsymbol{k}\, \left|\frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{(2\pi)^{3/2}}\right|^2 = \frac{k_F^3}{6\pi^2}\,. \tag{69}$$

It is independent of position, so $|\Phi_{k_F}\rangle$ looks like an appropriate ansatz for a homogeneous system. Moreover, it fulfills the stationarity condition (63): To create just a single excitation one of the creation operators in the Coulomb term of (68) must fill one of the annihilated states, i.e., $\boldsymbol{q} = 0$ or $\boldsymbol{q} = \boldsymbol{k} - \boldsymbol{k}'$. But this implies that the term is diagonal with $\boldsymbol{q} = 0$ giving the direct and $\boldsymbol{q} = \boldsymbol{k} - \boldsymbol{k}'$ the exchange contribution. Since the $\boldsymbol{q} = 0$ term is not present in the Hamiltonian, the eigenenergies of the Fock matrix are just the sum of the kinetic and the exchange terms

$$\varepsilon^{\mathrm{HF}}_{k,\sigma} = \frac{|\boldsymbol{k}|^2}{2} - \frac{1}{4\pi^2} \int_{|\boldsymbol{k}'|<k_F} d\boldsymbol{k}'\, \frac{1}{|\boldsymbol{k}-\boldsymbol{k}'|^2} = \frac{k^2}{2} - \frac{k_F}{\pi}\left(1 + \frac{k_F^2 - k^2}{2k_F k} \ln\left|\frac{k_F + k}{k_F - k}\right|\right) \tag{70}$$

It depends only on $k = |\boldsymbol{k}|$. Interestingly the slope of $\varepsilon^{\mathrm{HF}}_{\boldsymbol{k},\sigma}$ becomes infinite for $k \to k_F$. Thus, the density of states $D(\varepsilon_k)d\varepsilon = 4\pi k^2\, dk$, given by

$$D^{\mathrm{HF}}_\sigma(\varepsilon) = 4\pi k^2 \left(\frac{d\varepsilon^{\mathrm{HF}}_{k,\sigma}}{dk}\right)^{-1} = 4\pi k^2 \left(k - \frac{k_F}{\pi k}\left(1 - \frac{k_F^2 + k^2}{2k_F k} \ln\left|\frac{k_F + k}{k_F - k}\right|\right)\right)^{-1} \tag{71}$$

vanishes at the Fermi level (see Fig. 1). This is not quite what we expect from a respectable electron gas... It is clearly a defect of the Hartree-Fock approximation.

Instead of calculating the energy expectation value also directly in k-space, it is instructive to look at the exchange term in real space. To evaluate the electron-electron repulsion we need the

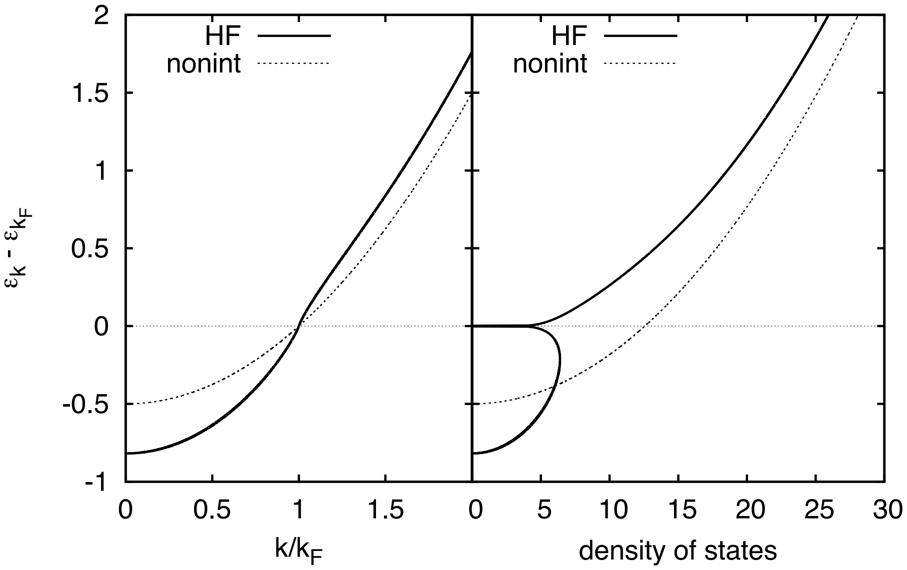

Fig. 1: *Hartree-Fock eigenvalues and density of states for the homogeneous solution* $|\Psi_{k_F}\rangle$ *of the homogeneous electron gas compared to non-interacting values.*

diagonal of the 2-body density matrix, which is given by (44) in terms of the one-body density matrix

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

where the one-body density matrix vanishes unless $\sigma' = \sigma$ where it is evaluated as in (69)

$$\begin{aligned} \Gamma_{\sigma\sigma}(\boldsymbol{r},\boldsymbol{r}') &= \langle\Phi_{k_F}|\hat{\Psi}^\dagger_{\sigma}(\boldsymbol{r})\hat{\Psi}_{\sigma}(\boldsymbol{r}')|\Phi_{k_F}\rangle \\ &= \int_{|\boldsymbol{k}|<k_F} d\boldsymbol{k}\,\frac{e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{(2\pi)^3} = \frac{1}{4\pi^2}\int_0^{k_F} dk\,k^2\int_{-1}^{1} d\cos\theta\, e^{ik|\boldsymbol{r}-\boldsymbol{r}'|\cos\theta} \\ &= \frac{k_F^3}{2\pi^2}\underbrace{\frac{\sin x - x\cos x}{x^3}}_{\xrightarrow{x\to 0} 1/3} = 3n_\sigma\,\frac{\sin x - x\cos x}{x^3} \end{aligned} \tag{72}$$

with $x = k_F|\boldsymbol{r}-\boldsymbol{r}'|$. Dividing the 2-body density matrix by n_σ^2 and subtracting the direct term (which is canceled by the contribution of the background charge) we obtain the exchange hole [10]

$$g_x(r,0) - 1 = -9\left(\frac{\sin k_F r - k_F r\cos k_F r}{(k_F r)^3}\right)^2. \tag{73}$$

It is shown in Fig. 2. The exchange energy per spin is then the Coulomb interaction of the charge density with its exchange hole

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

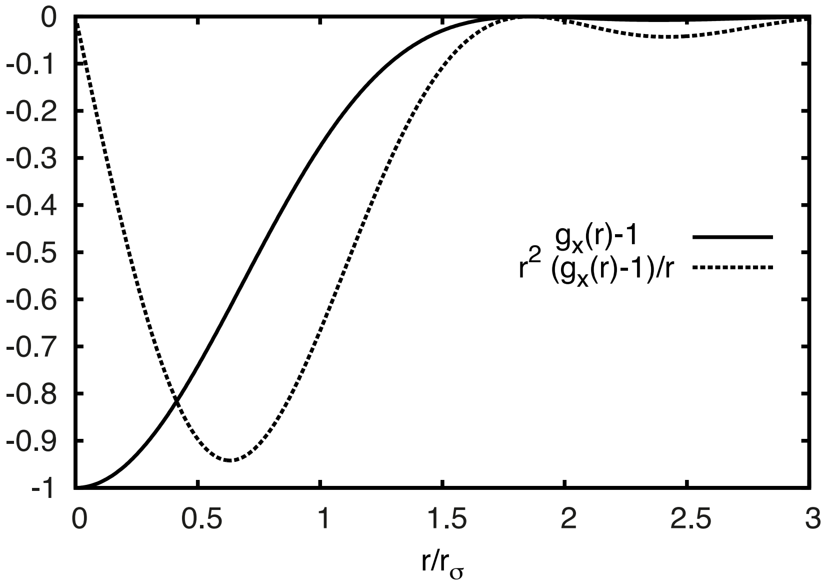

Fig. 2: *Exchange hole for a paramagnetic homogeneous electron gas in units of the spin Wigner-Seitz radius* $k_F\, r_\sigma = (9\pi/2)^{1/3}$. *In addition, the dotted line shows the contribution of the exchange hole to the Coulomb repulsion energy of Eq. (74).*

The exchange energy per electron of spin σ is thus

$$\varepsilon_x^\sigma = \frac{4\pi n_\sigma}{2}\int_0^\infty dr\, r^2\, \frac{g(r,0)-1}{r} = -\frac{9\cdot 4\pi n_\sigma}{2k_F^2}\underbrace{\int_0^\infty dx\, \frac{(\sin x - x\cos x)^2}{x^5}}_{=1/4} = -\frac{3k_F}{4\pi}\,. \qquad (74)$$

Together with the kinetic energy per electron of spin σ

$$\varepsilon_{\text{kin}}^\sigma = 4\pi\int_0^{k_F} dk\, k^2\, \frac{k^2}{2} \Big/ 4\pi\int_0^{k_F} dk\, k^2 = \frac{3k_F^2}{10} \qquad (75)$$

we obtain the total energy per electron

$$\varepsilon_{\text{HF}} = \frac{n_\uparrow(\varepsilon_{\text{kin}}^\uparrow + \varepsilon_x^\uparrow) + n_\downarrow(\varepsilon_{\text{kin}}^\downarrow + \varepsilon_x^\downarrow)}{n_\uparrow + n_\downarrow} = \frac{3(6\pi^2)^{2/3}}{10}\frac{n_\uparrow^{5/3} + n_\downarrow^{5/3}}{n} - \frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}\frac{n_\uparrow^{4/3} + n_\downarrow^{4/3}}{n}\,.$$

While the kinetic energy is lowest when $n_\uparrow = n_\downarrow$, exchange favors spin polarization. For reasonable electron densities the kinetic energy dominates, only at extremely low densities exchange dominates and the solution would be ferromagnetic.

A ferromagnetic Slater determinant would, of course, have two different Fermi momenta, $k_F^\uparrow \neq k_F^\downarrow$. It also would break the symmetry of the Hamiltonian under spin rotations. This is an example of how we can lower the energy expectation value by allowing Slater determinants that break a symmetry of the system. When we do not restrict the symmetry of the Slater determinant, the approach is called unrestricted Hartree-Fock. For the electron gas this approach actually gives Hartree-Fock states that even break translational symmetry, see, e.g., [11]

3.2.2 Hubbard model

As a simple example to illustrate the difference between restricted and unrestricted Hartree-Fock we consider the Hubbard model with two sites, $i = 1, 2$, between which the electrons can hop with matrix element $-t$ and with an on-site Coulomb repulsion U

$$\hat{H} = -t\sum_{\sigma}\left(c^{\dagger}_{2\sigma}c_{1\sigma} + c^{\dagger}_{1\sigma}c_{2\sigma}\right) + U\sum_{i\in\{1,2\}} n_{i\uparrow}n_{i\downarrow}\,. \tag{76}$$

The number of electrons N and the total spin projection S_z are conserved, so the Fock space Hamiltonian is block-diagonal in the Hilbert spaces with fixed number of up- and down-spin electrons $N_\uparrow$ and $N_\downarrow$ with dimensions

N	0	1		2			3		4	
$N_\uparrow$	0	1	0	2	1	0	2	1	2	
$N_\downarrow$	0	0	1	0	1	2	1	2	2	
dim	1	2	2	1	4	1	2	2	1	16

Exact solutions: The Hamiltonian for $N = N_\uparrow = 1$ is easily constructed. By introducing the basis states $c^{\dagger}_{1\uparrow}|0\rangle$ and $c^{\dagger}_{2\uparrow}|0\rangle$, we obtain the Hamiltonian matrix

$$\Big\langle 0\Big| \begin{pmatrix} c_{1\uparrow} \\ c_{2\uparrow} \end{pmatrix} \hat{H} \begin{pmatrix} c^{\dagger}_{1\uparrow} & c^{\dagger}_{2\uparrow} \end{pmatrix} \Big|0\Big\rangle = \begin{pmatrix} 0 & -t\,\langle 0|c_{1\uparrow}\, c^{\dagger}_{1\uparrow}c_{2\uparrow}\, c^{\dagger}_{2\uparrow}|0\rangle \\ -t\,\langle 0|c_{2\uparrow}\, c^{\dagger}_{2\uparrow}c_{1\uparrow}\, c^{\dagger}_{1\uparrow}|0\rangle & 0 \end{pmatrix} = \begin{pmatrix} 0 & -t \\ -t & 0 \end{pmatrix}.$$

This is easily diagonalized giving the familiar bonding and antibonding solution

$$|\varphi_\pm\rangle = \frac{1}{\sqrt{2}}\left(c^{\dagger}_{1\uparrow} \pm c^{\dagger}_{2\uparrow}\right)|0\rangle = c^{\dagger}_{\pm\uparrow}|0\rangle\,. \tag{77}$$

For $N_\uparrow = 1 = N_\downarrow$, we obtain a non-trivial interacting system

$$\Big\langle 0\Big| \begin{pmatrix} c_{1\uparrow}c_{2\downarrow} \\ c_{2\uparrow}c_{1\downarrow} \\ c_{1\uparrow}c_{1\downarrow} \\ c_{2\uparrow}c_{2\downarrow} \end{pmatrix} \hat{H} \begin{pmatrix} c^{\dagger}_{2\downarrow}c^{\dagger}_{1\uparrow} & c^{\dagger}_{1\downarrow}c^{\dagger}_{2\uparrow} & c^{\dagger}_{1\downarrow}c^{\dagger}_{1\uparrow} & c^{\dagger}_{2\downarrow}c^{\dagger}_{2\uparrow} \end{pmatrix} \Big|0\Big\rangle = \begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & -t & -t \\ -t & -t & U & 0 \\ -t & -t & 0 & U \end{pmatrix}. \tag{78}$$

To diagonalize the matrix, we transform the basis into linear combinations of covalent and ionic states

$$|\mathrm{cov}_\pm\rangle = \frac{1}{\sqrt{2}}\left(c^{\dagger}_{2\downarrow}c^{\dagger}_{1\uparrow} \pm c^{\dagger}_{1\downarrow}c^{\dagger}_{2\uparrow}\right)|0\rangle \tag{79}$$

$$|\mathrm{ion}_\pm\rangle = \frac{1}{\sqrt{2}}\left(c^{\dagger}_{1\downarrow}c^{\dagger}_{1\uparrow} \pm c^{\dagger}_{2\downarrow}c^{\dagger}_{2\uparrow}\right)|0\rangle \tag{80}$$

It is then easy to verify that $|\mathrm{cov}_-\rangle$ is an eigenstate with eigenvalue $\varepsilon_{\mathrm{cov}_-} = 0$ and that $|\mathrm{ion}_-\rangle$ has eigenenergy $\varepsilon_{\mathrm{ion}_-} = U$. The remaining two states mix

$$\begin{pmatrix} \langle\mathrm{cov}_+| \\ \langle\mathrm{ion}_+| \end{pmatrix} \hat{H} \begin{pmatrix} |\mathrm{cov}_+\rangle & |\mathrm{ion}_+\rangle \end{pmatrix} = \frac{1}{2}\left\{U - \begin{pmatrix} U & 4t \\ 4t & -U \end{pmatrix}\right\}. \tag{81}$$

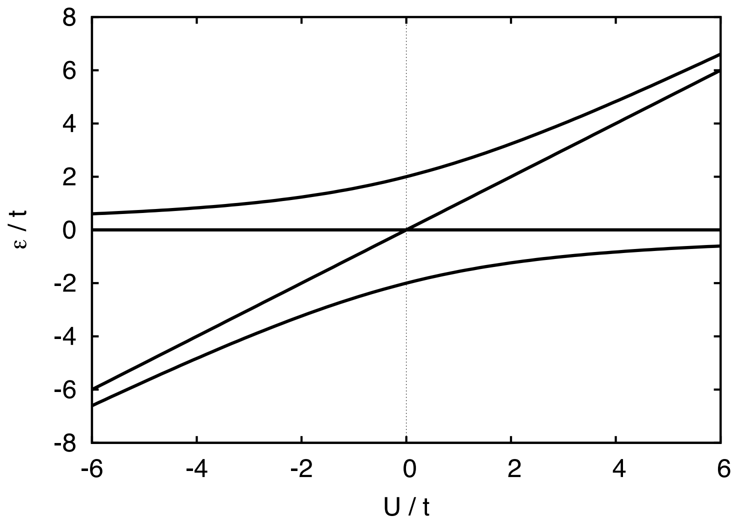

Fig. 3: *Spectrum of the two-site Hubbard model as a function of* U/t.

Rewriting the matrix

$$\begin{pmatrix} U & 4t \\ 4t & -U \end{pmatrix} = \sqrt{U^2+16t^2}\begin{pmatrix} \cos\Theta & \sin\Theta \\ \sin\Theta & -\cos\Theta \end{pmatrix}\,, \tag{82}$$

we find the ground state of the half-filled two-site Hubbard model

$$|\mathrm{gs}\rangle = \cos\Theta/2\,|\mathrm{cov}_+\rangle + \sin\Theta/2\,|\mathrm{ion}_+\rangle \tag{83}$$

$$= \frac{1}{\sqrt{2}}\left(\cos\tfrac{\Theta}{2}\,c^\dagger_{2\downarrow}c^\dagger_{1\uparrow} + \cos\tfrac{\Theta}{2}\,c^\dagger_{1\downarrow}c^\dagger_{2\uparrow} + \sin\tfrac{\Theta}{2}\,c^\dagger_{1\downarrow}c^\dagger_{1\uparrow} + \sin\tfrac{\Theta}{2}\,c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}\right)\,|0\rangle \tag{84}$$

with an energy of $\varepsilon_{\mathrm{gs}} = (U - \sqrt{U^2+16t^2})/2$. Without correlations ($U = 0 \rightsquigarrow \Theta = \pi/2$), all basis states have the same prefactor, so we can factorize the ground state, writing it as a product $c^\dagger_{+\downarrow}c^\dagger_{+\uparrow}|0\rangle$ of the operators defined in (77). For finite U this is no longer possible. In the strongly correlated limit $U \gg t$ ($\Theta \searrow 0$) the ground state becomes the maximally entangled state $|\mathrm{cov}_+\rangle$ and can not even approximately be expressed as a two-electron Slater determinant.

Hartree-Fock: We now want to see what Hartree-Fock can do in such a situation. Since the Hamiltonian is so simple, we can directly minimize the energy expectation value. The most general ansatz is a Slater determinant of an orbital $\varphi(\theta_\uparrow) = \sin(\theta_\uparrow)\,\varphi_1 + \cos(\theta_\uparrow)\,\varphi_2$ for the spin-up, and $\varphi(\theta_\downarrow) = \sin(\theta_\downarrow)\,\varphi_1 + \cos(\theta_\downarrow)\,\phi_2$ for the spin-down electron:

$$|\Phi(\theta_\uparrow,\theta_\downarrow)\rangle = \left(\sin(\theta_\downarrow)\,c^\dagger_{1\downarrow} + \cos(\theta_\downarrow)\,c^\dagger_{2\downarrow}\right)\,\left(\sin(\theta_\uparrow)\,c^\dagger_{1\uparrow} + \cos(\theta_\uparrow)\,c^\dagger_{2\uparrow}\right)\,|0\rangle\,. \tag{85}$$

The energy expectation value as a function of the parameters θ_σ is then

$$\begin{aligned}\langle\Phi(\theta_\uparrow,\theta_\downarrow)|\hat{H}|\Phi(\theta_\uparrow,\theta_\downarrow)\rangle &= -2t\,(\sin\theta_\uparrow\sin\theta_\downarrow + \cos\theta_\uparrow\cos\theta_\downarrow)\,(\cos\theta_\uparrow\sin\theta_\downarrow + \sin\theta_\uparrow\cos\theta_\downarrow) \\ &\quad + U\left(\sin^2\theta_\uparrow\sin^2\theta_\downarrow + \cos^2\theta_\uparrow\cos^2\theta_\downarrow\right)\,.\end{aligned} \tag{86}$$

If the Slater determinant respects the symmetry of the molecule under the exchange of sites (mirror symmetry of the H_2 molecule), it follows that the Hartree-Fock orbitals for both spins

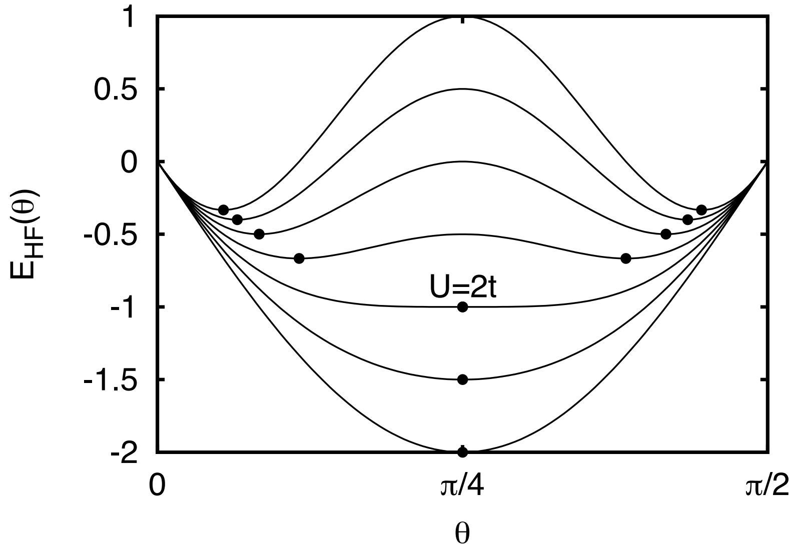

Fig. 4: *Energy expectation value for a Slater determinant $\Phi(\theta,\pi/2-\theta)$ for $U=0,\ t,\ 2t,\ \dots,\ 6t$. When $U \le 2t$ the minimum is at $\theta=\pi/4$. This is the Hartree-Fock solution with the bonding orbitals φ_+ occupied. For $U \ge 2t$, $\theta=\pi/4$ is still an extremal point (restricted Hartree-Fock solution), but an energy minimum is only attained when the symmetry is broken (unrestricted Hartree-Fock solution).*

are the bonding state φ_+ ($\theta=\pi/4$). This is the *restricted Hartree-Fock* solution. The corresponding energy is $E(\pi/4,\pi/4)=-2t+U/2$. The unrelaxed excited determinants are obtained by replacing occupied orbitals φ_+ with φ_-. Altogether we obtain the restricted Hartree-Fock spectrum

$$\begin{aligned} E(\ \ \pi/4,\ \ \pi/4) &= \ -2t+U/2 \\ E(\ \ \pi/4,-\pi/4) &= \qquad\quad U/2 \\ E(-\pi/4,\ \ \pi/4) &= \qquad\quad U/2 \\ E(-\pi/4,-\pi/4) &= \ \ \ 2t+U/2 \end{aligned} \tag{87}$$

Comparing to the energy for a state with both electrons of the same spin ($E=0$), we see that there is no spin-triplet, i.e., Hartree-Fock breaks the spin symmetry [12]. The states (87) are *spin-contaminated* [13]. Even worse, the Hartree-Fock ground state, and consequently all the states, are independent of U. The weight of the ionic states is always $1/2$, leading to an increase of the energy with $U/2$.

To avoid this, we can allow the Hartree-Fock solution to break the symmetry of the molecule (*unrestricted Hartree-Fock*), putting, e.g., more of the up-spin electron in the orbital on site 1 and more of the down-spin electron in orbital 2. In an extended system this corresponds to an antiferromagnetic spin-density wave. For $U<2t$ this does not lead to a state of lower energy. For larger U, however, there is a symmetry-broken ground state

$$\Phi_{\mathrm{UHF}}=\Phi(\theta,\pi/2-\theta)\ \ \text{with}\quad \theta(U)=\frac{\pi}{4}\pm\frac{1}{2}\arccos\left(\frac{2t}{U}\right). \tag{88}$$

Its energy is $E_{\mathrm{UHF}}=-2t^2/U$. Still there is no triplet state (spin contamination) and, for $U\to\infty$, the overlap with the true singlet ground state goes to $|\langle\Phi_{\mathrm{UHF}}|\Psi_-\rangle|^2=1/2$.

From Fig. 4 it might appear that there are just two degenerate unrestricted Hartree-Fock determinants. But, remembering that we can chose the spin quantization axis at will, we see that by rotating the spins by an angle α about the axis $\hat{n}$ (see App. C)

$$R_{\hat{n}}(\alpha) = e^{-i\hat{n}\cdot\vec{\sigma}\,\alpha/2} = \cos(\alpha/2) - i\sin(\alpha/2)\,\hat{n}\cdot\vec{\sigma}$$

we can produce a continuum of degenerate solutions $\hat{R}_{\hat{n}}(\alpha)|\Phi_{\mathrm{UHF}}\rangle$. As an example we consider the state we obtain when we rotate the spin quantization axis from the $\hat{z}$ into the $\hat{x}$ direction

$$R_{\hat{y}}(-\pi/2) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$$

which transforms the creation operators according to (16) as

$$\left(c^\dagger_{i\uparrow},\, c^\dagger_{i\downarrow}\right) R_{\hat{y}}(-\pi/2) = \left(\frac{1}{\sqrt{2}}\left(c^\dagger_{i\uparrow} - c^\dagger_{i\downarrow}\right),\, \frac{1}{\sqrt{2}}\left(c^\dagger_{i\uparrow} + c^\dagger_{i\downarrow}\right)\right).$$

The determinant (85) thus transforms to

$$\hat{R}_{\hat{y}}(-\pi/2)|\Phi(\theta_\uparrow,\theta_\downarrow)\rangle = \frac{1}{2}\Big(s_\downarrow(c^\dagger_{1\uparrow} + c^\dagger_{1\downarrow}) + c_\downarrow(c^\dagger_{2\uparrow} + c^\dagger_{2\downarrow})\Big)\Big(s_\uparrow(c^\dagger_{1\uparrow} - c^\dagger_{1\downarrow}) + c_\uparrow(c^\dagger_{2\uparrow} - c^\dagger_{2\downarrow})\Big)|0\rangle \tag{89}$$

where we introduced the abbreviations $s_\sigma = \sin\theta_\sigma$ and $c_\sigma = \cos\theta_\sigma$. Since the Hamiltonian (76) is invariant under spin rotations, $\hat{R}_{\hat{y}}(-\pi/2)\,\hat{H}\,\hat{R}^\dagger_{\hat{y}}(-\pi/2) = \hat{H}$, the energy expectation value of the rotated state is still given by (86).

Attractive Hubbard model For negative U allowing the spin orbitals to differ, $\Phi(\theta,\,\pi/2-\theta)$, does lower the energy expectation value. The minimum is always obtained for the restricted Hartree-Fock determinant $\Phi(\pi/4,\,\pi/4)$. In fact, for the attractive Hubbard model rather than breaking spin symmetry, we should try to break the charge symmetry: For $U < -2t$ the ansatz $\Phi(\theta,\theta)$ minimizes the energy for the two states $\theta(U) = \pi/4 \pm \arccos(-2t/U)$ with energy $E(U) = 2t^2/U + U$. Thus, the unrestricted Hartree-Fock ground state breaks the charge symmetry, i.e., is a charge-density wave state. On the other hand, looking back to (89) we see that $\Phi(\theta,\theta)$ is invariant under the spin rotation. This is actually true for any $\hat{R}_{\hat{n}}(\alpha)$ so that the unrestricted Hartree-Fock ground state of the attractive Hubbard model does not break spin symmetry.

It seems strange that for the attractive model we only find two unrestricted Hartree-Fock states, while for the repulsive model we have a continuum of states. To find the 'missing' states we consider a new kind of transformation that mixes creation and annihilation operators: When we exchange the role of the creation and annihilation operators for the up spins only, i.e.,

$$\tilde{c}^\dagger_{i\uparrow} = (-1)^i c_{i\uparrow} \quad \text{and} \quad \tilde{c}^\dagger_{i\downarrow} \to c^\dagger_{i\downarrow}, \tag{90}$$

the Hamiltonian (76) transforms into a two-site Hubbard model with the sign of U changed

$$\hat{H} = -t\sum_\sigma \left(\tilde{c}^\dagger_{2\sigma}\tilde{c}_{1\sigma} + \tilde{c}^\dagger_{1\sigma}\tilde{c}_{2\sigma}\right) - U\sum_{i\in\{1,2\}} \tilde{n}_{i\uparrow}\tilde{n}_{i\downarrow} + U(\tilde{n}_{1\downarrow} + \tilde{n}_{2\downarrow})\,. \tag{91}$$

Let us see what happens to the Slater determinant (85) when we apply the same transformation. In doing this, we have to remember that the vacuum state must vanish when acted on with an annihilator. For $|0\rangle$ this is no longer true for the transformed operators, but we can easily write down a state

$$|\tilde{0}\rangle = c^\dagger_{2\uparrow}c^\dagger_{1\uparrow}|0\rangle \tag{92}$$

that behaves as a suitable vacuum state: $\tilde{c}_{i\sigma}|\tilde{0}\rangle = 0$ and $\langle\tilde{0}|\tilde{0}\rangle$. We can then rewrite the transformed Slater determinant (85) as

$$\begin{aligned}
|\tilde{\Phi}(\theta_\uparrow,\theta_\downarrow)\rangle &= \Big(\sin(\theta_\downarrow)\,\tilde{c}^\dagger_{1\downarrow} + \cos(\theta_\downarrow)\,\tilde{c}^\dagger_{2\downarrow}\Big)\Big(\sin(\theta_\uparrow)\,\tilde{c}^\dagger_{1\uparrow} + \cos(\theta_\uparrow)\,\tilde{c}^\dagger_{2\uparrow}\Big)\,|\tilde{0}\rangle \\
&= \Big(\sin(\theta_\downarrow)\,c^\dagger_{1\downarrow} + \cos(\theta_\downarrow)\,c^\dagger_{2\downarrow}\Big)\Big(-\sin(\theta_\uparrow)\,c_{1\uparrow} + \cos(\theta_\uparrow)\,c_{2\uparrow}\Big)\,c^\dagger_{2\uparrow}c^\dagger_{1\uparrow}|0\rangle \\
&= \Big(\sin(\theta_\downarrow)\,c^\dagger_{1\downarrow} + \cos(\theta_\downarrow)\,c^\dagger_{2\downarrow}\Big)\Big(+\sin(\theta_\uparrow)\,c^\dagger_{2\uparrow} + \cos(\theta_\uparrow)\,c^\dagger_{1\uparrow}\Big)\,|0\rangle\;.
\end{aligned}$$

Thus, the transformation takes the unrestricted state $|\Phi(\theta,\pi/2-\theta)\rangle$ for the repulsive Hubbard model into the unrestricted state $|\Phi(\theta,\theta)\rangle$ for the attractive Hubbard model. Transforming the rotated state (89) in the same way, we find something remarkable:

$$\begin{aligned}
&\frac{1}{2}\Big(s_\downarrow(\tilde{c}^\dagger_{1\uparrow}+\tilde{c}^\dagger_{1\downarrow}) + c_\downarrow(\tilde{c}^\dagger_{2\uparrow}+\tilde{c}^\dagger_{2\downarrow})\Big)\Big(s_\uparrow(\tilde{c}^\dagger_{1\uparrow}-\tilde{c}^\dagger_{1\downarrow}) + c_\uparrow(\tilde{c}^\dagger_{2\uparrow}-\tilde{c}^\dagger_{2\downarrow})\Big)\,|\tilde{0}\rangle \\
&= \frac{1}{2}\Big(s_\downarrow(-c_{1\uparrow}+c^\dagger_{1\downarrow}) + c_\downarrow(c_{2\uparrow}+c^\dagger_{2\downarrow})\Big)\Big(s_\uparrow(-c_{1\uparrow}-c^\dagger_{1\downarrow}) + c_\uparrow(c_{2\uparrow}-c^\dagger_{2\downarrow})\Big)\,c^\dagger_{2\uparrow}c^\dagger_{1\uparrow}|0\rangle \\
&= \frac{1}{2}\Big((s_\downarrow c_\uparrow + c_\downarrow s_\uparrow)\big(c^\dagger_{1\downarrow}c^\dagger_{1\uparrow}+c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}\big)|0\rangle + 2\big(s_\downarrow s_\uparrow c^\dagger_{1\downarrow}c^\dagger_{2\uparrow} + c_\downarrow c_\uparrow c^\dagger_{2\downarrow}c^\dagger_{2\uparrow}\big)|0\rangle \\
&\qquad\quad + (s_\downarrow c_\uparrow - c_\downarrow s_\uparrow)\big(c^\dagger_{2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\uparrow}c^\dagger_{1\uparrow} - 1\big)|0\rangle \Big).
\end{aligned}$$

The energy expectation value of this state is by construction the same as for the charge-density state. For $\theta_\downarrow = \pi/2-\theta_\uparrow$ the new state has a uniform density, but the wave function no longer has a well-defined particle number, i.e., it breaks particle number conservation. It is still a product state in the transformed operators and vacuum, but it is a state in Fock space. States of this type are crucial for describing superconductivity.

3.3 BCS theory

Next we consider the BCS Hamiltonian

$$\hat{H}_{\text{BCS}} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}}\, c^\dagger_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}\sigma} - \sum_{\boldsymbol{k}\boldsymbol{k}'} G_{\boldsymbol{k}\boldsymbol{k}'}\, c^\dagger_{\boldsymbol{k}\uparrow}c^\dagger_{-\boldsymbol{k}\downarrow}c_{-\boldsymbol{k}'\downarrow}c_{\boldsymbol{k}'\uparrow} \tag{93}$$

with an attractive interaction between pairs of electrons of opposite spin and momentum (Cooper pairs). We now want to see if we can use the idea of product states in Fock space that we encountered for the attractive Hubbard model. To start, let us consider the determinant of plane wave states that we used for the homogeneous electron gas $|\Phi_{k_F}\rangle$. Since all states with momentum below k_F are occupied, we have

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

Thus $|\Phi_{k_F}\rangle$ behaves like a vacuum state for the transformed operators

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

Allowing the operators to mix, we can generalize this transformation to

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

The corresponding creation operators are obtained, of course, by taking the adjoint. Notice how states with $\boldsymbol{k}$ and $-\boldsymbol{k}$ are mixed. These Bogoliubov-Valatin operators fulfill the canonical anticommutation relations

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

when (the non-trivial anticommutators are $\{b_{\boldsymbol{k}\uparrow},\, b_{-\boldsymbol{k}\downarrow}\}$ and $\{b_{\boldsymbol{k}\sigma},\, b^\dagger_{\boldsymbol{k}\sigma}\}$)

$$u_k^2 + v_k^2 = 1\,. \tag{94}$$

A vacuum state for the new operators can be constructed from the generalized product state $\prod_{\boldsymbol{k}\sigma} b_{\boldsymbol{k}\sigma}|0\rangle$. Expanding the operators

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

and calculating the norm

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

we see from (94) that the BCS wavefunction

$$|\mathrm{BCS}\rangle = \prod_{\boldsymbol{k}} (u_k + v_k\, c^\dagger_{\boldsymbol{k}\uparrow} c^\dagger_{-\boldsymbol{k}\downarrow})\; |0\rangle \tag{95}$$

is the (normalized) vacuum for the Bogoliubov-Valatin operators.
To calculate physical expectation values we express the electron operators as

$$\begin{aligned} c_{\boldsymbol{k}\uparrow} &= u_k b_{\boldsymbol{k}\uparrow} + v_k b^\dagger_{-\boldsymbol{k}\downarrow} \\ c_{\boldsymbol{k}\downarrow} &= u_k b_{\boldsymbol{k}\downarrow} - v_k b^\dagger_{-\boldsymbol{k}\uparrow} \end{aligned}$$

The expectation value for the occupation of a plane wave state, e.g., is

$$\langle \mathrm{BCS}|\hat{n}_{\boldsymbol{k}\uparrow}|\mathrm{BCS}\rangle = \langle \mathrm{BCS}|(u_k b^\dagger_{\boldsymbol{k}\uparrow} + v_k b_{-\boldsymbol{k}\downarrow})(u_k b_{\boldsymbol{k}\uparrow} + v_k b^\dagger_{-\boldsymbol{k}\downarrow})|\mathrm{BCS}\rangle = v_k^2 = \langle \mathrm{BCS}|\hat{n}_{-\boldsymbol{k}\downarrow}|\mathrm{BCS}\rangle\,.$$

Unlike the electron gas Slater determinant $|\Phi_{k_F}\rangle$, where $n_{\boldsymbol{k}\sigma}$ is 1 below k_F and vanishes above, varying the parameter v_k in the BCS wave function allows us to get arbitrary momentum distributions $\langle n_{\boldsymbol{k}\sigma}\rangle$. Since the BCS wave function has contributions in all particle sectors with an even number of electrons, there are also less-conventional expectation values, e.g.,

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

When minimizing the energy expectation value, we have to introduce a chemical potential μ that is chosen to give the desired number of particles $N = \sum_{\boldsymbol{k}\sigma} v_k^2$. We get

$$\langle \mathrm{BCS}|\hat{H} - \mu\hat{N}|\mathrm{BCS}\rangle = \sum_{\boldsymbol{k}\sigma} (\varepsilon_{\boldsymbol{k}} - \mu)\, v_k^2 - \sum_{\boldsymbol{k},\boldsymbol{k}'} G_{\boldsymbol{k}\boldsymbol{k}'}\, u_k v_k u_{k'} v_{k'}\ . \tag{96}$$

Minimizing with respect to v_k (and remembering that $u_k = \sqrt{1 - v_k^2}$) we find the variational equations

$$4(\varepsilon_{\boldsymbol{k}} - \mu)\, v_k = 2 \sum_{\boldsymbol{k}'} G_{\boldsymbol{k}\boldsymbol{k}'} \left(u_k - \frac{v_k}{u_k} v_k \right) u_{k'} v_{k'}\ . \tag{97}$$

For simplicity we assume that $G_{\boldsymbol{k}\boldsymbol{k}'}$ is constant over a small range of $\boldsymbol{k}$ values around the Fermi surface and vanishes outside. We define

$$\varDelta := \sum_{\boldsymbol{k}'} G_{\boldsymbol{k}\boldsymbol{k}'}\, u_{k'} v_{k'} = G \sum_{\boldsymbol{k}:\text{close to FS}} u_k v_k \tag{98}$$

and obtain, squaring the variational equation and remembering that $1 - (u_k^2 + v_k^2)^2 = 0$,

$$4(\varepsilon_{\boldsymbol{k}} - \mu)^2 u_k^2 v_k^2 = (\varepsilon_{\boldsymbol{k}} - \mu)^2 \big(1 - (u_k^2 - v_k^2)^2\big) = \varDelta^2 (u_k^2 - v_k^2)$$

from which we get the momentum distribution

$$v_k^2 = \frac{1}{2} \left(1 - \frac{\varepsilon_{\boldsymbol{k}} - \mu}{\sqrt{(\varepsilon_{\boldsymbol{k}} - \mu)^2 + \varDelta^2}} \right) . \tag{99}$$

For $\varDelta = 0$ this is just the step function of a Fermi gas, for finite $\varDelta$ the transition is more smooth. We still have to determine the parameters μ and $\varDelta$. The chemical potential is fixed by

$$N = \sum_{\boldsymbol{k}} 2 v_k^2 = \sum_{\boldsymbol{k}} \left(1 - \frac{\varepsilon_{\boldsymbol{k}} - \mu}{\sqrt{(\varepsilon_{\boldsymbol{k}} - \mu)^2 + \varDelta^2}} \right) \tag{100}$$

while for $\varDelta$ we obtain from (98), solving (97) for $u_k v_k$ and summing over k, and using $u_k^2 - v_k^2 = 1 - 2v_k^2$

$$\varDelta = G \sum_{\boldsymbol{k}} u_k v_k = \frac{G}{2} \sum_{\boldsymbol{k}} \frac{\varDelta (u_k^2 - v_k^2)}{\varepsilon_{\boldsymbol{k}} - \mu} = \varDelta \frac{G}{2} \sum_{\boldsymbol{k}} \frac{1}{\sqrt{(\varepsilon_k - \mu)^2 + \varDelta^2}} \tag{101}$$

the self-consistent gap equation for $\varDelta$.

To see that $\varDelta$ is indeed a gap, consider the (unrelaxed) quasi-electron states

$$|\boldsymbol{k}\uparrow\rangle = \frac{1}{u_k} c^\dagger_{\boldsymbol{k}\uparrow} |\mathrm{BCS}\rangle = b^\dagger_{\boldsymbol{k}\uparrow} |\mathrm{BCS}\rangle. \tag{102}$$

Adding an electron of momentum $\boldsymbol{k}$ destroys its Cooper pair, changing $\langle n_{\boldsymbol{k}\uparrow} + n_{\boldsymbol{k}\downarrow}\rangle$ from $2v_k^2$ to 1 and removing the interaction of the pair with all others:

$$\begin{aligned} \langle \boldsymbol{k}\uparrow|\hat{H} - \mu\hat{N}|\boldsymbol{k}\uparrow\rangle - \langle \mathrm{BCS}|\hat{H} - \mu\hat{N}|\mathrm{BCS}\rangle &= (\varepsilon_{\boldsymbol{k}} - \mu)\,(1 - 2v_k^2) + 2\varDelta\, u_k v_k \\ = (\varepsilon_{\boldsymbol{k}} - \mu)\,(1 - 2v_k^2) + \frac{\varDelta^2}{\varepsilon_{\boldsymbol{k}} - \mu}(u_k^2 - v_k^2) &= \operatorname{sgn}(\varepsilon_{\boldsymbol{k}} - \mu)\,\sqrt{(\varepsilon_{\boldsymbol{k}} - \mu)^2 + \varDelta^2}. \end{aligned}$$

For $\varDelta =$ we recover Koopmans' Hartree-Fock result, while for $\varDelta > 0$ a gap opens around the Fermi level. Fig. 5 compares the quasi-electron dispersion and the corresponding density of states for the two cases.

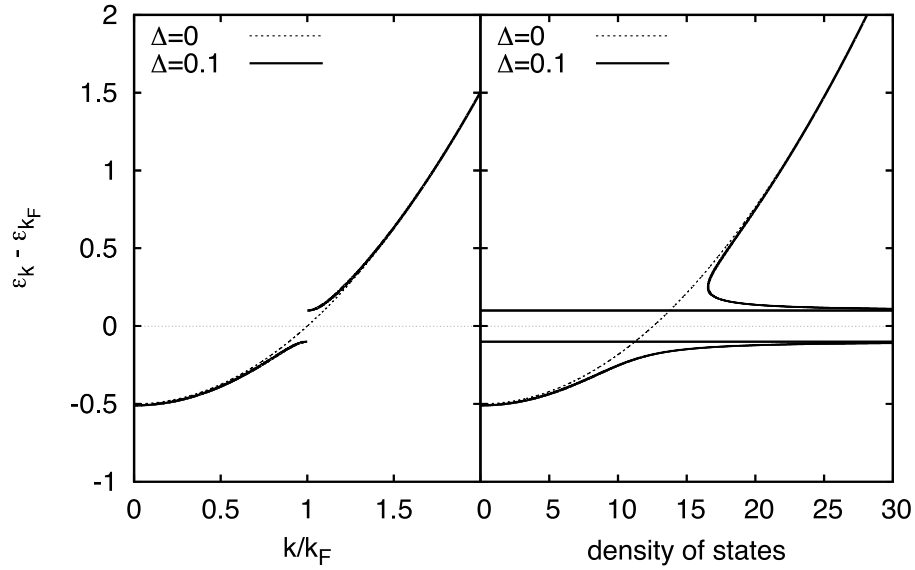

Fig. 5: *Quasi-electron energy and density of states for the BCS state with and without gap.*

4 Conclusion

We have seen that second quantization is an remarkable useful formalism. With just a few simple rules for the creation and annihilation operators and the corresponding vacuum, it converts dealing with many-electron states to straightforward algebraic manipulations. Moreover it is naturally suited for performing calculations in variational spaces spanned by a finite basis of orbitals. But its advantages go beyond a mere simplification. By abstracting from the coordinate representation, it allows us to express many-body operators in a way that is independent of the number of electrons. Because of this it becomes possible to consider Fock-space wave functions which do not have a definite number of electrons. This allows us to consider unrestricted mean-field states that not only break spatial or spin symmetries but also particle conservation. This additional freedom allows us to extend the concept of a Slater determinant to product states in Fock space, an example of which is the BCS wave function.

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A Basis orthonormalization

A general one-electron basis spanned by functions $|\chi_n\rangle$ will have an overlap matrix

$$S_{nm} = \langle\chi_n|\chi_m\rangle$$

that is positive definite (and hence invertible) and hermitian. The completeness relation is

$$\mathbb{1} = \sum_{k,l} |\chi_k\rangle (S^{-1})_{kl} \langle\chi_l| \,.$$

While we can work directly with such a basis, it is often more convenient to have an orthonormal basis, so that we do not have to deal with the overlap matrices in the definition of the second quantized operators and in the generalized eigenvalue problem.
To orthonormalize the basis $\{|\chi_n\rangle\}$, we need to find a basis transformation $\boldsymbol{T}$ such that

$$|\varphi_n\rangle := \sum_m |\chi_m\rangle\, T_{mn} \qquad \text{with} \quad \langle\varphi_n|\varphi_m\rangle = \delta_{mn} \,.$$

This implies that $\boldsymbol{T}^\dagger \boldsymbol{S} \boldsymbol{T} = \mathbb{1}$, or equivalently $\boldsymbol{S}^{-1} = \boldsymbol{T}\boldsymbol{T}^\dagger$. This condition does not uniquely determine $\boldsymbol{T}$. In fact there are many orthonormalization techniques, e.g., Gram-Schmidt orthonormalization or Cholesky decomposition.
Usually we will have chosen the basis functions $|\chi_n\rangle$ for a physical reason, e.g., atomic orbitals, so that we would like the orthonormal basis functions to be as close to the original basis as possible, i.e, we ask for the basis transformation $\boldsymbol{T}$ that minimizes

$$\begin{aligned}\sum_n \big\|\, |\varphi_n\rangle - |\chi_n\rangle \,\big\|^2 &= \sum_n \Big\| \sum_m |\chi_m\rangle (T_{mn} - \delta_{mn}) \Big\|^2 \\ &= \mathrm{Tr}\,(\boldsymbol{T}^\dagger - \mathbb{1})\, \boldsymbol{S}\, (\boldsymbol{T} - \mathbb{1}) \\ &= \mathrm{Tr}\,(\underbrace{\boldsymbol{T}^\dagger \boldsymbol{S} \boldsymbol{T}}_{=\mathbb{1}} - \boldsymbol{T}^\dagger \boldsymbol{S} - \boldsymbol{S}\boldsymbol{T} + \boldsymbol{S}) \,.\end{aligned}$$

Given an orthonormalization $\boldsymbol{T}$, we can obtain any other orthonormalization $\tilde{\boldsymbol{T}}$ by performing a unitary transformation, i.e., $\tilde{\boldsymbol{T}} = \boldsymbol{T}\boldsymbol{U}$. Writing $\boldsymbol{U} = \exp(i\lambda \boldsymbol{M})$, we obtain the variational condition

$$0 \overset{!}{=} \mathrm{Tr}\,(+i\boldsymbol{M}\boldsymbol{T}^\dagger \boldsymbol{S} - i\boldsymbol{S}\boldsymbol{T}\boldsymbol{M}) = i\,\mathrm{Tr}\,(\boldsymbol{T}^\dagger \boldsymbol{S} - \boldsymbol{S}\boldsymbol{T})\boldsymbol{M},$$

which is fulfilled for $\boldsymbol{S}\boldsymbol{T} = \boldsymbol{T}^\dagger \boldsymbol{S}$, i.e., $\boldsymbol{S}\boldsymbol{T}^2 = \boldsymbol{T}^\dagger \boldsymbol{S}\boldsymbol{T} = \mathbb{1}$. The second variation at $\boldsymbol{T} = \boldsymbol{S}^{-1/2}$

$$\frac{1}{2}\,\mathrm{Tr}\,(\boldsymbol{M}^2 \boldsymbol{S}^{1/2} + \boldsymbol{S}^{1/2} \boldsymbol{M}^2) > 0$$

is positive, since $\boldsymbol{S}$ and the square of the hermitian matrix $\boldsymbol{M}$ are both positive definite. Hence the Löwdin symmetric orthogonalization [14]

$$\boldsymbol{T}_{\text{Löwdin}} = \boldsymbol{S}^{-1/2}$$

minimizes the modification of the basis vectors.

B Some useful commutation relations

Expression of commutators of products of operators can be derived by adding and subtracting terms that differ only in the position of one operator, e.g.,

$$\begin{aligned}
[A_1A_2\cdots A_N,\,B] = &\ \ A_1A_2\cdots A_N B - BA_1A_2\cdots A_N \\
= &\ \ A_1A_2\cdots A_N B - A_1A_2\cdots BA_N \\
&+ A_1A_2\cdots BA_N - A_1\cdots BA_{N-1}A_N \\
&+ \qquad\qquad\quad \cdots \\
&+ A_1BA_2\cdots A_N - BA_1A_2\cdots A_N \\
= &\sum_i A_1\cdots A_{i-1}\,[A_i,\,B]\,A_{i+1}\cdots A_N
\end{aligned}$$

The following special cases are particularly useful

$$\begin{aligned}
[AB,\,C] &= A\,[B,\,C] + [A,\,C]\,B \\
&= A\{B,\,C\} - \{A,\,C\}B
\end{aligned}$$

$$\begin{aligned}
[A,\,BC] &= B\,[A,\,C] + [A,\,B]\,C \\
&= [A,\,B]\,C + B\,[A,\,C] \\
&= \{A,\,B\}C - B\{A,\,C\}
\end{aligned}$$

$$\begin{aligned}
[AB,\,CD] &= A\,[B,\,C]\,D + AC\,[B,\,D] + [A,C]\,DB + C\,[A,\,D]\,B \\
&= A\{B,\,C\}D - AC\{B,\,D\} + \{A,C\}DB - C\{A,\,D\}B
\end{aligned}$$

Important examples are

$$\begin{aligned}
\left[c_i^\dagger c_j,\,c_\gamma^\dagger\right] &= \ \ c_i^\dagger\delta_{j,\gamma} \\
\left[c_i^\dagger c_j,\,c_\gamma\right] &= -c_j\delta_{i,\gamma}
\end{aligned}$$

For the commutator of products of creation and annihilation operators appearing in one- and two-body operators we find

$$\left[c_i^\dagger c_j,\,c_\alpha^\dagger c_\beta\right] = \left[c_i^\dagger c_j,\,c_\alpha^\dagger\right]c_\beta + c_\alpha^\dagger\left[c_i^\dagger c_j,\,c_\beta\right] = \langle j|\alpha\rangle\,c_i^\dagger c_\beta - \langle\beta|i\rangle\,c_\alpha^\dagger c_j$$

and

$$\left[c_i^\dagger c_j^\dagger c_k c_l,\,c_\alpha^\dagger c_\beta\right] = \langle l|\alpha\rangle\,c_i^\dagger c_j^\dagger c_k c_\beta + \langle k|\alpha\rangle\,c_i^\dagger c_j^\dagger c_\beta c_l - \langle\beta|j\rangle\,c_i^\dagger c_\alpha^\dagger c_k c_l - \langle\beta|i\rangle\,c_\alpha^\dagger c_j^\dagger c_k c_l$$

C Pauli matrices and spin rotations

The Pauli or spin matrices are defined as

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

They are hermitian, i.e. $\sigma_i^\dagger = \sigma_i$, and $\sigma_i^2 = 1$. Therefore their eigenvalues are ± 1. The eigenvectors of σ_z are $|m_z\rangle$, $m_z = \pm 1$:

$$|+1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |-1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} .$$

For these vectors we find

$$\sigma_x|\,m_z\rangle = |\,-m_z\rangle \quad \sigma_y|\,m_z\rangle = im_z|\,-m_z\rangle \quad \sigma_z|\,m_z\rangle = m_z|\,m_z\rangle.$$

The products of the Pauli matrices are $\sigma_x\,\sigma_y = i\sigma_z$, where the indices can be permuted cyclically. From this follows for the commutator

$$[\sigma_x, \sigma_y] = 2i\sigma_z$$

while the anticommutator vanishes:

$$\{\sigma_x, \sigma_y\} = 0$$

Finally a rotation by an angle α about the axis $\hat{n}$ changes the spin matrices

$$R_{\hat{n}}(\alpha) = e^{-i\hat{n}\cdot\vec{\sigma}\,\alpha/2} = \cos(\alpha/2) - i\sin(\alpha/2)\,\hat{n}\cdot\vec{\sigma}\,.$$

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