2 Many-Electron States

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1   Indistinguishable particles

Everyday experience tells us that no two objects are the same. We can always find some properties in which they differ. We can even tell identical twins apart, if only we know them well enough: their characteristic traits give them individuality. It has therefore been argued that objects that cannot be distinguished must be identical, as Leibnitz did with his Principle of the Identity of Indiscernibles [1]. We might, however, imagine a replicator that could produce a perfect clone that is identical to the original in every respect. Still, being material objects, original and clone cannot be at the same place at the same time. So even then we could tell original and clone apart by closely following their trajectory in space. This is, of course, only possible in a classical setting. Quantum mechanically, our knowledge of the actual position is limited by the uncertainty principle.

While the idea of identical clones sounds like science fiction, it is standard fare in modern physics: with the discovery of the periodic table it was realized that all materials are built from a small set of different types of atoms, the elementary particles of chemistry. The notion of elementary particle seems, however, to depend on the energy range of interest. While from a chemist's point of view all atoms of a given element are identical, probing the atom at higher energies, we can actually find an internal structure, allowing us to distinguish atoms of the same type but in different excited states [2]. Probing at even higher energies, it turns out that atoms are built of more elementary particles: electrons and the nuclei. These are the elementary particles of condensed-matter physics and quantum chemistry. At still higher energies the nuclei turn out to be built of protons and neutrons, which at even higher energies appear to be built of *up* and *down* quarks.

The elementary particle we will mainly be concerned with here is the electron. For a system of two electrons we can write the wave function as $\Psi(x_1, x_2)$, where x_1 are the degrees of freedom, e.g., position and spin, of the first electron, and x_2 those of the second. As indistinguishable particles, the labeling as first and second electron is of course arbitrary, and we can ask how the wave function changes when we exchange the labels, putting the first electron at x_2 and the second at x_1. Such a reordering is performed by the permutation operator P:

$$P\Psi(x_1, x_2) = \Psi(x_2, x_1).$$

Indistinguishability implies that the observables do not change under a relabeling of the particles. This is true, in particular, for the probability density: $|\Psi(x_1, x_2)|^2 = |\Psi(x_2, x_1)|^2$, i.e.,

$$P\Psi(x_1, x_2) = e^{i\varphi}\Psi(x_1, x_2) \tag{1}$$

with some phase φ. When permuting twice gives the identity, $P^2 = \mathbb{1}$, then $e^{2i\varphi} = 1$, i.e., φ can only take two different values: $\varphi = 2\pi$, meaning that the wave function does not change (*symmetric*), or $\varphi = \pi$, which means that it changes sign (*antisymmetric*) under the permutation P. These are the irreducible representations of the permutation group. A particular consequence of antisymmetry is that for $\Psi(x_1, x_2 \to x_1) = 0$, i.e., the two particles can never be found at the same place. This is the Pauli principle.
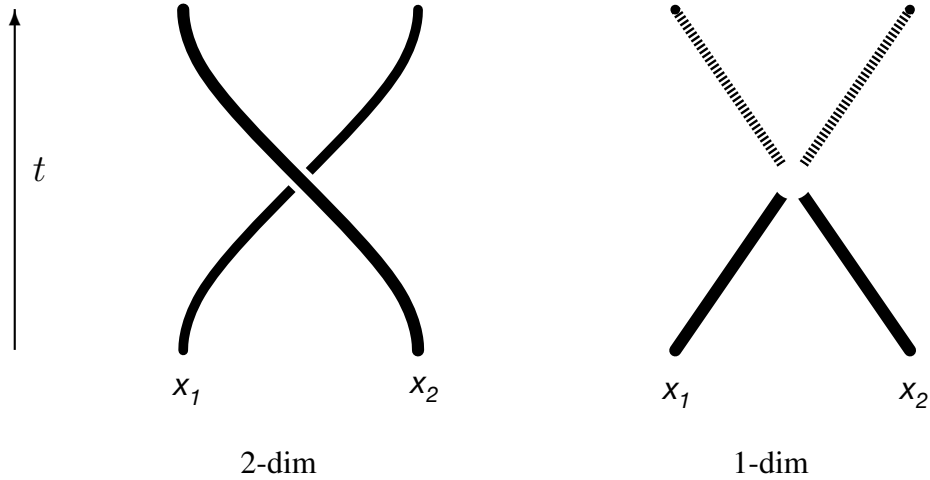
Fig. 1: *Permutation of particles: In 3-dimensional space the permutation is independent of the path along which the particles are exchanged. In 2-dimensional space it matters how the exchange paths wind around each other, giving rise to the braid group and fractional statistics. In 1-dimension, particles have to pass through each other in order to exchange their positions.*

The definition of indistinguishability is that no experiment can distinguish one particle from the other. Consequently, observables involving indistinguishable particles must remain unchanged when the particles are relabeled, or, more technically, they must commute with all possible permutations of the particles. This applies, in particular, to the Hamiltonian: $[P, H] = 0$. This implies that the symmetric and antisymmetric components of the many-body wave function are not mixed by the Hamiltonian: if the initial wave function is symmetric/antisymmetric, this does not change under time evolution.

There is an intriguing connection between the spin of the indistinguishable particles and the symmetry of their many-body wave function: for particles with integer spin (bosons) the wave function is symmetric under particle permutations, for fermions (half-integer spin) the wave function is antisymmetric. In non-relativistic quantum mechanics this *spin-statistics connection* is incorporated *ad hoc* via the initial conditions. In relativistic field-theory the connection between spin and statistics can be derived under fairly general assumptions on the axioms of the theory [3, 4]. For popular accounts, see [5, 6]. More recently there have been efforts to establish the spin-statistics connection in non-relativistic quantum mechanics. The basic idea of the approach is to perform the permutation of particles along a smooth path, where the spin picks up a geometric phase φ [7].

The concept of permuting particles by moving them along paths is also vital for understanding the statistics in lower-dimensional systems. Let us permute two particles by moving particle one along path $\gamma_1(t)$ from $\gamma_1(0) = x_1$ to $\gamma_1(1) = x_2$ and the other particle along $\gamma_2(t)$ from x_2 to x_1. If we call this operation P_γ, then P_γ^2 is given by moving particle one first along $\gamma_1(t)$ from x_1 to x_2 and then along $\gamma_2(t)$ from x_2 back to x_1 and likewise for the other particle. In three and higher dimensions these combined paths can be continuously deformed into the paths $\iota_1(t) = x_1$ and $\iota_2(t) = x_2$, which correspond to not moving the particles at all, i.e., the identity. Since the paths are homotopic, $P_\gamma^2 = \mathbb{1}$, as assumed above. In two dimensions this is not the

case. Let us assume the two paths $\gamma_1(t)$ and $\gamma_2(t)$ that exchange the particles wind around each other in clockwise direction as shown in Fig. 1. Applying this operation a second time, we obtain paths winding around each other twice to restore the original order of particles. These are however not homotopic to the paths corresponding to the identity $\mathbb{1}$, as deforming $\gamma_1(t)$ and $\gamma_2(t)$ into ι_1 and ι_2 would involve passing the curves through one another. Thus in two dimensions P_γ^2 need not be the identity and thus there is no restriction on the phase φ in (1). Since any phase is allowed, particles with such statistics are called anyons [8]. They appear, e.g., as quasiparticles in the fractional quantum Hall effect.

In one dimension two particles would have to pass through each other to exchange their positions. Therefore particles that cannot be at the same position, as is true for fermions, cannot exchange their positions. Then configuration space splits into equivalent parts, each with a specific ordering of the particles, separated from each other by nodes in the wave function where the coordinates of at least two particles agree. In each of these nodal pockets the ground state wave function is non-vanishing [9]. This is what makes many one-dimensional systems solvable [10].

1.1 Symmetric and antisymmetric wave functions

The (anti)symmetry of a many-body wave function has profound effects on the physical properties of the system. This can already be seen for a simple system of two particles, with one particle in a state $\varphi_a(x)$ and the other in state $\varphi_b(x)$. When the particles are distinguishable the many-body wave function could be

$$\Psi_{12}(x_1, x_2) = \varphi_a(x_1)\varphi_b(x_2) \quad \text{or} \quad \Psi_{21}(x_1, x_2) = \varphi_b(x_1)\varphi_a(x_2) \ . \tag{2}$$

For indistinguishable particles the wave functions is (anti)symmetric

$$\Psi_\pm(x_1, x_2) = \frac{1}{\sqrt{2}}\big(\Psi_{12}(x_1, x_2) \pm \Psi_{21}(x_1, x_2)\big) \ . \tag{3}$$

We can then calculate the expectation value of the squared distance

$$\big\langle (x_1 - x_2)^2 \big\rangle = \big\langle x_1^2 \big\rangle + \big\langle x_2^2 \big\rangle - 2 \big\langle x_1 x_2 \big\rangle \ . \tag{4}$$

For wave function Ψ_{12}, assuming that the single-electron states are normalized, we obtain

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

Giving the expectation value in terms of single-electron expectation values

$$\big\langle (x_1 - x_2)^2 \big\rangle_{12} = \big\langle x^2 \big\rangle_a + \big\langle x^2 \big\rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \ . \tag{5}$$

Due to the symmetry $(x_1 - x_2)^2 = (x_2 - x_1)^2$ we obtain the same expectation value for Ψ_{21}. For indistinguishable particles additional cross terms appear in the expectation value of an operator M

$$\langle M \rangle_\pm = \frac{1}{2}\Big(\langle M \rangle_{12} \pm \langle \Psi_{12} | M | \Psi_{21} \rangle \pm \langle \Psi_{21} | M | \Psi_{12} \rangle + \langle M \rangle_{21} \Big) \ . \tag{6}$$
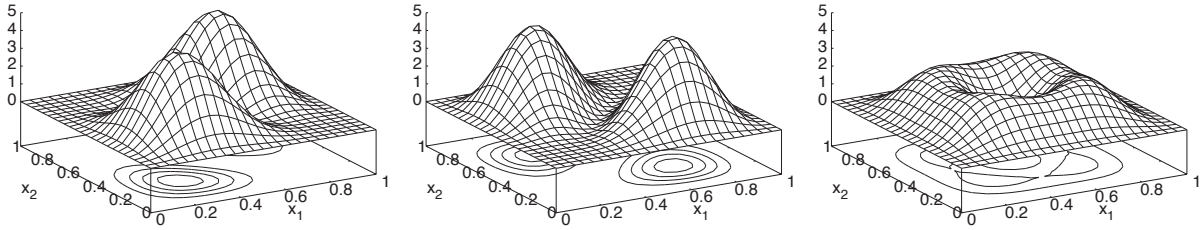
Fig. 2: *Probability distribution $|\Psi(x_1, x_2)|^2$ for two identical particles in a one-dimensional infinite potential well with one particle in the ground and the other in the first excited state. For the symmetric wave function, shown on the left, the probability of finding the electrons is largest on the line $x_1 = x_2$, for the antisymmetric wave function, shown in the centre, the probability vanishes there. For comparison, the right-most plot shows the probability distribution for independent particles.*

For observables involving only one coordinate like $M = x_1^2$, and similarly for x_2^2, these terms are of the form

$$\langle \Psi_{12} | x_1^2 | \Psi_{21} \rangle = \int dx_1 \, x_1^2 \, \overline{\varphi_a(x_1)} \varphi_b(x_1) \int dx_2 \, \overline{\varphi_b(x_2)} \varphi_a(x_2) \,, \tag{7}$$

which vanishes if the two states φ_a and φ_b are orthogonal. For operators like $M = x_1 x_2$ involving both coordinates they do not vanish, even for orthogonal states

$$\langle \Psi_{12} | x_1 x_2 | \Psi_{21} \rangle = \int dx_1 \, x_1 \, \overline{\varphi_a(x_1)} \varphi_b(x_1) \int dx_2 \, x_2 \, \overline{\varphi_b(x_2)} \varphi_a(x_2) = \langle x \rangle_{ab} \cdot \overline{\langle x \rangle}_{ab} \,. \tag{8}$$

These non-vanishing cross terms are called exchange terms. They make expectation values for symmetric and antisymmetric wave functions different. In the present case

$$\left\langle (x_1 - x_2)^2 \right\rangle_\pm = \left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b - 2 \left(\langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2 \right) \tag{9}$$

we see that the exchange terms decrease (increase) the expectation value of the squared distance by $2|\langle x \rangle_{ab}|^2$ for symmetric (antisymmetric) wave functions compared to the result for distinguishable particles. I.e., indistinguishable fermions tend to avoid each other while bosons tend to move closer together. For two identical particles in a one-dimensional box this tendency is readily apparent from the probability density $|\Psi(x_1, x_2)|^2$ shown in Fig. 2.

The effect of (anti)symmetry thus has to do with the overlap of the of the single-particle states that are involved. When this overlap vanishes for some reason, the symmetry of the wave function makes no difference. An extreme example is two electrons that are strictly localized in non-overlapping regions in space. In this case all integrals of the type (8) vanish, and there is no observable to distinguish an (anti)symmetric from a non-symmetrized state. This makes sense, since their localization in different regions of space makes them actually distinguishable. Such a situation is, of course, never perfectly realized. And in principle we would have to antisymmetrize the states of all electrons in the universe. Except for the rare case that we have sent an electron of an entangled pair to our far-away friend Bob, it is, however, safe to assume

that the electrons on the moon have negligible overlap with those in our (terrestrial) laboratory. We can then consider them distinguishable from those in our experiment, so that we need only antisymmetrize the wave function with respect to the electrons in our apparatus.

Often we have a similar situation where we can use the spin to tell electrons apart: When the Hamiltonian of our system does not affect the spin $[\vec{S}, H] = 0$, and we are only interested in observables that commute with the spin, we can distinguish two types of electrons by their spin direction S_z. In that case we need not antisymmetrize all electrons, but only the spin-up and the spin-down electrons separately. This is a typical example of how quantum numbers that are conserved in the processes we are interested in make can elementary particles distinguishable. This is how the concept of elementary particle becomes dependent on what energy scale we are interested in.

2   Reduced density matrices

By definition, observables on an N-particle Hilbert space that do not distinguish between the particles must be symmetric under particle permutations. For example, a single-particle operator $M(x)$ takes the form $\sum_{i=1}^{N} M(x_i)$ in the N-particle Hilbert space. We can write a general operator as a sum of n-particle operators

$$
\begin{aligned}
M(\mathbf{x}) &= M_0 + \sum_i M_1(x_i) + \frac{1}{2!} \sum_{i \neq j} M_2(x_i, x_j) + \frac{1}{3!} \sum_{i \neq j \neq k} M_3(x_i, x_j, x_k) + \cdots \quad (10) \\
&= M_0 + \sum_i M_1(x_i) + \sum_{i<j} M_2(x_i, x_j) + \sum_{i<j<k} M_3(x_i, x_j, x_k) + \cdots , \quad (11)
\end{aligned}
$$

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, e.g. $M_2(x_i, x_i)$ only acts on a single coordinate and should be included in M_1.

To evaluate expectation values it is useful to introduce *density matrices* [11]

$$
\Gamma^{(p)}(x'_1, \ldots, x'_p; x_1, \ldots, x_p) :=
$$
$$
\binom{N}{p} \int dx_{p+1} \cdots dx_N \, \overline{\Psi(x'_1, \ldots, x'_p, x_{p+1}, \ldots, x_N)} \, \Psi(x_1, \ldots, x_p, x_{p+1}, \ldots, x_N) , \quad (12)
$$

where we integrate over all except p coordinates of the normalized N-particle wave function Ψ. When $x = (r, \sigma)$ denotes the coordinate and the spin of the particle, the integral over x means integration over space and summation over spin. The density matrices are obviously related by

$$
\Gamma^{(p)}(x'_1, \ldots, x'_p; x_1, \ldots, x_p) = \frac{p+1}{N-p} \int dx_{p+1} \Gamma^{(p+1)}(x'_1, \ldots, x'_p, x_{p+1}; x_1, \ldots, x_p, x_{p+1}) \quad (13)
$$

They are Hermitean, e.g. $\Gamma^{(2)}(x'_1, x'_2; x_1, x_2) = \overline{\Gamma^{(2)}(x_1, x_2; x'_1, x'_2)}$, and (anti)symmetric in each set of their arguments, e.g. $\Gamma^{(2)}(x'_1, x'_2; x_1, x_2) = -\Gamma^{(2)}(x'_2, x'_1; x_1, x_2)$. The p-body density matrix contains all the information needed for evaluating expectation values of operators up to

order p. The expectation value of a single-electron operator, e.g., the expectation value of the kinetic energy $T = -1/2 \sum_i \Delta_{r_i}$ is obtained from the one-body density matrix as

$$\langle \Psi | T | \Psi \rangle = -\frac{1}{2} \int dx \, \Delta_r \, \Gamma^{(1)}(x'; x) \Big|_{x'=x} \, , \tag{14}$$

where we first keep $x' \neq x$ to make sure that the derivative only operates on the second argument, $x = (r, \sigma)$, but after that set $x' = x$ so both arguments are summed over. For a local operator like the Coulomb potential we can directly work with the diagonal elements of the density matrix. For the interaction of the electrons with a nucleus of charge Z at R this gives

$$\langle V \rangle = -Z \int dx \, \frac{\Gamma^{(1)}(x; x)}{|r - R|} \, . \tag{15}$$

Similarly, the Coulomb repulsion between the electrons is given by

$$\langle U \rangle = \int dx \, dx' \, \frac{\Gamma^{(2)}(x, x'; x, x')}{|r - r'|} \, . \tag{16}$$

We see that for calculating the eigenenergies of a many-body Hamiltonian describing a system of N electrons moving around nuclei of charge Z_α at position R_α

$$H = -\frac{1}{2} \sum_i \Delta_i - \sum_{i,\alpha} \frac{Z_\alpha}{|r_i - R_\alpha|} + \sum_{i<j} \frac{1}{|r_i - r_j|} \tag{17}$$

we do not need the full eigenfunction but only the corresponding one-body density matrix and the diagonal elements of the two-body density matrix. It is then tempting to try to calculate the ground state energy of an N-electron system by finding the two-electron density matrix that leads to the lowest energy expectation value. This is known as *Coulson's Challenge* [12]. The approach is, however, not practical since we know no criterion that would tell us what function of four arguments is actually a fermionic density matrix, i.e., one that can be obtained via (12) from an antisymmetric N-electron wave function. For the single-electron density matrix there is such a criterion: for any $\Gamma(x'; x)$ with eigenvalues $\gamma_i \in [0, 1]$ and trace $\mathrm{Tr}\,\Gamma(x'; x) = N$ there exists a normalized N-electron wave function with single-electron density matrix $\Gamma(x'; x)$.

Since we made sure that the N-electron wave function is normalized, the diagonal elements of the density matrices have straightforward physical interpretations. From the definition (12) we see that the single-electron density matrix gives the electron density $\Gamma^{(1)}(x; x) = n(x)$, while the two-electron density matrix $2\Gamma^{(2)}(x, x'; x, x') = n(x, x')$ gives the conditional electron density, i.e., the electron density at x', given that one electron is at x. They are normalized accordingly

$$\int dx \, \Gamma^{(1)}(x; x) = N \quad \text{and} \quad \int dx \, dx' \, \Gamma^{(2)}(x, x'; x, x') = \frac{N(N-1)}{2} \, . \tag{18}$$

The way the two-electron density differs from the simple product of the one-electron densities describes the correlation of the electrons

$$n(x, x') = n(x) n(x') \, g(x, x') \, . \tag{19}$$

The factor $g(x, x')$ is called the *pair-correlation function*. Since by the Pauli principle no two electrons can occupy the same state, it vanishes for $x = x'$. From (13) we find

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

which gives the sum rule

$$\int dx'\, n(x') \left(g(x, x') - 1\right) = -1 \ , \tag{20}$$

which implies that the integrand vanishes for $|r - r'| \to \infty$. In practice $n(x')\,(g(x, x') - 1)$ is, as a function of x', quite localized around x. It is called the *exchange-correlation hole*. With this we can write the Coulomb repulsion energy between the electrons as

$$\langle U \rangle = \frac{1}{2} \int dx\, dx'\, \frac{n(x)n(x')}{|r - r'|} + \frac{1}{2} \int dx\, dx'\, \frac{n(x)n(x')\left(g(x, x') - 1\right)}{|r - r'|} \ , \tag{21}$$

where the first term is the long ranged Coulomb interaction between the uncorrelated charge densities (Hartree energy), while the second term is the interaction of the charge density with its rather localized exchange-correlation hole.

3 Slater determinants

When dealing with indistinguishable particles, we need only consider many-body wave functions that are (anti)symmetric under particle permuations. This can be ensured by explicitly (anti)symmetrizing an arbitrary wave function

$$\mathcal{S}_\pm \Psi(x_1, \ldots, x_N) := \frac{1}{\sqrt{N!}} \sum_P (\pm 1)^P \Psi\left(x_{p(1)}, \ldots, x_{p(N)}\right) \ , \tag{22}$$

where $(\pm 1)^P$ 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 expensive operation. Since (anti)symmetrization only involves a relabeling of coordinates, in integrals, i.e., matrix elements, we can save some work by observing that in matrix elements only one of the wave functions needs to be properly (anti)symmetrized [11]

$$\int d\mathbf{x}\, \overline{(\mathcal{S}_\pm \Psi_a(\mathbf{x}))}\, M(\mathbf{x})\, (\mathcal{S}_\pm \Psi_b(\mathbf{x})) = \sqrt{N!} \int d\mathbf{x}\, \overline{\Psi_a(\mathbf{x})}\, M(\mathbf{x})\, (\mathcal{S}_\pm \Psi_b(\mathbf{x})) \ , \tag{23}$$

where $\mathbf{x} = x_1, \ldots, x_N$ and the observable M commutes with particle permutations.

It is remarkable that for products of single-electron states antisymmetrization can be performed very efficiently: it is simply the prescription for calculating a determinant, which can be calculated with $\mathcal{O}(N^3)$ operations. Interestingly, the corresponding operation for bosons, the symmetrized of a product of single-electron states, called the permanent, cannot be performed effi-

ciently. Given a set of spin-orbitals $\varphi_\alpha(x)$ we write the *Slater determinant*

$$\Phi_{\alpha_1\cdots\alpha_N}(\mathbf{x}) := \mathcal{S}_- \, \varphi_{\alpha_1}(x_1)\cdots\varphi_{\alpha_N}(x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}.$$
(24)

Obviously, replacing the orbitals by linear combinations $\tilde{\varphi}_{\alpha_n}(x) = \sum_{m=1}^N a_{n,m}\,\varphi_{\alpha_m}(x)$ among themselves produces the same Slater determinant, merely changing the normalization by $\det(A)$, which is non-zero as long as A is invertible.

For $N = 1$ a Slater determinant is simply the one-electron orbital $\varphi_\alpha(x)$; for $N = 2$ it has the familiar form $(\varphi_\alpha(x)\varphi_\beta(x') - \varphi_\beta(x)\varphi_\alpha(x'))/\sqrt{2}$.

Slater determinants are popular electronic wave functions because operations can be calculated efficiently, even for large numbers N of electrons, using standard methods of linear algebra. As an example, using (23), we see that the overlap of two Slater determinants is simply the determinant of the overlap matrix of their single electron orbitals:

$$\int dx_1 \cdots dx_N \, \overline{\Phi_{\alpha_1\cdots\alpha_N}(x_1,\ldots,x_N)}\, \Phi_{\beta_1\cdots\beta_N}(x_1,\ldots,x_N) = \det\left(\langle\varphi_{\alpha_n}|\varphi_{\beta_m}\rangle\right).$$
(25)

It follows that Slater determinants constructed from a set of orthonormal spin-orbitals $\varphi_\mu(x)$ are normalized – except when they contain an orbital more than once, in which case the determinant, obeying the Pauli principle, vanishes. Likewise, it follows that two Slater determinants $\Phi_{\alpha_1\cdots\alpha_N}(x_1,\ldots,x_N)$ and $\Phi_{\beta_1\cdots\beta_N}(x_1,\ldots,x_N)$ are orthogonal except when they are built from the same set of orbitals, i.e., $\{\alpha_1,\ldots,\alpha_N\} = \{\beta_1,\ldots,\beta_N\}$. Thus, if we fix some ordering of the orbitals, e.g., $\alpha_1 < \alpha_2 < \cdots < \alpha_N$, the determinants formed from all possible choices of N spin-orbitals from the set of K orthonormal single-electron functions $\varphi_\mu(x)$ forms an orthonormal set in the N-electron Hilbert space. 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:

$$\frac{K!}{N!(K-N)!} = \binom{K}{N}.$$
(26)

They span the antisymmetrized N-particle Hilbert space. Thus, the choice of an orthonormal set of single-electron functions $\{\varphi_\mu(x)\,|\,\mu = 1\ldots K\}$ induces an orthonormal basis

$$\left\{\Phi_{\alpha_1\cdots\alpha_N}(x_1,\ldots,x_N)\,\middle|\,\alpha_1 < \alpha_2 < \cdots < \alpha_N \in \{1,\ldots,K\}\right\}$$
(27)

in the corresponding N-electron space. Given a set of one-electron functions, we can thus, by the variational principle, approach the exact solution of the many-body problem in the corresponding N-electron Hilbert space by including more and more of these determinants. This is called the *configuration interaction* (CI) method. It becomes exact on this space when we include all $\binom{K}{N}$ basis determinants (exact diagonalization or full CI). Even though these calculation very quickly involve unimaginable numbers of determinants – for $N = 25$ electrons in $K = 100$ orbitals the number of basis functions already exceeds 10^{23} – the result is still not exact, as the single electron basis is not complete. This is illustrated in Fig. 3.
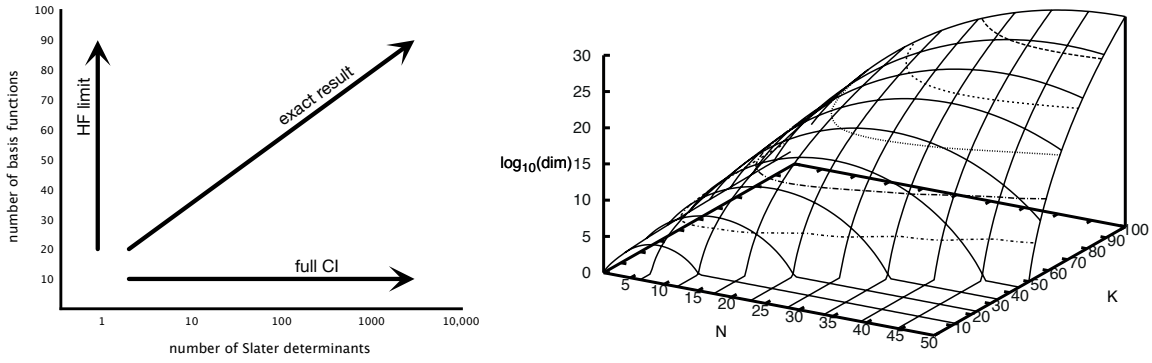
Fig. 3: *Left: Convergence of a calculation for an N-electron system with K basis functions. The dimension of the Hilbert space for configuration interaction is $\dim = \binom{K}{N}$. The plot on the right shows the $\log_{10}$ of this as a function of the number of electrons N and orbitals K.*

3.1 Hartree-Fock

To calculate expectation values for Slater determinants we take again the route via the reduced density matrices described in Sec. 2. To calculate the one-body density matrix, we expand the Slater determinant along its first row

$$\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \dots, x_N) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} (-1)^{1+n} \varphi_{\alpha_n}(x_1) \, \Phi_{\alpha_{i \neq n}}(x_2, \dots, x_N) \,, \tag{28}$$

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. The integral for obtaining the one-body density matrix is then just of the type (25), so that

$$\Gamma^{(1)}(x';x) = \frac{1}{N} \sum_{n,m} (-1)^{n+m} \overline{\varphi_{\alpha_n}(x')} \, \varphi_{\alpha_m}(x) \, \frac{\det(\langle \varphi_{\alpha_{j \neq n}} | \varphi_{\alpha_{k \neq m}} \rangle)}{\det(\langle \varphi_{\alpha_j} | \varphi_{\alpha_k} \rangle)} \tag{29}$$

where we have introduced the normalization factor of the Slater determinant. For orthonormal orbitals this simplifies to the familiar expressions

$$\Gamma^{(1)}(x';x) = \sum_n \overline{\varphi_{\alpha_n}(x')} \, \varphi_{\alpha_n}(x) \quad \text{and} \quad n(x) = \sum_n |\varphi_n(x)|^2 \,. \tag{30}$$

For higher-order density matrices, we could expand the $N-1$ Slater determinants further. A simpler way to generalize (28) is, however, to realize that we can write the permutations of a set of N objects by considering all possible partitions of this set into two sets and taking all permutations among the elements of these sets. This lets us write a Slater determinant as the sum over products of two smaller Slater determinants:

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

$$\tag{31}$$

For $p = 2$ we get the general form of the two-body density matrix for a Slater determinant

$$\Gamma^{(2)}(x_1', x_2'; x_1, x_2) = \sum_{\substack{n'<m' \\ n<m}} (-1)^{n'+m'+n+m} \overline{\Phi_{\alpha_{n'},\alpha_{m'}}(x_1', x_2')} \, \Phi_{\alpha_n,\alpha_m}(x_1, x_2) \frac{\det(\langle \varphi_{\alpha_{j\neq n',m'}} | \varphi_{\alpha_{k\neq n,m}} \rangle)}{\det(\langle \varphi_{\alpha_j} | \varphi_{\alpha_k} \rangle)} \tag{32}$$

Since the summation indices are ordered, for orthogonal orbitals only the terms with $(n', m') = (n, m)$ remain, giving the generalization of (30) to $p = 2$

$$\Gamma^{(2)}(x_1' x_2'; x_1, x_2) = \sum_{n<m} \overline{\Phi_{\alpha_n,\alpha_m}(x_1', x_2')} \, \Phi_{\alpha_n,\alpha_m}(x_1, x_2) \tag{33}$$

and

$$n(x_1, x_2) = \sum_{n,m} |\Phi_{\alpha_n,\alpha_m}(x_1, x_2)|^2 \ , \tag{34}$$

where the factor of 2 is included by summing over all combinations (n, m), not only the ordered ones, and $m = n$ can be included, since in that case the determinant vanishes. In terms of the orbitals this becomes

$$n(x_1, x_2) = \sum_{n,m} \left(|\varphi_{\alpha_n}(x_1)|^2 |\varphi_{\alpha_m}(x_2)|^2 - \overline{\varphi_{\alpha_n}(x_1)} \varphi_{\alpha_m}(x_1) \, \overline{\varphi_{\alpha_m}(x_2)} \varphi_{\alpha_n}(x_2) \right) , \tag{35}$$

from which it is easy to find the pair correlation function

$$g(x_1, x_2) = 1 - \frac{\sum_{n,m} \overline{\varphi_{\alpha_n}(x_1)} \varphi_{\alpha_m}(x_1) \, \overline{\varphi_{\alpha_m}(x_2)} \varphi_{\alpha_n}(x_2)}{n(x_1) \, n(x_2)} \ . \tag{36}$$

Given the explicit form of the two-body density matrix (32), we can meet Coulson's challenge for the Hamiltonian (17), albeit restricted to density matrices that arise from Slater determinants. This procedure is equivalent to the *Hartree-Fock* method, which gives the Slater determinant for which the total energy is stationary.

For a homogeneous electron gas, i.e., the Hamiltonian (17) without ionic potentials (except for a homogeneous neutralizing background), one such stationary point is, by symmetry, the Slater determinant of plane waves of wave vectors k with $|k| \leq k_F$. For this simple case we can calculate the pair correlation function (36) explicitly

$$g(r_1, \sigma_1, r_2, \sigma_2) - 1 = -9 \frac{\left(\sin(k_F r) - k_F r \cos(k_F r) \right)^2}{(k_F r)^6} \delta_{\sigma_1, \sigma_2} \tag{37}$$

with $r = r_2 - r_1$. This shows how electrons of the same spin avoid getting close to each other because of the antisymmetry requirement (*exchange hole*), while for a Slater determinant electrons of opposite spin are uncorrelated.

The exchange hole decays rapidly with distance and becomes more localized with increasing density, approaching a delta function in the limit $k_F \to \infty$. As shown in Fig. 4, the exchange hole is essentially contained in a sphere of the Wigner-Seitz radius $r_\sigma = 2^{1/3} r_s$, i.e., the radius of a sphere containing one electron of a given spin. Since this condition is somewhat
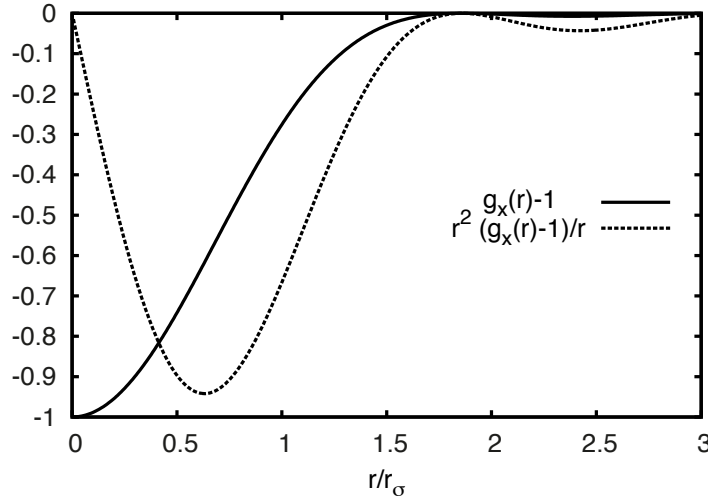
Fig. 4: *Exchange hole for a paramagnetic homogeneous electron gas in units of the spin Wigner-Seitz radius $k_F r_\sigma = (9\pi/2)^{1/3}$. In addition, the dotted line shows the contribution of the exchange hole to the Coulomb repulsion energy of Eq. (21).*

similar to the sum rule (20) for the pair-correlation function, this is not entirely unexpected. Including correlation effects, which are missing in Hartree-Fock, could increase the range of the exchange-correlation hole, while, missing exchange effects, the correlation hole for electrons of different spin should be more localized. This is in fact what is found in quantum Monte Carlo calculations, see, e.g., Fig. 1 of Ref. [13].

We note in passing that the homogeneous electron gas is not necessarily the Hartree-Fock ground state. Allowing the Slater determinant to break the symmetry of the Hamiltonian, we might obtain a lower energy solution [14]. Enforcing the symmetry of the Slater determinant is called restricted Hartree-Fock, allowing it to have a lower symmetry is unrestricted Hartree-Fock. See, e.g., Ref. [15] for a simple example.

To go beyond Hartree-Fock we could now derive the matrix elements of n-particle operators between different Slater determinants, so that we could represent the operators, e.g., in the orthonormal basis (27). For this we could introduce generalized density matrices with two different many-body wave functions [11]. A much more transparent approach is, however, provided by the formalism of second quantization. It addresses the main inconvenience when working with Slater determinants: keeping track of the sign for sub-determinants. In second quantization these signs are simply stored in the relative positions of certain operators. For this to work, these operators have to change sign when exchanging the order of two of them – they have to anti-commute.

4 Second quantization

The first object to be successfully quantized was the electron. It was no longer described as a classical point-particle but by a quantum mechanical Schrödingier field. Later, for studying the interaction of radiation with matter, also the electromagnetic field had to be quantized, giving rise to quantum particles – photons. This process, pioneered by Dirac [16], was called

the second quantization. Shortly after, Jordan, Klein, and Wigner used a similar approach to quantize the Schrödingier field and found that it could be used to write antisymmetric states in a very convenient way using particle-type operators [17, 18].

When working with Slater determinants of the form (24) we are working in a real-space basis. Like in fundamental quantum mechanics, it is, however, often useful to abstract from a specific basis and work with 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

$$\Phi_{\alpha\beta}(x_1, x_2) = \frac{1}{\sqrt{2}} \left(\varphi_\alpha(x_1)\varphi_\beta(x_2) - \varphi_\beta(x_1)\varphi_\alpha(x_2)\right). \tag{38}$$

We could do the same for Dirac states, defining a two-particle Dirac state

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

The idea of second quantization is then to specify the states using operators

$$c_\beta^\dagger c_\alpha^\dagger |0\rangle = |\alpha, \beta\rangle. \tag{39}$$

When these operators change sign when they are reordered, antisymmetry of the wave function will be automatically ensured

$$|\alpha, \beta\rangle = c_\beta^\dagger c_\alpha^\dagger |0\rangle = -c_\alpha^\dagger c_\beta^\dagger |0\rangle = -|\beta, \alpha\rangle. \tag{40}$$

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

4.1   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 operators with these properties to represent Slater determinants. We start by motivating the properties of the new operators.

To be able to construct many-electron states, we start from the simplest such state: $|0\rangle$ the state with no electron, i.e., the *vacuum state*, which we assume to be normalized $\langle 0|0\rangle = 1$. Next we introduce for each single-electron state $|\alpha\rangle$ (corresponding to an orbital $\varphi_\alpha(x)$) an operator $c_\alpha^\dagger$. We call it a *creation operator*, since we ask that applying $c_\alpha^\dagger$ to an N-electron state adds an electron in state $|\alpha\rangle$ to that state, making it an $N+1$ electron state. In effect, the operator should be constructed such as to mimic the effect of adding an extra column φ_α and an extra row x_{N+1} to the Slater determinant (24). Since the order in which we add rows/columns matters for the sign of the Slater determinant, we postulate that the operators change sign when exchanged: $c_\alpha^\dagger c_\beta^\dagger = -c_\beta^\dagger c_\alpha^\dagger$. This is more conveniently written as $\{c_\alpha^\dagger, c_\beta^\dagger\} = 0$ by introducing the *anti-commutator*

$$\{A, B\} := A\,B + B\,A. \tag{41}$$

The simplest state we can produce with these operators is the single-electron state $|\alpha\rangle = c_\alpha^\dagger|0\rangle$. When we want to calculate its norm, we have to consider the adjoint of $c_\alpha^\dagger|0\rangle$, formally obtaining $\langle\alpha|\alpha\rangle = \langle 0|c_\alpha c_\alpha^\dagger|0\rangle$, or, more generally, $\langle\alpha|\beta\rangle = \langle 0|c_\alpha c_\beta^\dagger|0\rangle$. This must mean that c_α, the adjoint of a creation operator, must remove an electron from the state, otherwise the overlap of $c_\alpha c_\beta^\dagger|0\rangle$ 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 $c_\alpha|0\rangle = 0$. Moreover, by taking the adjoint or the anti-commutator of the creation operators, we see that also the annihilation operators anti-commute: $\{c_\alpha, c_\beta\} = 0$. Moreover, to obtain the proper normalization of the single-electron states, we postulate the commutation relation $\{c_\alpha, c_\beta^\dagger\} = \langle\alpha|\beta\rangle$.

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

$$
\boxed{
\begin{array}{ll}
c_\alpha|0\rangle = 0 & \{c_\alpha, c_\beta\} = 0 = \{c_\alpha^\dagger, c_\beta^\dagger\} \\[2mm]
\langle 0|0\rangle = 1 & \{c_\alpha, c_\beta^\dagger\} = \langle\alpha|\beta\rangle
\end{array}
}
\tag{42}
$$

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 the *Fock space*. It is also remarkable that the mixed anti-commutator is the only place where the orbitals that distinguish different operators enter.

One type of operators is particularly useful for making contact with the real-space picture: The operators $\hat{\Psi}^\dagger(x)$, with $x = (r, \sigma)$, that create an electron of spin σ at position r, i.e., in state $|x\rangle = |r, \sigma\rangle$. Because of their importance they get a special name, *field operators*, and a special symbol $\hat{\Psi}^\dagger(x)$ instead of $c_x^\dagger$, but really they are just ordinary creation operators for the states corresponding to a delta function at r and a spin σ. The anti-commutator for the field-operators obviously follow from (42)

$$
\{\hat{\Psi}(x), \hat{\Psi}(x')\} = 0 = \{\hat{\Psi}^\dagger(x), \hat{\Psi}^\dagger(x')\} \quad \text{and} \quad \{\hat{\Psi}(x), \hat{\Psi}^\dagger(x')\} = \delta(x - x') .
\tag{43}
$$

Given the single-electron wave functions in real space $\varphi_\alpha(x)$, we can express any creation operator in terms of the field operators

$$
c_\alpha^\dagger = \int dx\, \varphi_\alpha(x)\hat{\Psi}^\dagger(x) .
\tag{44}
$$

Using (43), it is easy to see that these operator indeed fulfill all properties (42) required of the creation operators.

Conversely, if we have a complete set of single electron states $\{\varphi_{\alpha_n}(x)\}$, we can expand the field operators in terms of the corresponding creators and annihilators. Given the overlap matrix $S = (\langle\alpha_n|\alpha_m\rangle)$ we can use the Cholesky factorization $S^{-1} = T^\dagger T$ to orthonormalize the orbitals $\tilde{\varphi}_{\alpha_n}(x) = \sum T_{n,m}\, \varphi_{\alpha_m}(x)$. The completeness relation is then

$$
\sum_{n,m} \overline{\varphi_{\alpha_n}(x)}\, \left(S^{-1}\right)_{n,m}\, \varphi_{\alpha_m}(x') = \sum_j \overline{\tilde{\varphi}_{\alpha_j}(x)}\, \tilde{\varphi}_{\alpha_j}(x') = \delta(x - x') .
\tag{45}
$$

Using this together with the commutation relations (42) we see that the operators

$$\hat{\Psi}(x) = \sum_n \tilde{\varphi}_{\alpha_n}(x)\, c_{\alpha_n}\ , \tag{46}$$

fulfill the commutation relations (43) of the field operators.

4.2   Representation of Slater determinants

We now show that we can write a Slater determinant in terms of the algebra (42) we have just defined. For this we consider an N-electron state $\prod c_\alpha^\dagger |0\rangle$ and prove that its real-space representation, obtained via the field operators is just the corresponding Slater determinant

$$\Phi_{\alpha_1\alpha_2\ldots\alpha_N}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \left\langle 0 \left| \hat{\Psi}(x_1)\hat{\Psi}(x_2)\ldots\hat{\Psi}(x_N)\, c_{\alpha_N}^\dagger \ldots c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger \right| 0 \right\rangle \tag{47}$$

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 special case of an anti-commutation relation

$$\{\hat{\Psi}(x), c_\alpha^\dagger\} = \int dx'\, \varphi_\alpha(x')\, \{\hat{\Psi}(x), \hat{\Psi}^\dagger(x')\} = \varphi_\alpha(x) \tag{48}$$

we see that

$$\left\langle 0 \left| \hat{\Psi}(x_1)\, c_{\alpha_1}^\dagger \right| 0 \right\rangle = \left\langle 0 \left| \varphi_{\alpha_1}(x_1) - c_{\alpha_1}^\dagger \hat{\Psi}(x_1) \right| 0 \right\rangle = \varphi_{\alpha_1}(x_1) \tag{49}$$

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

$$
\begin{aligned}
\left\langle 0 \left| \hat{\Psi}(x_1)\hat{\Psi}(x_2)\, c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger \right| 0 \right\rangle &= \left\langle 0 \left| \hat{\Psi}(x_1)\left(\varphi_{\alpha_2}(x_2) - c_{\alpha_2}^\dagger \hat{\Psi}(x_2)\right) c_{\alpha_1}^\dagger \right| 0 \right\rangle \\
&= \left\langle 0 \left| \hat{\Psi}(x_1)c_{\alpha_1}^\dagger \right| 0 \right\rangle \varphi_{\alpha_2}(x_2) - \left\langle 0 \left| \hat{\Psi}(x_1)c_{\alpha_2}^\dagger \hat{\Psi}(x_2)c_{\alpha_1}^\dagger \right| 0 \right\rangle \\
&= \varphi_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_2) - \varphi_{\alpha_2}(x_1)\varphi_{\alpha_1}(x_2)\ .
\end{aligned}
\tag{50}
$$

We see how anti-commuting automatically produces appropriate sign 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

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

Using (47) 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 (47) for N-electron states. Thus we see that instead of working with the Slater determinant $\Phi_{\alpha_1 \alpha_2 \ldots \alpha_N}(x_1, x_2, \ldots, x_N)$ we can work with the corresponding N-electron product state $\prod c_\alpha^\dagger \left|0\right\rangle$. In particular, instead of working with the basis of Slater determinants (27) induced by an orthonormal set of single-electron states $\{\varphi_{\alpha_n}(x)\}$, we can work with the corresponding basis of product states

$$\left\{ \prod_{\alpha_1 < \cdots < \alpha_N} c_{\alpha_N}^\dagger \cdots c_{\alpha_1}^\dagger \left|0\right\rangle \right\} . \tag{51}$$

4.3 Representation of n-body operators

Having established the relation between product states and Slater determiants, it is straightforward to express the matrix elements of a general n-body operator (11)

$$M(\mathbf{x}) = M_0 + \sum_i M_1(x_i) + \sum_{i<j} M_2(x_i, x_j) + \sum_{i<j<k} M_3(x_i, x_j, x_k) + \cdots \tag{52}$$

with N-electron Slater determinants:

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

$$= \left\langle 0 \left| c_{\beta_1} \cdots c_{\beta_N} \, \hat{M} \, c_{\alpha_N}^\dagger \cdots c_{\alpha_1}^\dagger \right| 0 \right\rangle \tag{53}$$

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

$$\hat{M} = \frac{1}{N!} \int dx_1 \cdots x_N \, \hat{\Psi}^\dagger(x_N) \cdots \hat{\Psi}^\dagger(x_1) \, M(x_1, \cdots, x_N) \, \hat{\Psi}(x_1) \cdots \hat{\Psi}(x_N) . \tag{54}$$

Note that this form of the operator is only valid when applied to N-electron states. But from here on, we can work entirely in terms of our algebra (42).

To see what (54) means we look at its parts (52). As usual, we start with the simplest case, the zero-body operator, which, up to trivial prefactor, is $M_0(x_1, \cdots, x_N) = 1$. Operating on an N-electron wave function, it gives

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

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

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

$$\vdots$$

$$= \frac{1}{N!} \, 1 \cdot 2 \, \cdots \, N = 1 \tag{55}$$

where we have used that

$$\int dx \, \hat{\Psi}^\dagger(x) \hat{\Psi}(x) = \hat{N} \tag{56}$$

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 apparently does not depend on the number of electrons in the wave function that it is applied to. This was not the case for the original expression (54).

Next we consider one-body operators $M(x_1, \ldots, x_N) = \sum_j M_1(x_j)$

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

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

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

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

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 $\hat{\Psi}(x_j)|N$-electron state$\rangle$.

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

$$\hat{M}_1 = \sum_{n,m} \int dx \, \overline{\varphi_{\alpha_n}(x)} \, M(x) \, \varphi_{\alpha_m}(x) \, c^\dagger_{\alpha_n} c_{\alpha_m} = \sum_{n,m} \langle \alpha_n | M_1 | \alpha_m \rangle \, c^\dagger_{\alpha_n} c_{\alpha_m} \; . \qquad (57)$$

Also here we find a form for $\hat{M}_1$ that is apparently independent of the number of electrons N and can be evaluated directly in the basis states (51).

For the two-body operators $M(x_1, \ldots, x_N) = \sum_{i<j} M_2(x_i, x_j)$ 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. This time we are left with a zero-body operator for $N-2$ electrons:

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

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

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

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

Expanding in an orthonormal basis, we get

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

$$= \frac{1}{2} \sum_{n,n',m,m'} \langle \alpha_n \alpha_{n'} | M_2 | \alpha_m \alpha_{m'} \rangle \qquad\qquad c^\dagger_{\alpha_{n'}} c^\dagger_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}} \quad (58)$$

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. Obviously, from the symmetry $M_2(x, x') = M_2(x', x)$ follows $\langle \alpha_n \alpha_{n'} | M_2 | \alpha_m \alpha_{m'} \rangle = \langle \alpha_{n'} \alpha_n | M_2 | \alpha_{m'} \alpha_m \rangle$.

The procedure 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 (52) that was explicitly formulated in an N-electron Hilbert space, the results (55), (57), and (58) 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.

4.4 Vacuum state and electron-hole transformation

We have introduced the state $|0\rangle$ as the state with no electrons, $N = 0$. The whole formalism of second quantization requires, however, only (42), i.e., that $|0\rangle$ is normalized and annihilated by the annihilation operators. We can exploit this to obtain more convenient descriptions of many-electron systems. As a first example, see [19] for the physics background, let us consider the d-states of an atom. Denoting the operator for putting an electron of spin σ in the d-orbital with directional quantum number m by $d^\dagger_{m\sigma}$, we can describe a d^N configuration, i.e., a state with N d-electrons as a linear combination of product states $\prod_{n=1}^{N} d^\dagger_{m_n\sigma}|0\rangle$. Here $|0\rangle$ is the state without electrons. This is the description we have used so far. It specifies the states the electrons are in. For an almost full shell it might, however, be more convenient to specify the state in terms of the non-occupied states. We can do this by introducing a new "vacuum" state

$$|\text{full shell}\rangle = d^\dagger_{-2\downarrow} d^\dagger_{-1\downarrow} \cdots d^\dagger_{2\downarrow} d^\dagger_{-2\uparrow} d^\dagger_{-1\uparrow} \cdots d^\dagger_{2\uparrow}|0\rangle = \prod_\sigma \prod_{m=2}^{-2} d^\dagger_{m\sigma}|0\rangle \,, \tag{59}$$

corresponding to a filled d-shell. $|\text{full shell}\rangle$ certainly does not fulfill the requirements for a vacuum state, since $d_{m\sigma}|\text{full shell}\rangle \neq 0$. Thanks to the Pauli principle it is, however, annihilated by any electron creation operator $c^\dagger_\delta$ in the space of d-orbitals. Thus, when we relabel these electron creation operators as hole annihilation operators, $h_\delta = c^\dagger_{\bar\delta}$, then $|\text{full shell}\rangle$ behaves as a vacuum state for these newly labeled operators h_δ. We pick the relation between the hole state δ and the corresponding electron states $\bar\delta$ such that form of the anti-commutation relations remain unchanged: $\{h_\alpha, h^\dagger_\beta\} = \{c^\dagger_{\bar\alpha}, c_{\bar\beta}\} = \langle \bar\beta | \bar\alpha \rangle = \langle \alpha | \beta \rangle$. Having established an isomorphism between the algebra of electron operators and that of the corresponding hole operators, we can relate electron expectation values to those of hole-states, e.g., $\langle 0 | c_\alpha c^\dagger_\beta | 0 \rangle = \langle \text{full} | h_{\bar\alpha} h^\dagger_{\bar\beta} | \text{full} \rangle$.

A common choice is to take the complex conjugate state $\varphi_{\bar\delta}(x) = \overline{\varphi_\delta(x)}$.

We can now ask what kind of particles the operators $h^\dagger_\delta$ create. This is most easily done in the basis $d^\dagger_{m\sigma}$ of spherical harmonics; the general $h^\dagger_\delta$ follow then by expanding them in the $d^\dagger_{m\sigma}$. A full d-shell has total orbital momentum $L = 0$ and total spin $S = 0$. Removing an electron in state $|m\sigma\rangle$ thus changes L_z from 0 to $-m$ and S_z from 0 to $-\sigma$. The corresponding creator therefore creates a hole with directional quantum number $-m$ and spin $-\sigma$. We express this by writing the electron-hole transformation as $h^\dagger_{m\sigma} = d_{-m,-\sigma}$. We can make a similar argument

for a completely filled band

$$|\text{full band}\rangle = \prod_{\sigma}\prod_{k} b_{k\sigma}^{\dagger}|0\rangle\,, \tag{60}$$

with hole operators $h_{k\sigma}^{\dagger} = b_{-k,-\sigma}$.

We can then relate the matrix elements for N-electron states of type $|e\rangle = \prod c_{\alpha_n}^{\dagger}|0\rangle$ and the related N-hole states $|h\rangle = \prod h_{\bar{\alpha}_n}^{\dagger}|\text{full}\rangle$, where $|\text{full}\rangle = \prod_{n=1}^{N_{\text{states}}} c_{\alpha_n}^{\dagger}|0\rangle$ is assumed to be normalized, as is required of a vacuum state. Working with orthonormal operators, we find that the matrix elements for a one-body operator (57) change sign and have a constant shift on the diagonal

$$\langle h'|\hat{M}_1|h\rangle = \sum_{n,m}\langle\alpha_n|M_1|\alpha_m\rangle\,\langle h'|c_{\alpha_n}^{\dagger}c_{\alpha_m}|h\rangle \tag{61}$$

$$= \sum_{n,m}\langle\alpha_n|M_1|\alpha_m\rangle\,\langle h'|h_{\bar{\alpha}_n}h_{\bar{\alpha}_m}^{\dagger}|h\rangle \tag{62}$$

$$= \sum_{n,m}\langle\alpha_n|M_1|\alpha_m\rangle\left(\underbrace{\langle\bar{\alpha}_n|\bar{\alpha}_m\rangle}_{\langle\text{full}|c_{\alpha_n}^{\dagger}c_{\alpha_m}|\text{full}\rangle}\langle h'|h\rangle - \underbrace{\langle h'|h_{\bar{\alpha}_m}^{\dagger}h_{\bar{\alpha}_n}|h\rangle}_{=\langle e'|c_{\alpha_m}^{\dagger}c_{\alpha_n}|e\rangle}\right) \tag{63}$$

$$= \langle\text{full}|\hat{M}_1|\text{full}\rangle\,\delta_{h',h} - \langle e'|\hat{M}_1|e\rangle\,. \tag{64}$$

In going to the second line, we converted from writing the matrix element in electron operators to the formulation in hole operators. The identity of the matrix elements for the N-hole and N-electron states in the third line follows from the fact that the operators $c_{\bar{\alpha}}$ and h_{α} form, with their respective vacua, the same algebra. For two-body operators (58) we use

$$h_{\alpha}h_{\beta}h_{\gamma}^{\dagger}h_{\delta}^{\dagger} = h_{\delta}^{\dagger}h_{\gamma}^{\dagger}h_{\beta}h_{\alpha} - \langle\alpha|\gamma\rangle\,h_{\beta}h_{\delta}^{\dagger} + \langle\alpha|\delta\rangle\,h_{\beta}h_{\gamma}^{\dagger} - \langle\beta|\gamma\rangle\,h_{\delta}^{\dagger}h_{\alpha} + \langle\beta|\delta\rangle\,h_{\gamma}^{\dagger}h_{\alpha}\,. \tag{65}$$

Collecting contributions of the direct two-body terms to $\langle h'|\hat{M}_2|h\rangle$ we get

$$\frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\beta\alpha|M_2|\gamma\delta\rangle\langle h'|\delta_{\alpha\delta}\,h_{\beta}h_{\gamma}^{\dagger} - \delta_{\beta\gamma}h_{\delta}^{\dagger}\,h_{\alpha}|h\rangle = \frac{1}{2}\sum_{\alpha\beta}\langle\beta\alpha|M_2|\beta\alpha\rangle\,\delta_{h',h} - \sum_{\alpha\beta\gamma}\langle\beta\alpha|\gamma\alpha\rangle\langle h'|h_{\gamma}^{\dagger}h_{\beta}|h\rangle$$

and similarly for minus the exchange terms

$$\frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\beta\alpha|M_2|\gamma\delta\rangle\langle h'|\delta_{\alpha\gamma}\,h_{\beta}h_{\delta}^{\dagger} - \delta_{\beta\delta}h_{\gamma}^{\dagger}\,h_{\alpha}|h\rangle = \frac{1}{2}\sum_{\alpha\beta}\langle\beta\alpha|M_2|\alpha\beta\rangle\,\delta_{h',h} - \sum_{\alpha\beta\gamma}\langle\beta\alpha|\alpha\gamma\rangle\langle h'|h_{\gamma}^{\dagger}h_{\beta}|h\rangle$$

The first terms only contribute to diagonal matrix elements and give the expectation value of the full shell $\langle\text{full}|\hat{M}_2|\text{full}\rangle$. The one-body terms also contribute only to the diagonal when the full shell is symmetric (atomic shell: radial symmetry, filled band: $k = 0$) and M_2 conserves the corresponding quantum numbers (atomic shell: $m_1 + m_2 = m_3 + m_4$, filled band: $k_1 + k_2 = k_3 + k_4$): fixing, e.g., $\alpha = \gamma$ then also fixes $\beta = \delta$. Moreover, all terms $\sum_{\alpha}\langle\beta\alpha|M_2|\beta\alpha\rangle$ or the corresponding exchange term are independent of $|\beta\rangle$ for orbitals of the same symmetry (just rotate the basis to the desired $|\beta'\rangle$) so that, again, there is just a constant shift of the diagonal elements

$$\langle h'|\hat{M}_2|h\rangle = \left(\langle\text{full}|\hat{M}_2|\text{full}\rangle + N\sum_{\alpha}(\langle\beta\alpha|M_2|\beta\alpha\rangle - \langle\beta\alpha|M_2|\alpha\beta\rangle)\right)\delta_{e',e} + \langle e'|\hat{M}_2|e\rangle\,. \tag{66}$$

An interesting new situation arises when we consider product states that are not closed shells. A popular example is the Fermi sea for a homogeneous electron gas

$$|\text{Fermi sea}\rangle = \prod_\sigma \prod_{|k|\leq k_F} c^\dagger_{k\sigma}|0\rangle . \tag{67}$$

We can now introduce new annihilation operators as

$$h_{k\sigma} = \begin{cases} c^\dagger_{-k,-\sigma} & \text{for } |k| \leq k_F \\ c_{k,\sigma} & \text{for } |k| > k_F \end{cases} \tag{68}$$

They are of hole-type for states occupied in $|\text{Fermi sea}\rangle$, while for empty states they are of electron type. This mixing of character has an interesting consequence: electron creation operators in a basis other than that used for defining the new vacuum are transformed to operators with mixed creator/annihilator contributions. As an example, the field operator

$$\hat{\Psi}_\sigma(r) = \int dk\, e^{ikr}\, c_k = \int_{|k|\leq k_F} dk\, e^{ikr}\, h^\dagger_{-k,-\sigma} + \int_{|k|>k_F} dk\, e^{ikr}\, h_{k,\sigma} \tag{69}$$

is no longer a pure annihilation operator in the hole picture. I.e., we no longer get the full algebra (42) but are restricted to operators defined in the basis that was used to generate the new vacuum.

5 Many-body states

We now consider small model Hamiltonians to illustrate the techniques introduced so far. This will also allow us to discuss characteristic many-body states without too much complication.

5.1 Hubbard model

As the first example we study 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

$$H = -t \sum_\sigma \left(c^\dagger_{2\sigma}c_{1\sigma} + c^\dagger_{1\sigma}c_{2\sigma} \right) + U \sum_{i\in\{1,2\}} n_{i\uparrow}n_{i\downarrow} . \tag{70}$$

The number of electrons N and 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

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

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

This is easily diagonalized giving the familiar bonding and antibonding solution

$$|\pm\rangle = \frac{1}{\sqrt{2}} \left(c_{1\uparrow}^\dagger \pm c_{2\uparrow}^\dagger \right) |0\rangle = c_{\pm\uparrow}^\dagger|0\rangle. \tag{71}$$

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

$$\langle 0| \begin{pmatrix} c_{1\uparrow}c_{2\downarrow} \\ c_{2\uparrow}c_{1\downarrow} \\ c_{1\uparrow}c_{1\downarrow} \\ c_{2\uparrow}c_{2\downarrow} \end{pmatrix} H \begin{pmatrix} c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger & c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger & c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger & c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger \end{pmatrix} |0\rangle = \begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & -t & -t \\ -t & -t & U & 0 \\ -t & -t & 0 & U \end{pmatrix}. \tag{72}$$

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

$$|\text{cov}_\pm\rangle = \frac{1}{\sqrt{2}} \left(c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger \pm c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle \tag{73}$$

$$|\text{ion}_\pm\rangle = \frac{1}{\sqrt{2}} \left(c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger \pm c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle \tag{74}$$

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

$$\begin{pmatrix} \langle\text{cov}_+| \\ \langle\text{ion}_+| \end{pmatrix} H \begin{pmatrix} |\text{cov}_+\rangle & |\text{ion}_+\rangle \end{pmatrix} = \frac{1}{2}\left\{ U - \begin{pmatrix} U & 4t \\ 4t & -U \end{pmatrix} \right\}. \tag{75}$$

Rewriting the matrix

$$\begin{pmatrix} U & 4t \\ 4t & -U \end{pmatrix} = \sqrt{U^2 + 16t^2} \begin{pmatrix} \cos\Theta & \sin\Theta \\ \sin\Theta & -\cos\Theta \end{pmatrix}, \tag{76}$$

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

$$|\text{gs}\rangle = \cos\Theta/2\,|\text{cov}_+\rangle + \sin\Theta/2\,|\text{ion}_+\rangle \tag{77}$$

$$= \frac{1}{\sqrt{2}} \left(\cos\tfrac{\Theta}{2}\, c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger + \cos\tfrac{\Theta}{2}\, c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger + \sin\tfrac{\Theta}{2}\, c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger + \sin\tfrac{\Theta}{2}\, c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger \right) |0\rangle \tag{78}$$

with an energy of $\varepsilon_{\text{gs}} = (U - \sqrt{U^2 + 16t^2})/2$. 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 $c_{+\downarrow}^\dagger c_{+\uparrow}^\dagger|0\rangle$ of the operators defined in (71). 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 $|\text{cov}_+\rangle$
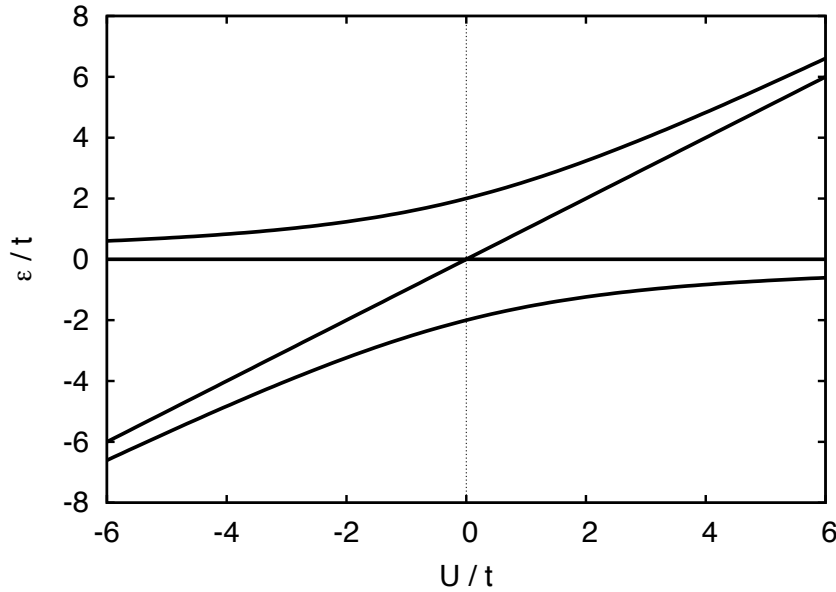
Fig. 5: *Spectrum of the two-site Hubbard model as a function of U/t.*

and can not even approximately be expressed as a two-electron Slater determinant. See [15] for a more detailed discussion, but beware that there the basis was chosen slightly differently to make the symmetry of the singlet/triplet state apparent.

We can, however, construct a product state, exploiting the freedom we gained by introducing second quantization: the product wave function in Fock space

$$|\text{VB}\rangle \;=\; \left(1 + c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger\right)\left(1 + c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger\right)|0\rangle \tag{79}$$

$$=\; \underbrace{|0\rangle}_{N=0} + \underbrace{\left(c_{2\downarrow}^\dagger c_{1\uparrow}^\dagger + c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger\right)|0\rangle}_{N_\uparrow = 1 = N_\downarrow} + \underbrace{c_{2\downarrow}^\dagger c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger c_{1\uparrow}^\dagger |0\rangle}_{N=4} \tag{80}$$

has a component in the two-electron Hilbert space that is just the covalent state $|\text{cov}_+\rangle$. It would be very desirable to generalize this approach to a half-filled state without double occupancies, i.e., a *Mott state* and to models with more than two sites. We might try an ansatz

$$|\text{VB?}\rangle = \prod_{\langle ij\rangle}\left(1 + c_{j\downarrow}^\dagger c_{i\uparrow}^\dagger + c_{i\downarrow}^\dagger c_{j\uparrow}^\dagger\right)|0\rangle \tag{81}$$

that has the advantage of not producing doubly occupied sites. The product is over pairs of sites, i.e., bonds, where each site only occurs in one such bond (if a site i participated in two bonds $\langle ij\rangle$ and $\langle ik\rangle$, there would be terms with doubly occupied site i, e.g., $c_{k\downarrow}^\dagger c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{k\uparrow}^\dagger$). There are, however, many ways we could partition the lattice sites into bonds, and to maintain the symmetry of the lattice we would have to sum over them. Alternatively, we could take products of all bond states and use a Gutzwiller projection to eliminate the doubly occupied sites. This is the idea of the *resonating valence bond* (RVB) state [20]. Unfortunately, neither approach to the Mott state is easy to handle.

In the *negative-U Hubbard model* we do not have such problems. For $U \ll t$ the ground state is a linear combination of doubly occupied sites $|\text{ion}_+\rangle$, which can be obtained from

$$|\text{pair}\rangle = \frac{1}{2} \left(1 + c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger\right) \left(1 + c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger\right) |0\rangle. \tag{82}$$

As each pair of creation operators in the product involves only a single site, this ansatz readily generalizes to larger lattices

$$|\text{pair}\rangle = \prod_i \frac{1}{\sqrt{2}} \left(1 + c_{i\downarrow}^\dagger c_{i\uparrow}^\dagger\right) |0\rangle. \tag{83}$$

The idea of such grand-canonical product states in Fock space are central for understanding the superconducting state.

5.2 BCS state

We now turn from the Hubbard model to the BCS Hamiltonian

$$H_{\text{BCS}} = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k,k'} V_{k,k'} \, c_{-k'\downarrow}^\dagger c_{k'\uparrow}^\dagger c_{k\uparrow} c_{-k\downarrow} \tag{84}$$

in which the interaction term scatters Cooper pairs of electrons $(k \uparrow, -k \downarrow)$ with different values of k. We start again by looking at a two-site model. With periodic boundary conditions, the bonding and antibonding states (71) become states with $k = 0$ and $k = \pi$, respectively. Note that for both values ($k = \pi$ being at the boundary of the Brillouin zone) we have $k = -k$. Setting $V_{0,\pi} = -I$, we obtain the two-site Hamiltonian

$$H = \sum_{k \in \{0,\pi\},\sigma} \varepsilon_k \, n_{k\sigma} - I \left(c_{\pi\downarrow}^\dagger c_{\pi\uparrow}^\dagger c_{0\uparrow} c_{0\downarrow} + c_{0\downarrow}^\dagger c_{0\uparrow}^\dagger c_{\pi\uparrow} c_{\pi\downarrow}\right). \tag{85}$$

For $N_\uparrow = 1 = N_\downarrow$ the Hamiltonian matrix is

$$\langle 0| \begin{pmatrix} c_{0\uparrow} c_{\pi\downarrow} \\ c_{\pi\uparrow} c_{0\downarrow} \\ c_{0\uparrow} c_{0\downarrow} \\ c_{\pi\uparrow} c_{\pi\downarrow} \end{pmatrix} H \begin{pmatrix} c_{\pi\downarrow}^\dagger c_{0\uparrow}^\dagger & c_{0\downarrow}^\dagger c_{\pi\uparrow}^\dagger & c_{0\downarrow}^\dagger c_{0\uparrow}^\dagger & c_{\pi\downarrow}^\dagger c_{\pi\uparrow}^\dagger \end{pmatrix} |0\rangle = \begin{pmatrix} \varepsilon_0 + \varepsilon_\pi & 0 & 0 & 0 \\ 0 & \varepsilon_0 + \varepsilon_\pi & 0 & 0 \\ 0 & 0 & 2\varepsilon_0 & -I \\ 0 & 0 & -I & 2\varepsilon_\pi \end{pmatrix} \tag{86}$$

To find the ground state, we need only consider the subspace of the Cooper pairs

$$|\text{pair}_k\rangle = c_{-k\downarrow}^\dagger c_{k\uparrow}^\dagger |0\rangle. \tag{87}$$

Writing $\bar{\varepsilon} = (\varepsilon_0 + \varepsilon_\pi)/2$ and $\Delta = \varepsilon_\pi - \varepsilon_0$

$$\begin{pmatrix} 2\varepsilon_0 & -I \\ -I & 2\varepsilon_\pi \end{pmatrix} = 2\bar{\varepsilon} - \begin{pmatrix} \Delta & I \\ I & -\Delta \end{pmatrix} = 2\bar{\varepsilon} - \sqrt{I^2 + \Delta^2} \begin{pmatrix} \cos\Theta & \sin\Theta \\ \sin\Theta & -\cos\Theta \end{pmatrix} \tag{88}$$

2.24

we diagonalize, just as we did in the case of the Hubbard model, to find the ground state of the half-filled two-site BCS-model for $I > 0$

$$|\text{gs}\rangle = \cos\Theta/2 \,|\text{pair}_0\rangle + \sin\Theta/2 \,|\text{pair}_\pi\rangle = \left(\cos\tfrac{\Theta}{2}\, c_{0\downarrow}^\dagger c_{0\uparrow}^\dagger + \sin\tfrac{\Theta}{2}\, c_{\pi\downarrow}^\dagger c_{\pi\uparrow}^\dagger\right)|0\rangle \qquad (89)$$

It is similar in form to the ground state (82) of the negative-U two-site Hubbard model, except that the two pairs can have different amplitudes, as the pair with lower band energy ε_k is preferred. Introducing $\Theta_0 = \Theta$ and $\Theta_\pi = \pi - \Theta$ we can recover this state (for any $I > 0$, not just in the limit of large interaction as for the negative-U Hubbard model) from the Fock-space product-state

$$|\text{BCS}\rangle = \prod_{k\in\{0,\pi\}} \frac{1}{\sqrt{1 + \cos^2\tfrac{\Theta_k}{2}}} \left(1 + \cos\tfrac{\Theta_k}{2}\, c_{-k\downarrow}^\dagger c_{k\uparrow}^\dagger\right)|0\rangle . \qquad (90)$$

This readily generalizes to larger numbers of k-points, where it becomes the BCS wave function.

6   Conclusions

We have studied the consequences of one of the most bizarre features of quantum mechanics, the existence of indistinguishable particles. To treat such particles, we have to introduce artificial labels but must make sure that no observable depends on them. The invariance under permutations of these labels implies that many-particle wave functions must be properly (anti)symmetrized. The type of symmetry is given by the spin-statistics connection. Unfortunately, imposing the correct (anti)symmetry on a generic N-particle wave function is a computationally hard problem as there are $N!$ permutations. One way to get around this problem is to integrate-out all degrees of freedom that are not explicitly considered. This gives rise to the reduced density matrices. Another is to exploit the fact that products of single-particle wave functions can be efficiently anti-symmetrized by forming the Slater determinant. Working with Slater determinants is made more convenient by introducing operators that are designed to encode the Fermi sign in their position. This technique of second quantization has two important benefits: we are no longer restricted to calculating with Slater determinants in configuration-space representation but can work with abstract Dirac states instead. Even more importantly, creation and annihilation operators are defined in Fock space. They enable us to write observables in a unified way on Fock space. Moreover, they allow us to also write wave functions in Fock space. Using this additional degree of freedom, it is possible to write non-Fermi-liquid states as generalized Slater determinants (product states), the most famous being the BCS state.

Acknowledgment

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