

2 Quantum systems with many particles

QM I mainly dealt with one-particle quantum mechanics. Even the two-body hydrogen atom can essentially be mapped onto a one-particle problem.

For any more complicated atom or molecule with more electrons, this is no longer possible, and we have to deal with the full many-body problem.

Other applications that we may have in mind are ensembles (gases, liquids) of quantum particles with mutual interactions.

2.1 Many-particle Hilbert space

Let us consider systems that arise from the coupling of N subsystems (e.g. one-particle systems).

Then the Hilbert space of the total system can be described by a tensor product of the subsystem's Hilbert spaces $\mathcal{H}_1, \mathcal{H}_2, \dots, \mathcal{H}_N$:

$$\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \dots \otimes \mathcal{H}_N \quad (2.1)$$

The tensor product of states is written as

$$|\psi_1 \psi_2 \dots \psi_N\rangle = |\psi_1\rangle \otimes |\psi_2\rangle \otimes \dots \otimes |\psi_N\rangle \quad (2.2)$$

The tensor product is linear in each factor, such that the scalar product in the subsystems induces a scalar product in the total system:

$$\langle \phi_1 \dots \phi_N | \psi_1 \dots \psi_N \rangle = \langle \phi_1 | \psi_1 \rangle \langle \phi_2 | \psi_2 \rangle \dots \langle \phi_N | \psi_N \rangle. \quad (2.3)$$

Operators ($\hat{=}$ observables) acting on the subsystems can form an observable of the total system by means of the tensor product:

$$A_i : \mathcal{H}_i \rightarrow \mathcal{H}_i$$

$$(A_1 \otimes A_2 \otimes \dots \otimes A_N) |\psi_1 \dots \psi_N\rangle = |A_1 \psi_1\rangle \otimes |A_2 \psi_2\rangle \otimes \dots \otimes |A_N \psi_N\rangle \quad (2.4)$$

In order to completely characterize states of the total system, one can use orthonormalized base states of each subsystem that are induced by complete sets of compatible observables.

Let $|\xi_i^j\rangle$ be a set of base states

in \mathcal{H}_i . Then the product states

$$|\xi'_1\rangle \otimes \dots \otimes |\xi'_N\rangle = |\xi'_1, \dots, \xi'_N\rangle \quad (2.5)$$

form a basis of \mathcal{H} . An example of such base states is given by position and spin eigenstates of each subsystem:

$$|\vec{x}_1 s_1, \dots, \vec{x}_N s_N\rangle = |\vec{x}_1 s_1\rangle \otimes \dots \otimes |\vec{x}_N s_N\rangle \quad (2.6)$$

An arbitrary state in the total system then can be decomposed as

$$|\psi\rangle = \sum_{s_1, \dots, s_N} \int d^3x_1 \dots d^3x_N \psi(\vec{x}_1 s_1, \dots, \vec{x}_N s_N) |\vec{x}_1 s_1, \dots, \vec{x}_N s_N\rangle \quad (2.7)$$

where $\psi(\vec{x}_1 s_1, \dots, \vec{x}_N s_N)$ denotes the N -particle wave function. If all states are properly normalized, $\psi(\vec{x}_1 s_1, \dots, \vec{x}_N s_N)$ is the probability amplitude (and $|\psi|^2$ the probability) to detect one particle at position \vec{x}_1 with spin s_1 and one particle at position \vec{x}_2 and spin s_2, \dots etc.

2.2 Identical particles

An important special case is the coupling of subsystems of identical particles. Identical really means that each two particles cannot be distinguished from one another. Consider two electrons: the fact that two electrons are identical means that the state in which one sits at \vec{x}_1 and the other at \vec{x}_2 and the state in which the other is at \vec{x}_1 and the first one at \vec{x}_2 are the same.

The concept of particles being identical means that they cannot be labeled as, e.g., classical billiard balls.

This poses a practical problem for our formalism, since we typically have to attach labels to our quantities. E.g. let

$$|\xi_1 \dots \xi_N\rangle$$

be the state vector of a system of N identical particles. The normalized wave function

$$\psi(\xi_1 \dots \xi_N) = \langle \xi_1 \dots \xi_N | \psi \rangle \quad (2.8)$$

now is a probability amplitude to find the first particle in state ξ_1 and the second in state ξ_2 , etc.

The property of the particles being identical now has to be implemented "by hand":

exchanging two identical particles should lead to the same state with the same probabilities.

Let π denote the permutation of N objects,

e.g. $N=3$: $\pi(1) = 3, \pi(2) = 1, \pi(3) = 2$,

then

$$|\xi_1 \xi_2 \dots \xi_N\rangle \quad \text{and} \quad |\xi_{\pi(1)} \xi_{\pi(2)} \dots \xi_{\pi(N)}\rangle \quad (2.9)$$

should describe the same physics. As only the probabilities described by these two states need be the same, the two states in (2.9) do not have to be equal, but only the following relation has to hold:

$$P(\pi) |\xi_1 \dots \xi_N\rangle = |\xi_{\pi(1)} \dots \xi_{\pi(N)}\rangle, \quad (2.10)$$

where $P(\pi)$ is unitary

$$P(\pi)^\dagger = P(\bar{\pi})^{-1} \quad (2.11)$$

(Unitarity implies probability conservation.)

By definition, no observable can distinguish between the left- and right-hand sides of (2.10)

Observables of the total system thus must be symmetric in, e.g., the coordinates of the particle coordinates. Typical observables are the total momentum or angular momentum,

$$\vec{P} = \sum_i \vec{P}_i, \quad \vec{L} = \sum_i \vec{L}_i \quad (2.12)$$

or a Hamilton - operator of the type

$$H = \frac{1}{2m} \sum_i \vec{P}_i^2 + \sum_{i < j} V(|x_i - x_j|) \quad (2.13)$$

For any symmetric operator A , we have

$$\langle \xi_1 \dots \xi_N | A | \xi_1 \dots \xi_N \rangle = \langle \xi_{\pi(1)} \dots \xi_{\pi(N)} | A | \xi_{\pi(1)} \dots \xi_{\pi(N)} \rangle$$

$$\stackrel{(2.10)}{=} \langle \xi_1 \dots \xi_N | P(\pi)^\dagger A P(\pi) | \xi_1 \dots \xi_N \rangle \quad (2.14)$$

As this holds for any state $|\xi_1 \dots \xi_N\rangle$, we have

$$A = P(\pi)^\dagger A P(\pi) \quad (2.15)$$

and with (2.11)

$$P(\bar{i}) A = A P(\bar{i}), \quad (2.16)$$

i.e. permutations and symmetric operators commute.

This implies that for any energy eigenstate $|\psi\rangle$

$$H(P|\psi\rangle) = PH|\psi\rangle = PE|\psi\rangle = E(P|\psi\rangle), \quad (2.17)$$

also $P|\psi\rangle$ is an energy eigenstate with the same energy eigenvalue. This degeneracy is typical for systems of identical particles. It is called "exchange degeneracy".

Let us study (2.10) for the simple case of two identical particles. Exchanging the particles twice trivially leads to the same state:

$$\begin{aligned} P_{(\bar{i})}^2 |\xi_1 \xi_2\rangle &= P_{(\bar{i})} |\xi_2 \xi_1\rangle = |\xi_1 \xi_2\rangle \\ &= |\xi_1 \xi_2\rangle \end{aligned} \quad (2.18)$$

i.e.

$$P_{(\bar{i})}^2 = \mathbb{1} \quad (2.19)$$

This implies that the eigenvalues of P are equal to ± 1 . The corresponding eigenstates are given by symmetric and antisymmetric combinations,

$$|\xi_1 \xi_2\rangle_S = |\xi_1 \xi_2\rangle + |\xi_2 \xi_1\rangle \quad (2.20)$$

$$|\xi_1 \xi_2\rangle_A = |\xi_1 \xi_2\rangle - |\xi_2 \xi_1\rangle$$

$$\Rightarrow P(\bar{1}12) |\xi_1 \xi_2\rangle_S = |\xi_1 \xi_2\rangle_S \quad (2.21)$$

$$P(\bar{1}12) |\xi_1 \xi_2\rangle_A = -|\xi_1 \xi_2\rangle_A$$

Now, it is an experimental fact that wave functions of two identical particles are always either symmetric or anti-symmetric, i.e. are always eigenfunctions of the permutation operator. If the wave function is antisymmetric

$$P(\bar{1}12) |\xi_1 \xi_2\rangle_A = -|\xi_1 \xi_2\rangle_A$$

we call the corresponding particles "fermions".

If the wave function is symmetric

$$P(\bar{\pi}_2) |\xi_1 \xi_2\rangle_S = |\xi_1 \xi_2\rangle_S$$

we are dealing with "bosons".

It turns out that the first case of fermions applies to particles with half-integer spin, such as electrons, protons, neutrons, He^3 -atoms, etc.

whereas the second case of bosons applies to integer-spin particles (π mesons, photons, He^4 atoms).

The underlying deep connection between spin and statistics (permutations of particles) can be explained within relativistic quantum field theory ("spin-statistics theorem"), but is beyond the scope of this lecture course.

These findings can straightforwardly be generalized to systems with more particles. In the case of bosons, any permutation leaves the

wave function invariant,

$$P(\pi) |\psi\rangle = |\psi\rangle, \quad \text{bosons} \quad (2.22)$$

whereas for fermions, we have

$$P(\pi) |\psi\rangle = \text{sign}(\pi) |\psi\rangle \quad (2.23)$$

where $\text{sign}(\pi) = 1$ if π consists of an even number of permutations and $\text{sign}(\pi) = -1$ for an odd number of permutations.

In the case of fermions, the antisymmetry of the wave function has an immediate consequence: from

$$\psi(\xi_1, \xi_2, \dots) = -\psi(\xi_2, \xi_1, \dots), \quad (2.24)$$

we deduce that

$$\psi(\xi_1, \xi_1, \dots) = 0 \quad (2.25)$$

This formalizes Pauli's exclusion principle: two identical fermions cannot be in the same quantum state.

2.3 Non-interacting identical particles

The exact treatment of systems of interacting particles is usually very difficult. In practice approximate methods such as perturbation theory etc. are used. In such cases the zeroth-order approximation is the non-interacting system.

Then, the Hamiltonian is just the sum of one-particle Hamiltonians,

$$H_0 = \sum_{i=1}^N H(i) \quad (2.26)$$

Let $|m_i\rangle$ denote the stationary states of the one-particle problem

$$H(i) |m_i\rangle = \epsilon_m |m_i\rangle, \quad (2.27)$$

with ϵ_m being the one-particle energy, then the full Hamiltonian is diagonalized by the product state

$$H |\psi\rangle = E |\psi\rangle \quad (2.28)$$

with $|\psi\rangle = |m_1 m_2 \dots m_N\rangle$

$$\text{and } E = \epsilon_1 + \epsilon_2 + \dots + \epsilon_N \quad (2.29)$$

Because of the exchange degeneracy, there are many solutions with the same energy. In particular, many product states arising from (2.29) by permutation

$$P(\pi) |m_1 \dots m_N\rangle \quad (2.30)$$

have the same energy as $|4\rangle$.

Now, for identical particles, we need to construct those solutions which are fully symmetric (for bosons) or anti-symmetric (for fermions).

For bosons, the symmetric wave function is obtained by summing over all permutations ($N!$ for N particles)

$$|m_1 \dots m_N\rangle_S \sim \sum_{\pi} |m_{\pi(1)} \dots m_{\pi(N)}\rangle \quad (2.31)$$

For fermions, the corresponding anti-symmetric state is obtained from

$$|m_1 \dots m_N\rangle_S = \frac{1}{\sqrt{N!}} \sum_{\pi} \text{sign}(\pi) |m_{\pi(1)} \dots m_{\pi(N)}\rangle \quad (2.32)$$

Let ξ_i collectively denote position and spin space, $\xi_i = \vec{x}_i s_i$, then also the projection of

(2.32) onto position and spin space is antisymmetric, ²⁷

$$\begin{aligned}\Psi_{n_1 \dots n_N}(\xi_1, \dots, \xi_N) &= \frac{1}{\sqrt{N!}} \sum_{\pi} \text{Sign}(\pi) \langle \xi_1, \dots, \xi_N | \psi_{n_1} \dots \psi_{n_N} \rangle \\ &= \frac{1}{\sqrt{N!}} \sum_{\pi} \text{Sign}(\pi) \psi_{n_{\pi(1)}}(\xi_1) \dots \psi_{n_{\pi(N)}}(\xi_N)\end{aligned}$$

(2.33)

This sum can also be represented as a determinant

$$\Psi_{n_1 \dots n_N}^{SD}(\xi_1, \dots, \xi_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_{n_1}(\xi_1) & \psi_{n_1}(\xi_2) & \dots & \psi_{n_1}(\xi_N) \\ \psi_{n_2}(\xi_1) & \psi_{n_2}(\xi_2) & & \\ \vdots & & \ddots & \\ \psi_{n_N}(\xi_1) & & & \psi_{n_N}(\xi_N) \end{pmatrix}$$

(2.34)

Slater determinant

Again, the exclusion principle is obvious as the determinant is zero if the matrix has a rank lower than N . This is automatically the case, if two sets of quantum numbers n_i, n_j are equal $n_i = n_j$. As this exclusion principle applies to the set of all quantum numbers including spin, each atomic energy level

can be filled by two electrons with opposite spin orientation (spin-up, spin-down).

2.4 Ideal Fermi gas

Due to the exclusion principle, already the ideal Fermi gas shows some interesting features different from an ideal classical gas.

The exclusion principle inhibits that all fermions in a gas sit in the ground state. Only a few fermions can occupy the states with minimal energy. So even if the gas is very cold ("ultra-cold"), some fermions will have comparatively high energy. The highest energy occurring in a Fermi gas at lowest possible temperature is called the Fermi energy E_F .

Let us assume the Fermi gas lives in a volume $V = L^3$
cubic

Ignoring surface as well as interaction effects, the eigenstates will be eigenstates of the free one-particle

Hamiltonian

$$H = \frac{\hat{p}^2}{2m} \quad (2.35)$$

i.e. plane waves:

$$\Psi_{\vec{k}}(\vec{x}, m_s) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{x}} |S m_s\rangle \quad (2.36)$$

with energy
$$E(\vec{k}) = \frac{\hbar^2}{2m} k^2 \quad (2.37)$$

Let the boundary conditions of the box be such that the wave function is periodic (the details of the boundary conditions are not so relevant in what follows); then the wave vectors are quantized:

$$\vec{k} = \frac{2\pi}{L} \vec{\nu}, \quad \vec{\nu} \in \mathbb{Z}^3 \quad (2.38)$$

The ket $|S m_s\rangle$ characterizes the spin state of the wave function with S being the quantum number of the total spin, say $S = \frac{1}{2}$ for electrons, and

$$m_s \in \{-S, -S+1, \dots, S\} \quad (2.39)$$

being the "magnetic" quantum number for the third component of the spin, i.e. $\pm \frac{1}{2}$ for electrons or protons. The measure for counting the number of possible states in S and k space

is thus given by:

$$\begin{aligned}
 dN &= (2s+1) dv_x dv_y dv_z \\
 &\stackrel{(2.38)}{=} (2s+1) \frac{L^3}{(2\pi)^3} d^3k \\
 &= (2s+1) \frac{V}{(2\pi)^3} d^3k \tag{2.40}
 \end{aligned}$$

The ground state of the ideal Fermi gas is characterized by the lowest-possible highest energy E_F , the Fermi energy. The corresponding momentum p_F or wave vector k_F

$$E_F = \frac{p_F}{2m} = \frac{\hbar^2 k_F^2}{2m} \tag{2.41}$$

is called Fermi momentum and separates the occupied states with $p < p_F$ from the unoccupied states with $p > p_F$ in momentum (or k space). In k space, this separating momentum is a surface (in 3d or a line in 2d) which is called the Fermi surface.

The Fermi energy etc can be computed from filling up all states for a given number of N fermions in a gas. First, we note that

$$d\varepsilon(k) = \frac{\hbar^2}{2m} 2k dk, \quad (2.42)$$

such that $(k = \sqrt{\frac{2m\varepsilon}{\hbar^2}})$

$$d^3k = \underbrace{d\Omega_k}_{\substack{\text{surface element} \\ \text{in } k \text{ space}}} k^2 dk = \frac{1}{2} d\Omega_k \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon} d\varepsilon$$

This yields for the measure (2.40) (number density) per volume:

$$\frac{dN}{V} = \frac{(2s+1)}{(2\pi)^3} \frac{1}{2} d\Omega_k \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon} d\varepsilon \quad (2.43)$$

Integrating over the directions in k space, we obtain the number density per volume and energy interval ($\int d\Omega_k = 4\pi$)

$$\frac{dN}{V} = \frac{2s+1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon} d\varepsilon =: \mathcal{D}(\varepsilon) d\varepsilon \quad (2.44)$$

where $D(\varepsilon)$ is called spectral density.

Integrating (2.44) with the total number of fermions N corresponding to the Fermi energy ε_F , we get:

$$\frac{N}{V} = \int_0^{\varepsilon_F} D(\varepsilon) d\varepsilon =: \left(\frac{\varepsilon_F}{\gamma} \right)^{3/2}, \quad \gamma = \left(\frac{6\pi^2}{2s+1} \right)^{2/3} \frac{\hbar^2}{2m}$$

where we introduced the constant γ . (2.45)

For electrons, we have

$$\gamma_e = (3\pi^2)^{2/3} \frac{\hbar^2}{2m} \simeq 0.3646 \dots \text{ eV nm}^2 \quad (2.46)$$

As we have neglected interactions and surface effects, the ideal Fermi gas is homogeneous inside the volume, such that $\frac{N}{V}$ is equal to the spatially constant density of fermions:

$$\Rightarrow \quad \varepsilon_F = \frac{p_F^2}{2m} = \gamma n^{2/3} \quad (2.47)$$

Fermi energy as well as Fermi momentum increase with increasing density.

The total energy per volume is obtained from

$$\frac{E}{V} = \int_0^{\epsilon_F} \epsilon D(\epsilon) d\epsilon = \frac{3}{5} \gamma n^{5/3}. \quad (2.48)$$

At zero temperature, this is identical to the internal energy of the gas:

$$\begin{aligned} U(T=0) &= E = \frac{E}{V} \cdot V = \frac{3}{5} \gamma n^{5/3} \cdot V \\ &\stackrel{(2.45)}{=} \frac{3}{5} \gamma n^{5/3} \cdot \frac{N}{\left(\frac{\epsilon_F}{\gamma}\right)^{3/2}} \stackrel{(2.47)}{=} \frac{3}{5} N \epsilon_F \quad (2.49) \end{aligned}$$

If we wish to compress a Fermi gas, we need to put energy into the system, as compression goes along with increasing the density, c.f. (2.48).

This is also reflected by the pressure that by simple thermodynamical relations follows from

$$\begin{aligned} P &= - \left(\frac{\partial U}{\partial V} \right)_N = - \frac{\partial}{\partial V} \left(\frac{3}{5} \gamma \underbrace{n^{5/3}}_{\left(\frac{N}{V}\right)^{5/3}} \cdot V \right)_N \\ &= \frac{2}{5} \gamma n^{5/3}. \quad (2.50) \end{aligned}$$

Let us apply these findings to atomic nuclei.

Scattering experiments with electrons tell us that nuclei show an approximately constant proton density, which can be approximated by the core density

$$\rho_{\text{nucl.}} \approx n(r=0) \approx 0.17 \frac{\text{Nucleons (protons + neutrons)}}{(10^{-15} \text{ m})^3} \quad (2.51)$$

Furthermore ignoring interactions, we can approximate the nuclei by an ideal Fermi gas. As the volume of the nuclei scales roughly with the mass number A (number of protons + number of neutrons),

with $N \approx Z \approx \frac{A}{2}$ (proton and neutron gases have to be treated separately), we find for the maximum energy,

$$\begin{aligned} \mathcal{E}_F &= \gamma_{\text{proton, neutron}} \overset{2/3}{m} \approx 37 \text{ MeV} \\ &= \frac{1}{2} \rho_{\text{nucl.}} \end{aligned} \quad (2.52)$$

which is small compared to the the nucleus's rest mass of $\approx 1 \text{ GeV}$. As also the

excitation energies of a nucleus are of order \sim GeV, small nuclei can be considered as a strongly degenerate Fermi gas. Effects from transmuting kinetic energy into excitations can only be expected for larger nuclei, as the total kinetic energy is

$$E = \frac{3}{5} \left(\frac{A}{2} \epsilon_F^m + \frac{A}{2} \epsilon_F^p \right) = \frac{3}{5} A \epsilon_F \quad (2.53)$$

For $A \geq 50$ this becomes of order GeV.

2.5 Hartree-Fock Approximation

The Hartree-Fock method is an approximation technique to determine the ground state of a many-body quantum system. It is built on the Rayleigh-Ritz variational principle. To remind you of the latter, consider the expectation value of the Hamiltonian with respect to a state $|\Psi\rangle$ as a functional of $|\Psi\rangle$: normalized

$$E[\Psi] := \langle \bar{\Psi} | H | \bar{\Psi} \rangle \quad (2.54)$$

The energy functional is minimized by definition by the ground state. In turn, for a set of trial states $\bar{\Psi}_i$, $i=1, \dots$, the state

$$\Psi_{\min} = \min_i E[\bar{\Psi}_i] \quad (2.55)$$

gives the best approximation of the ground state energy among the set of trial states.

The difficulty in using the variational principle in practice consists in finding an appropriate set of trial states.

The Hartree-Fock approximation starts from

the assumption that the ground state of a many-body state can be "sufficiently-well" approximated by a product state of one-particle states. This is in general not true, but in practice results in quantitatively satisfactory results for ground state energies. The reason is, roughly speaking, that this approximation is able to take the essential part of the interparticle interaction into account.

For fermionic many-body systems, the trial state is written as a Slater determinant

$$\Psi^{SD}(\xi_1, \dots, \xi_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(\xi_1) & \psi_1(\xi_2) & \dots & \psi_1(\xi_N) \\ \psi_2(\xi_1) & \psi_2(\xi_2) & \dots & \psi_2(\xi_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\xi_1) & \psi_N(\xi_2) & \dots & \psi_N(\xi_N) \end{pmatrix}, \quad (2.56)$$

where the functions $\psi_i(\xi_j)$ are one-particle wave functions to be determined by a suitable algorithmic scheme, that preserves the orthonormality property of the wave functions ψ_i .

As a concrete example, we consider a many-electron atom (a many-electron system in a central potential V_c),

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i=1}^N V_c(\vec{x}_i) + V_{ee} \quad (2.57)$$

where

$$V_c(\vec{x}_i) = -\frac{Ze^2}{r_i} \quad , \quad r_i = |\vec{x}_i| \quad (2.58)$$

and

$$V_{ee} = \frac{e^2}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \quad (2.59)$$

denotes the inter-electron potential with

$$r_{ij} = |\vec{x}_i - \vec{x}_j| \quad (2.60)$$

being a two-particle operator.

In this case, ξ_i represents position and spin of the electrons: $\xi_i \hat{=} (\vec{x}_i, m_i)$, $m_i = \pm \frac{1}{2}$.

Using the orthonormality of the one-particle wave functions

$$\begin{aligned} \int d\xi_i \psi_j(\xi_i) \psi_u(\xi_i) &= \delta_{ju} \\ &= \sum_{m_i} \int d^3x_i \end{aligned}$$

and $(\text{sign}(u))^2 = 1$ (2.61)

it is easy to see that the expectation value of one-particle operators such as the kinetic and central-potential term in (2.57) with respect to the Slater determinant boil down to the sum ^{over} expectation values ~~in~~ in each one-particle sector:

$$\begin{aligned} & \langle \Psi^{SD} | \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} | \Psi^{SD} \rangle \\ &= \frac{\hbar^2}{2m} \sum_{i=1}^N \sum_{m=\pm\frac{1}{2}} \int d^3x |\nabla \psi_i(\vec{x}, m)|^2 \end{aligned} \quad (2.62)$$

and $\langle \Psi^{SD} | V_c | \Psi^{SD} \rangle$

$$= -Ze^2 \sum_{i=1}^N \sum_{m=\pm\frac{1}{2}} \int d^3x \frac{|\psi_i(\vec{x}, m)|^2}{r} \quad (2.63)$$

In order to understand the expectation value of V_{ee} w.r.t Ψ^{SD} , let us write Ψ^{SD} as, c.f. (2.33)

$$\Psi^{SD} = \frac{1}{\sqrt{N!}} \sum_{\pi} \text{sign}(\pi) \psi_{\pi(1)}(\xi_1) \dots \psi_{\pi(N)}(\xi_N) \quad (2.64)$$

The two-particle operator r_{ij} (2.60) in V_{ee} now acts on the one-particle wave functions with corresponding arguments ξ_i and ξ_j , i.e.

$$V_{ee} \Psi^{SD} = \frac{e^2}{2} \frac{1}{\sqrt{N!}} \sum_{i \neq j} \sum_{\pi} \text{sign}(\pi) \frac{1}{r_{ij}} \Psi_{\pi(i)}(x_i, m_i) \Psi_{\pi(j)}(x_j, m_j) \prod_{k \notin \{i, j\}} \Psi_{\pi(k)}(x_k, m_k) \quad (2.65)$$

In the expectation value $\langle \Psi^{SD} | V_{ee} | \Psi^{SD} \rangle$, only identical permutations contribute due to orthogonality of the $\Psi_{\pi(k)}$, except for a possible exchange of i and j ; (in total, these are $(N-2)!$ permutations)

Let $\pi(i) = q, \pi(j) = p$, then

$$\langle \Psi^{SD} | V_{ee} | \Psi^{SD} \rangle = \frac{e^2}{2} \frac{(N-2)!}{N!} \sum_{P \neq q} \sum_{m, m'} \sum_{i \neq j} \int d^3x \int d^3x' \left[\Psi_q^\dagger(x, m) \Psi_p^\dagger(x', m') \frac{1}{|x-x'|} \Psi_q(x, m) \Psi_p(x', m') - \Psi_p^\dagger(x, m) \Psi_q^\dagger(x', m') \frac{1}{|x-x'|} \Psi_q(x, m) \Psi_p(x', m') \right] \quad (2.66)$$

As all terms depend trivially on the spin state m , we define a mean kinetic energy and charge density of the i 'th one-particle state,

$$t_i(\vec{x}) = \frac{\hbar^2}{2m} \sum_m |\nabla \psi_i(\vec{x}, m)|^2 \quad (2.67)$$

$$n_i(\vec{x}) = \sum_m |\psi_i(\vec{x}, m)|^2$$

With these abbreviations, the expectation value of the Hamiltonian reads

$$\begin{aligned} \langle \psi^{SD} | H | \psi^{SD} \rangle = & \sum_i \int_{\vec{x}} \left(t_i(\vec{x}) - Z e^2 \frac{n_i(\vec{x})}{r} \right) \\ & + \frac{e^2}{2} \sum_{i \neq j} \int_{\vec{x}, \vec{y}} \frac{n_i(\vec{x}) n_j(\vec{y})}{|\vec{x} - \vec{y}|} - A, \end{aligned} \quad (2.68)$$

where A is the "exchange energy"

$$A = \frac{e^2}{2} \sum_{i \neq j, m, m'} \int_{\vec{x}, \vec{y}} \frac{\psi_j^\dagger(\vec{x}, m) \psi_j(\vec{y}, m) \psi_i^\dagger(\vec{y}, m') \psi_i(\vec{x}, m')}{|\vec{x} - \vec{y}|} \quad (2.69)$$

Whereas the first three terms could as well be interpreted as the energy of classical electron clouds in a central potential with self-interactions, the exchange energy is a pure quantum phenomenon of identical particles.

Finally $\langle \psi^{SD} | H | \psi^{SD} \rangle$ has to be minimized under the constraint that

$$\langle \psi^{SD} | \psi^{SD} \rangle = 1. \quad (2.70)$$

The variation of $\langle \psi^{SD} | H | \psi^{SD} \rangle$ yields

$$\delta \langle \psi^{SD} | H | \psi^{SD} \rangle =$$

$$\sum_{i,m} \int d^3x \delta \psi_i^\dagger(x,m) \left\{ \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} + e^2 \sum_{j \neq i} \int d^3y \frac{m_j(\vec{y})}{|\vec{x}-\vec{y}|} \right) \psi_i(x,m) \right. \\ \left. - e^2 \sum_{j \neq i, m'} \int d^3y \frac{\psi_i(\vec{y}, m') \psi_j^\dagger(\vec{y}, m')}{|\vec{x}-\vec{y}|} \psi_j(x,m) \right\} \quad (2.71)$$

Implementing the constraint (2.70) by means of a Lagrange multiplier ϵ_i for every one particle component ψ_i , we obtain the Hartree-Fock equations

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} + e^2 \sum_{j \neq i} \int d^3y \frac{m_j(\vec{y})}{|\vec{x}-\vec{y}|} - \epsilon_i \right) \psi_i(\vec{x}, m) \\ = e^2 \sum_{j \neq i, m'} \int d^3y \frac{\psi_i(\vec{y}, m') \psi_j^\dagger(\vec{y}, m')}{|\vec{x}-\vec{y}|} \psi_j(\vec{x}, m), \quad i=1, \dots, N \quad (2.72)$$

(The Lagrange multipliers ϵ_i acquire the meaning of one-particle energies).

These equations are coupled non-linear integro-differential equations which are difficult to solve (hardly any non-trivial solutions are known).

In practice, a good strategy towards the solution is a numerical iteration.

As zeroth-order solution, one typically chooses one-particle eigenstates of hydrogen-like atoms (with charge Z), computes the \vec{y} integrals and then solves numerically for $\psi_i(\vec{x}_i, m)$. The latter constitutes the next-order solution which is plugged into the \vec{y} integrals and so on... (hoping for convergence)

For light atoms, the strategy works very well. An application to heavy atoms is numerically very expensive.

3 Summation of angular momentum

For systems with rotational invariance, the total angular momentum is conserved. In the case of many-particle systems (e.g. atoms), the total angular momentum can consist of the angular momenta of the single-particle subsystems. Even for one-particle system, the total angular momentum can consist of, say, an orbital angular momentum \vec{L} and a spin \vec{S} , $\vec{J} = \vec{L} + \vec{S}$. Hence, we have to learn how to add angular momenta. This is not as easy in quantum mechanics as in classical mechanics (where only classical 3-vectors have to be added), but the combination of different state spaces have to be mapped onto the state space of the total angular momentum.

3.1 Special properties of angular momentum

Let us first recall basic facts about angular momentum, as known from QM 1. The components of angular momentum satisfy

$$[J_i, J_j] = i\hbar \epsilon_{ijk} J_k \quad (3.1)$$

In the following, we will choose the convention $\hbar = 1$ for notational simplicity.

The maximum set of compatible operators consists, for instance, of \vec{J}^2 and J_z with corresponding eigenvalue equations

$$\begin{aligned} \vec{J}^2 |jm\rangle &= j(j+1) |jm\rangle & , j \in \frac{1}{2}\mathbb{N}_0 \\ J_z |jm\rangle &= m |jm\rangle & , m = -j, \dots, j \end{aligned} \quad (3.2)$$

The eigenstates can be generated from the ladder operators

$$J_{\pm} = J_x \pm iJ_y, \quad J_-^{\dagger} = J_+ \quad (3.3)$$

which act on the eigenstates as follows

$$\begin{aligned} J_{\pm} |jm\rangle &= C_{jm}^{\pm} |j, m \pm 1\rangle \\ \text{where } C_{jm}^{\pm} &= \sqrt{j(j+1) - m(m \pm 1)} \end{aligned} \quad (3.4)$$

The quantum number j classifies the $(2j+1)$ -dimensional irreducible representation of the angular momentum algebra. Let us denote the representation space as \mathfrak{h}_j ,