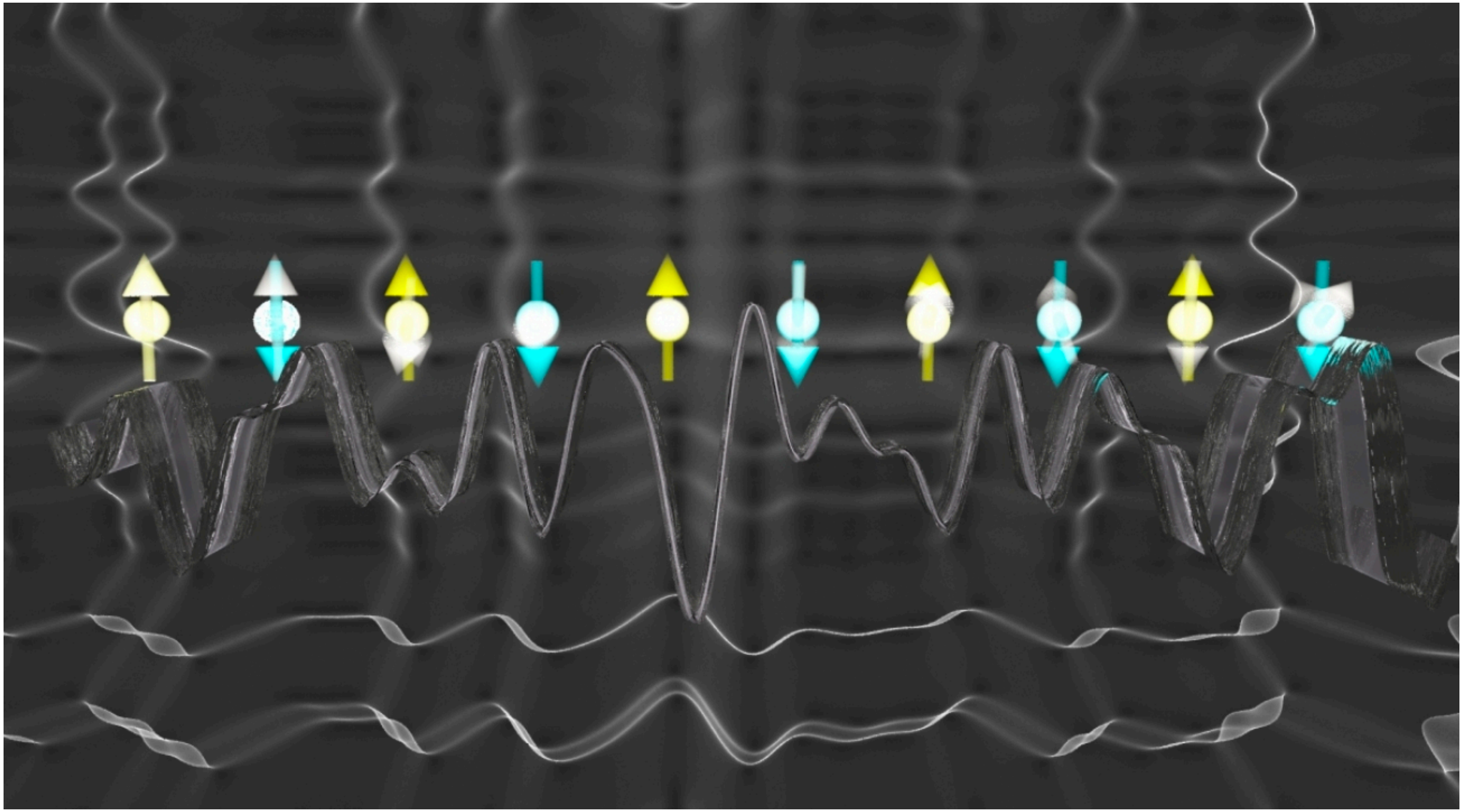
Quantum mechanics

Chapter VI Many-Particle Systems



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Consider a system consisting of N particles with masses m_1, m_2 , m_3 , ..., m_N . Let r_j , j = 1, 2, 3, ..., N, be the position vector of the jth particle. The wave function of such a system will depend on the position vectors of all the particles and time:

$$\psi = \psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_N, t).$$

The Schrödinger equation for this N-particle system is written as

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_N, t),$$

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where the Hamiltonian H is given by

$$\hat{H} = -\sum_{j=1}^{N} \frac{\hbar^2}{2m_j} \vec{\nabla}_j^2 + V(\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_N).$$

Here, $V(r_1, r_2, r_3, ..., r_N)$ is the potential energy of the system, and the Laplace operator with respect to the coordinates of the jth particle is

$$\vec{\nabla}_j^2 = \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2}.$$

In analogy with the single-particle case, the quantity

$$|\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_N, t)|^2 d\tau_1 d\tau_2 d\tau_3 ... d\tau_N,$$

is interpreted as the probability, at a given instant t, of finding the particle 1 in the infinitesimal volume element $d\tau_1$, particle 2 in the infinitesimal volume element $d\tau_2$, and so on,

Therefore, as earlier, the normalization for the wave function is written as

$$\int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2 \int_{-\infty}^{+\infty} d\tau_3 \ldots \int_{-\infty}^{+\infty} d\tau_N |\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N, t)|^2 = 1.$$

If the potential, V, is time independent, the stationary states of an N-particle system are characterized by the wave functions of the form

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N, t) = \phi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N) e^{-\frac{i}{\hbar}Et},$$

where E is the total energy of the system and the function ϕ satisfies the following time independent Schrödinger equation

$$-\sum_{j=1}^{N}\frac{\hbar^2}{2m_j}\vec{\nabla}_j^2\phi(\vec{r}_1,...,\vec{r}_N)+V(\vec{r}_1,...,\vec{r}_N)\phi(\vec{r}_1,...,\vec{r}_N)=E\phi(\vec{r}_1,...,\vec{r}_N).$$

The expectation value of operator, A

$$\langle\psi|\hat{A}|\psi\rangle=\int_{-\infty}^{+\infty}\phi^*(\vec{r}_1,...,\vec{r}_N)\,\hat{A}\,\phi(\vec{r}_1,...,\vec{r}_N)\,d\tau_1 d\tau_2 d\tau_3...d\tau_N,$$

The operators representing observables related to different particles commute, while those related to a given particle satisfy the commutation relations valid for a single-particle system.

For instance, the position and momentum operators satisfy the following commutation relations

$$[(\hat{r}_\alpha)_k, (\hat{p}_\beta)_\ell] = i\hbar\delta_{k\ell}\delta_{\alpha\beta},$$

where the Roman indices, k, l,..., stand for the particle's number (1,2,3,...,N) in the system, while the Greek indices $\alpha,\beta,\ldots$, represent the Cartesian components of the position vector, r, and momentum, p.

In summary, the coordinate and momentum operators of different particles commute, while the coordinate and momentum operators of the same particle satisfy the usual single-particle commutation relations.

When the particles belonging to a quantum mechanical system do not interact among themselves and are subject solely to an externally applied potential, they are called independent.

For such a system, the potential can be written as

$$V(\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_N) = \sum_{j=1}^{N} V_j(\vec{r}_j),$$

If, in addition, the particles can be distinguished from each other in terms of one or several individual properties, they are called distinguishable. The system of particles is then said to be consisting of distinguishable independent particles.

The separation of variables leading to N independent single-particle Schrödinger equations

$$-\frac{\hbar^2}{2m_j}\vec{\nabla}_j^2\phi(\vec{r}_j)+V(\vec{r}_j)\phi_j(\vec{r}_j)=E_j\phi_j(\vec{r}_j), \qquad j=1,2,3,...,N.$$

The stationary state wave function of the system is then given by the product of the single-particle wave functions

$$\psi(\vec{r}_1,...,\vec{r}_N,t)=\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\phi_3(\vec{r}_3)...\phi_N(\vec{r}_N)\ e^{-\frac{i}{\hbar}(E_1+E_2+E_3+...+E_N)t}$$

$$=\left(\prod_{j=1}^{N}\phi_j(\vec{r}_j)\right)\ e^{-\frac{i}{\hbar}Et},$$

with energy

$$E=E_1+E_2+E_3+...+E_N=\sum_{j=1}^{N}E_j.$$

Let all the particles constituting the system be identical, that is, they all have the same physical characteristics.

In classical mechanics, these particles, despite being identical, may be distinguished from each other.

There is no way to distinguish between identical particles in quantum mechanics. Clearly, identical particles are inevitably indistinguishable in quantum mechanics.

let us define the so-called permutation operator P_{jk}, which interchanges the particles that are at the positions r_j and r_k.

$$\hat{P}_{jk}\phi(\vec{r}_1,\vec{r}_2,\ldots,\underbrace{\vec{r}_j,\ldots,\vec{r}_k},\ldots,\vec{r}_N) = \phi(\vec{r}_1,\vec{r}_2,\ldots,\underbrace{\vec{r}_k,\ldots,\vec{r}_j},\ldots,\vec{r}_N).$$

Since the particles are indistinguishable, no experiment can determine which of the particles of the system is at r_j and which one is at r_k. The probability density, therefore, should remain unchanged, that is,

$$|\phi(\vec{r}_1,\vec{r}_2,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N)|^2 = |\phi(\vec{r}_1,\vec{r}_2,...,\vec{r}_k,...,\vec{r}_j,...,\vec{r}_N)|^2.$$

This, in turn, gives

$$\phi(\vec{r}_1,\vec{r}_2,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N) = \pm\phi(\vec{r}_1,\vec{r}_2,...,\vec{r}_k,...,\vec{r}_j,...,\vec{r}_N).$$

As a consequence, the wave function of a system of N identical particles can either be symmetric or anti-symmetric with respect to the interchange of any pair of particles of the system.

In nature, as confirmed by experiments, particles with integer spin have symmetric wave functions, while the particles with half-odd integer spin are characterized by the anti-symmetric wave functions.

The Hamiltonian of a system of N identical particles is a sum of the kinetic energy operators and the potential energy operators of all the particles

$$\hat{H}(\vec{r}_1,\vec{r}_2,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N)=\sum_{j=1}^{N}\frac{\hat{\vec{p}}_j^2}{2m}+\hat{V}(\vec{r}_1,\vec{r}_2,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N)$$

If we exchange any pair of particles, say the jth and the kth, the potential energy must remain unchanged, that is,

$$\hat{V}(\vec{r}_1,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N) \rightarrow \hat{V}(\vec{r}_1,...,\vec{r}_k,...,\vec{r}_j,...,\vec{r}_N) = \hat{V}(\vec{r}_1,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N).$$

If it is not so, the particles will be distinguishable and that will contradict the quantum mechanical assertion that identical particles are indistinguishable.

Consider the eigenvalue problem

$$\hat{H}(\vec{r}_1,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N)\phi(\vec{r}_1,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N) = E\phi(\vec{r}_1,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N).$$

The wave functions corresponding to all possible permutations of particles of the system will have one and the same energy E. That is, the eigenstates of the Hamiltonian are degenerate. This is called the exchange degeneracy.

Furthermore, we have

$$\hat{H}\hat{P}_{jk}\phi(\vec{r}_1,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N)=\hat{H}\phi(\vec{r}_1,...,\vec{r}_k,...,\vec{r}_j,...,\vec{r}_N)$$

$$=E\phi(\vec{r}_1,...,\vec{r}_k,...,\vec{r}_j,...,\vec{r}_N)=E\hat{P}_{jk}\phi(\vec{r}_1,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N)$$

$$=\hat{P}_{jk}E\phi(\vec{r}_1,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N)=\hat{P}_{jk}\hat{H}\phi(\vec{r}_1,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N).$$

In other words,

$$(\hat{H}\hat{P}_{jk}-\hat{P}_{jk}\hat{H})\phi(\vec{r}_1,...,\vec{r}_j,...,\vec{r}_k,...,\vec{r}_N)=0.$$

The last equation shows that the operator P_{jk} commutes with the Hamiltonian

$$(\hat{H}\hat{P}_{jk}-\hat{P}_{jk}\hat{H})\equiv[\hat{H},\hat{P}_{jk}]=0.$$

It means that the symmetry property of the wave function of a system of N identical particles is conserved in time

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Let $\phi_{n1}(\xi_1)$, $\phi_{n2}(\xi_2)$, $\phi_{n3}(\xi_3)$,…, $\phi_{nN}(\xi_N)$ be the normalized single- particle wave functions, where each of the indices n_1, n_2, n_3 ,…, n_N stands for the total set of quantum numbers relevant to the problem at hand. We shall assume, for now, that n_1, n_2, n_3,…,n_N are all different.

The symmetric and the anti-symmetric wave functions, $\phi_s(\xi_1, \xi_2, \xi_3,…, \xi_N)$ and $\phi_a(\xi_1, \xi_2, \xi_3, …, \xi_N)$ respectively, of the system of N identical and indistinguishable particles are written as

$$\phi_s(\xi_1, \xi_2, \xi_3, ..., \xi_N) = \frac{1}{\sqrt{N!}} \sum_P P\{\phi_{n_1}(\xi_1)\phi_{n_2}(\xi_2)\phi_{n_3}(\xi_3)...\phi_N(\xi_N)\},$$

$$\phi_a(\xi_1, \xi_2, \xi_3, ..., \xi_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P\{\phi_{n_1}(\xi_1)\phi_{n_2}(\xi_2)\phi_{n_3}(\xi_3)...\phi_N(\xi_N)\}$$

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where the sum stands for the summation over all possible permutations (N! in all) of the particles.

It is worth noting that in the case of the anti-symmetric wave function, $(-1)^P = +1$, if $(\xi_1, \xi_2, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N)$ (resulting from the interchange of the ith and the jth particles) is an even permutation of $(\xi_1, \xi_2, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N)$, while $(-1)^P = -1$, if $(\xi_1, \xi_2, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N)$ is an odd permutation of $(\xi_1, \xi_2, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N)$.

According to this prescription, the symmetric wave function for a system of two indistinguishable particles assumes the form

$$\phi_s(\xi_1,\xi_2) = \frac{1}{\sqrt{2}}\left[\phi_{n_1}(\xi_1)\phi_{n_2}(\xi_2) + \phi_{n_1}(\xi_2)\phi_{n_2}(\xi_1)\right],$$

while the anti-symmetric wave function for the same system can be written as

$$\phi_a(\xi_1,\xi_2) = \frac{1}{\sqrt{2}}\left[\phi_{n_1}(\xi_1)\phi_{n_2}(\xi_2) - \phi_{n_1}(\xi_2)\phi_{n_2}(\xi_1)\right].$$

The factor in these formulae, comes from normalization of the two-particle wave function

Similarly, for a three-particle system, the symmetric wave function has the form

$$\phi_s(\xi_1,\xi_2,\xi_3) = \frac{1}{\sqrt{3!}}\,[\phi_{n_1}(\xi_1)\phi_{n_2}(\xi_2)\phi_{n_3}(\xi_3)+\phi_{n_1}(\xi_2)\phi_{n_2}(\xi_3)\phi_{n_3}(\xi_1)$$
$$+\,\phi_{n_1}(\xi_3)\phi_{n_2}(\xi_1)\phi_{n_3}(\xi_2)+\phi_{n_1}(\xi_1)\phi_{n_2}(\xi_3)\phi_{n_3}(\xi_2)$$
$$+\,\phi_{n_1}(\xi_3)\phi_{n_2}(\xi_2)\phi_{n_3}(\xi_1)+\phi_{n_1}(\xi_2)\phi_{n_2}(\xi_1)\phi_{n_3}(\xi_3)],$$

while the anti-symmetric wave function for the three-particle system can be written as

$$\phi_a(\xi_1,\xi_2,\xi_3) = \frac{1}{\sqrt{3!}}\,[\phi_{n_1}(\xi_1)\phi_{n_2}(\xi_2)\phi_{n_3}(\xi_3)+\phi_{n_1}(\xi_2)\phi_{n_2}(\xi_3)\phi_{n_3}(\xi_1)$$
$$+\,\phi_{n_1}(\xi_3)\phi_{n_2}(\xi_1)\phi_{n_3}(\xi_2)-\phi_{n_1}(\xi_1)\phi_{n_2}(\xi_3)\phi_{n_3}(\xi_2)$$
$$-\,\phi_{n_1}(\xi_3)\phi_{n_2}(\xi_2)\phi_{n_3}(\xi_1)-\phi_{n_1}(\xi_2)\phi_{n_2}(\xi_1)\phi_{n_3}(\xi_3)].$$

The anti-symmetric wave functions can also be written as determinants:

$$\phi_a(\xi_1,\xi_2)=\frac{1}{\sqrt{2}}\begin{vmatrix}\phi_{n_1}(\xi_1) & \phi_{n_1}(\xi_2)\\ \phi_{n_2}(\xi_1) & \phi_{n_2}(\xi_2)\end{vmatrix},$$

$$\phi_a(\xi_1,\xi_2,\xi_3)=\frac{1}{\sqrt{3!}}\begin{vmatrix}\phi_{n_1}(\xi_1) & \phi_{n_1}(\xi_2) & \phi_{n_1}(\xi_3)\\ \phi_{n_2}(\xi_1) & \phi_{n_2}(\xi_2) & \phi_{n_2}(\xi_3)\\ \phi_{n_3}(\xi_1) & \phi_{n_3}(\xi_2) & \phi_{n_3}(\xi_3)\end{vmatrix}.$$

Pauli Exclusion Principle

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In general, the N-particle anti-symmetric wave function can be written as

$$\phi_a(\xi_1, \xi_2, \xi_3, ..., \xi_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{n_1}(\xi_1) & \phi_{n_1}(\xi_2) & \cdots & \phi_{n_1}(\xi_N) \\ \phi_{n_2}(\xi_1) & \phi_{n_2}(\xi_2) & \cdots & \phi_{n_2}(\xi_N) \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \phi_{n_N}(\xi_1) & \phi_{n_N}(\xi_2) & \cdots & \phi_{n_N}(\xi_N) \end{vmatrix}.$$

This is known as the Slater determinant. Note that interchanging any two identical particles is equivalent to interchanging the corresponding columns of the Slater determinant. From the properties of the determinants, we know that interchanging two columns of a determinant results in the multiplication of the determinant by (−1).

Pauli Exclusion Principle

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What will be the expressions for the functions ϕ_s and ϕ_a when some (or may be all) of n_j, j = 1,2,3,...,N coincide?

If some of these n_j coincide, then we have to avoid double counting. For instance, if n_1 occurs m_1 times, n_2 occurs m_2 times, ..., n_N occurs m_N times, then the total number of distinct permutation of N indices will be

$$P = \frac{N!}{m_1!m_2!m_3!...m_N!},$$

and hence, the symmetric wave function of the system will be

$$\phi_s(\xi_1,...,\xi_N) = \sqrt{\frac{m_1!m_2!m_3!...m_N!}{N!}} \sum_P \hat{P}\left\{\phi_{n_1}(\xi_1)\phi_{n_2}(\xi_2)...\phi_{n_N}(\xi_N)\right\}.$$

Pauli Exclusion Principle

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For anti-symmetric wave function, all n_j have to be different, otherwise the wave function will vanish.

In a system of N identical fermions, no two fermions can occupy the same single-particle state at a time; every single-particle state can be occupied by (at most) one fermion only. This is known as the Pauli exclusion principle.

Note that ξ includes spatial as well as spin variables. The wave function of a particle is written as a product of the spatial and the spin parts

$$\phi(\xi) = \phi(\vec{r}, \vec{S}) = \phi(\vec{r})\chi(\vec{S}).$$

Pauli Exclusion Principle

Generalizing it to the system of N identical particles, we have

$$\phi(\vec{r}_1, ..., \vec{r}_N, \vec{S}_1, ..., \vec{S}_N) = \phi(\vec{r}_1, ..., \vec{r}_N)\,\chi(\vec{S}_1, ..., \vec{S}_N).$$

In the case of identical bosons, when the wave function must be symmetric, the spatial and the spin parts must have the same parity, that is, they are both either symmetric or anti-symmetric. Thus,

$$\phi_s(\vec{r}_1, ..., \vec{r}_N, \vec{S}_1, ..., \vec{S}_1) = \begin{cases} \phi_s(\vec{r}_1, ..., \vec{r}_N)\,\chi_s(\vec{S}_1, ..., \vec{S}_N) \\ \phi_a(\vec{r}_1, ..., \vec{r}_N)\,\chi_a(\vec{S}_1, ..., \vec{S}_N), \end{cases}$$

where the suffixes s and a stand for the symmetric and the anti-symmetric wave functions, respectively.

Pauli Exclusion Principle

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For a system of N identical fermions, the wave function must be overall anti-symmetric and, therefore, the spatial and the spin parts of the wave function must have opposite parities, that is, if one of them is symmetric, the other has to be anti-symmetric, and vice versa. Thus,

$$\phi_a(\vec{r}_1,...,\vec{r}_N,\vec{S}_1,...,\vec{S}_1) = \begin{cases} \phi_s(\vec{r}_1,...,\vec{r}_N)\,\chi_a(\vec{S}_1,...,\vec{S}_N) \\ \phi_a(\vec{r}_1,...,\vec{r}_N)\,\chi_s(\vec{S}_1,...,\vec{S}_N). \end{cases}$$

$$\chi_a = \frac{1}{\sqrt{2}}\left\{\uparrow_1\downarrow_2 - \uparrow_2\downarrow_1\right\} m_s = 0;\ S=0,\ \text{singlet state}$$

$$\chi_s = \begin{bmatrix} \uparrow_1\uparrow_2 & m_s = 1 \\ \frac{1}{\sqrt{2}}\left\{\uparrow_1\downarrow_2 + \uparrow_2\downarrow_1\right\} & m_s = 0 \\ \downarrow_1\downarrow_2 & m_s = -1 \end{bmatrix};\ S=1,\ \text{triplet state}$$

The Hamiltonian for the one-dimensional harmonic oscillator (a particle of mass m attached to a spring) is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2\hat{x}^2,$$

Let us introduce the following operators

$$\hat{a} = \frac{1}{\sqrt{2m\hbar\omega}}(i\hat{p} + m\omega\hat{x}), \qquad \hat{a}^\dagger = \frac{1}{\sqrt{2m\hbar\omega}}(-i\hat{p} + m\omega\hat{x}).$$

Consider the product

$$\hat{a}\hat{a}^\dagger = \frac{1}{2m\hbar\omega}(i\hat{p} + m\omega\hat{x})(-i\hat{p} + m\omega\hat{x}) = \frac{1}{2m\hbar\omega}(\hat{p}^2 + m^2\omega^2\hat{x}^2 - im\omega[\hat{x},\hat{p}])$$

$$= \frac{1}{2m\hbar\omega}(\hat{p}^2 + m^2\omega^2\hat{x}^2 + m\hbar\omega) = \frac{1}{\hbar\omega}\left(\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega\hat{x}^2\right) + \frac{1}{2} = \frac{\hat{H}}{\hbar\omega} + \frac{1}{2}$$

We get that

$$\hat{H} = \hbar\omega\left(\hat{a}\hat{a}^\dagger - \frac{1}{2}\right).$$

Similarly, we have

$$\hat{a}^\dagger\hat{a} = \frac{1}{2m\hbar\omega}(-i\hat{p} + m\omega\hat{x})(i\hat{p} + m\omega\hat{x}) = \frac{1}{2m\hbar\omega}(\hat{p}^2 + m^2\omega^2\hat{x}^2 + im\omega[\hat{x},\hat{p}])$$
$$= \frac{1}{2m\hbar\omega}(\hat{p}^2 + m^2\omega^2\hat{x}^2 - m\hbar\omega) = \frac{1}{\hbar\omega}\left(\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega\hat{x}^2\right) - \frac{1}{2} = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2}$$

and

$$\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)$$

The following commutation relation between a and a+

$$[\hat{a},\hat{a}^\dagger] = 1.$$

Second quantization

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The Schrödinger equation is completely equivalent to any of the following equations

$$\hbar\omega\left(\hat{a}^{\dagger}\hat{a}+\frac{1}{2}\right)\phi=E\phi,\quad \text{or}\quad \hbar\omega\left(\hat{a}\hat{a}^{\dagger}-\frac{1}{2}\right)\phi=E\phi.$$

Assume that ϕ_n is an eigenfunction of the Hamiltonian H with energy E_n. Then, $a^+\phi_n$ is an eigenfunction of the Hamiltonian with energy ($E_n+\hbar\omega$).

$$\hat{H}\hat{a}^{\dagger}\phi_n=\hbar\omega\left(\hat{a}^{\dagger}\hat{a}+\frac{1}{2}\right)\hat{a}^{\dagger}\phi_n=\hbar\omega\left(\hat{a}^{\dagger}\hat{a}\hat{a}^{\dagger}+\frac{1}{2}\hat{a}^{\dagger}\right)\phi_n$$

$$=\hbar\omega\left\{\hat{a}^{\dagger}\left(1+\hat{a}^{\dagger}\hat{a}\right)+\frac{1}{2}\hat{a}^{\dagger}\right\}=\hat{a}^{\dagger}\left[\hbar\omega\left(\hat{a}^{\dagger}\hat{a}+\frac{1}{2}\right)\phi_n+\hbar\omega\phi_n\right]$$

$$=\hat{a}^{\dagger}\left[\hat{H}\phi_n+\hbar\omega\phi_n\right]=\hat{a}^{\dagger}\left[E_n\phi_n+\hbar\omega\phi_n\right]=\left(E_n+\hbar\omega\right)\hat{a}^{\dagger}\phi_n.$$

Second quantization

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Similarly

$$\hat{H}\hat{a}\phi_n = \hbar\omega\left(\hat{a}\hat{a}^\dagger - \frac{1}{2}\right)\hat{a}\phi_n = \hbar\omega\left(\hat{a}\hat{a}^\dagger\hat{a} - \frac{1}{2}\hat{a}\right)\phi_n$$

$$= \hbar\omega\left\{\hat{a}\left(\hat{a}\hat{a}^\dagger - 1\right) - \frac{1}{2}\hat{a}\right\}\phi_n = \hat{a}\left[\hbar\omega\left(\hat{a}\hat{a}^\dagger - \frac{1}{2}\right)\phi_n - \hbar\omega\phi_n\right]$$

$$= \hat{a}\left[\hat{H}\phi_n - \hbar\omega\phi_n\right] = \hat{a}\left[E_n\phi_n - \hbar\omega\phi_n\right] = \left(E_n - \hbar\omega\right)\hat{a}\ \phi_n.$$

Thus, while acting on the eigenfunction ϕ_n of H with energy E_n, the operator a lowers the energy by one unit of $\hbar\omega$. The operators a^+ and a are called ladder operators. The operator a^+ is also known as creation operator, while the operator a is also called annihilation operator.

All what we said earlier suggests that there must exist the lowest energy state (lowest rung in the ladder) whose wave function $\phi_0(x)$ must satisfy the equation

$$\hat{a}\phi_0(x) = 0.$$

We can use this to determine $\phi_0(x)$. We have

$$\frac{1}{\sqrt{2m\hbar\omega}}\left(i\hat{p} + m\omega\hat{x}\right)\phi_0(x) = 0.$$

Or,

$$\frac{d\phi_0(x)}{dx} = -\frac{m\omega}{\hbar}x\phi_0(x).$$

Integrating, we get

$$\int \frac{d\phi_0(x)}{\phi_0(x)} = -\frac{m\omega}{\hbar}\int x dx. \quad \Rightarrow \quad \phi_0(x) = A_0\, e^{-\frac{m\omega}{2\hbar}x^2} \equiv A_0\, e^{-\frac{x^2}{2x_0^2}},$$

where A_0 is a constant to be determined and

$$x_0 = \sqrt{\hbar/m\omega}$$

The wave function of the first excited state is obtained as

$$\phi_1(x) = \hat{a}^\dagger \phi_0(x) = \frac{1}{\sqrt{2m\omega\hbar}}\left(-\hbar\frac{d}{dx} + m\omega x\right) A_0\, e^{-\frac{x^2}{2x_0^2}} = \sqrt{\frac{2}{\sqrt{\pi}x_0^3}}\, x\, e^{-\frac{x^2}{2x_0^2}}.$$

Since, by acting on an eigenstate of the Hamiltonian, the creation operator increases its energy by one unit of $\hbar\omega$, the energy of the first excited state is $3\hbar\omega/2$.

Second quantization

Let us introduce an operator

$$\hat{N} = \hat{a}^{\dagger}\hat{a}$$

It is called the occupation number operator or, simply, the number operator.

First, we notice that the number operator commutes with the Hamiltonian:

$$[\hat{N},\hat{H}] = \left[\hat{N},\hat{N}+\frac{1}{2}\right]\hbar\omega = \hbar\omega[\hat{N},\hat{N}] + \frac{\hbar\omega}{2}[\hat{N},\hat{I}] = 0.$$

Since, N and H commute, they must have a common set of eigenvectors. Let |n⟩ be the nth joint eigenvector of these operators:

$$\hat{N}|n\rangle = n\,|n\rangle,$$

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and

$$\hat{H}|n\rangle = E_n|n\rangle,$$

where n is a positive integer and E_n, n=1,2,3,... are the energy eigenvalues.

Next, we compute the commutator of a and a^+ with N. We have

$$[\hat{a}^\dagger\hat{a},\hat{a}] = \hat{a}^\dagger[\hat{a},\hat{a}] + [\hat{a}^\dagger,\hat{a}]\hat{a} = -\hat{a}.$$

Similarly,

$$[\hat{N},\hat{a}^\dagger] = \hat{a}^\dagger.$$

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Therefore,

$$\hat{N}(\hat{a}|n\rangle) = \hat{a}(\hat{N}-1)|n\rangle = (n-1)\hat{a}|n\rangle,$$

$$\hat{N}(\hat{a}^{\dagger}|n\rangle) = \hat{a}^{\dagger}(\hat{N}+1)|n\rangle = (n+1)\hat{a}^{\dagger}|n\rangle.$$

By acting on the state |n⟩, the operator a decreases the number n by unity and generates a new eigenstate |n − 1⟩, that is,

$$\hat{a}|n\rangle = a_n|n-1\rangle.$$

Similarly, the operator a+, when acting on |n⟩, increases n by unity and generates a new eigenstate, |n + 1⟩ of N , that is

$$\hat{a}^{\dagger}|n\rangle = b_n|n+1\rangle$$

On the other hand

$$(\langle n|\hat{a}^{\dagger})\cdot(\hat{a}|n\rangle) = |a_n|^2\langle n-1|n-1\rangle = |a_n|^2$$

Therefore, we must have

$$|a_n|^2 = n. \quad \Rightarrow \quad a_n = \sqrt{n}.$$

Similarly, we arrive at

$$|b_n|^2 = n+1. \quad \Rightarrow \quad b_n = \sqrt{n+1}.$$

We can now apply the creation operator a^+ on $|0\rangle$ to generate all possible excited state energy eigenvectors.

$$|1\rangle = \hat{a}^{\dagger}|0\rangle,$$

$$|2\rangle = \frac{1}{\sqrt{2}}\hat{a}^{\dagger}|1\rangle = \frac{1}{\sqrt{2!}}\hat{a}^{\dagger 2}|0\rangle,$$

$$|3\rangle = \frac{1}{\sqrt{3}}\hat{a}^{\dagger}|2\rangle = \frac{1}{\sqrt{3!}}\hat{a}^{\dagger 3}|0\rangle,$$

......................................,

......................................,

$$|n\rangle = \frac{1}{\sqrt{n}}\hat{a}^{\dagger}|n-1\rangle = \frac{1}{\sqrt{n!}}\hat{a}^{\dagger n}|0\rangle.$$

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Hence, to find any excited state eigenvector |n⟩, we need to apply the creation operator n successive times to the vacuum state |0⟩.

Any two of the energy eigenvectors |n′⟩ and |n⟩ (corresponding to different eigenvalues) are orthogonal, and the sequence of the vectors {|0⟩, |1⟩, |2⟩ |3⟩,. . . ,|n⟩} constitutes an orthonormal and complete basis:

$$\langle n'|n\rangle = \delta_{n'n}, \qquad \sum_{n=0}^{\infty} |n\rangle\langle n| = \hat{I}.$$

Occupation number representation

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The set of occupation numbers contains all the information necessary to construct an appropriately symmetrized or antisymmetrized basis vector, denoted

$$|\Phi\rangle = |n_1, n_2, \ldots, n_\alpha, \ldots\rangle.$$

For bosons, n_α must be a non-negative integer; for fermions, the Pauli exclusion principle restricts n_α to be either 0 or 1. There is a unique vacuum or no-particle state:

$$|0\rangle = |0, 0, 0, 0, \ldots\rangle.$$

The single-particle states can be represented

$$|\alpha\rangle = |0, 0, \ldots, 0, n_\alpha = 1, 0, \ldots\rangle \equiv |0_1, 0_2, \ldots, 0_{\alpha-1}, 1_\alpha, 0_{\alpha+1}, \ldots\rangle.$$

Let us define the bosonic creation operator $a^\dagger_\alpha$ by

$$a_\alpha^\dagger|n_1, n_2, \ldots, n_{\alpha-1}, n_\alpha, n_{\alpha+1}, \ldots\rangle = \sqrt{n_\alpha + 1}\,|n_1, n_2, \ldots, n_{\alpha-1}, n_\alpha + 1, n_{\alpha+1}, \ldots\rangle,$$

and the corresponding annihilation operator a_α by

$$a_\alpha|n_1, n_2, \ldots, n_{\alpha-1}, n_\alpha, n_{\alpha+1}, \ldots\rangle = \sqrt{n_\alpha}\,|n_1, n_2, \ldots, n_{\alpha-1}, n_\alpha - 1, n_{\alpha+1}, \ldots\rangle.$$

We can define the number operator

$$N_\alpha = a_\alpha^\dagger a_\alpha,$$

such that

$$N_\alpha|n_1, n_2, \ldots, n_\alpha, \ldots\rangle = n_\alpha|n_1, n_2, \ldots, n_\alpha, \ldots\rangle$$

and

$$N = \sum_\alpha N_\alpha.$$

Occupation number representation

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The simplest application of the creation and annihilation operators involves the single-particle states:

$$a_\alpha^\dagger|0\rangle = |\alpha\rangle, \qquad a_\alpha|\beta\rangle = \delta_{\alpha,\beta}|0\rangle.$$

When applied to multi-particle states, the properties of the creation and annihilation operators must be consistent with the symmetry of bosonic states under pairwise interchange of particles.

For any pair of single particle states $|\alpha\rangle$ and $|\beta\rangle$, and for any vector $|\Psi\rangle$ in the Fock space, we have

$$a_\alpha^\dagger a_\beta^\dagger|\Psi\rangle = a_\beta^\dagger a_\alpha^\dagger|\Psi\rangle \qquad a_\alpha a_\beta|\Psi\rangle = a_\beta a_\alpha|\Psi\rangle.$$

Occupation number representation

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$a_\alpha^\dagger a_\beta|\Psi\rangle = a_\beta a_\alpha^\dagger|\Psi\rangle$ for $\alpha \neq \beta$. $a_\alpha a_\alpha^\dagger|\Psi\rangle - a_\alpha^\dagger a_\alpha|\Psi\rangle = (N_\alpha+1)|\Psi\rangle - N_\alpha|\Psi\rangle = |\Psi\rangle$

The properties described in the preceding paragraph can be summarized in the commutation relations

$$[a_\alpha^\dagger, a_\beta^\dagger] = [a_\alpha, a_\beta] = 0, \qquad [a_\alpha, a_\beta^\dagger] = \delta_{\alpha,\beta} I.$$

One consequence of these commutation relations is that any multi-particle basis state can be written

$$|n_1, n_2, \ldots, n_\alpha, \ldots\rangle = \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} \ldots \left(a_\alpha^\dagger\right)^{n_\alpha} \ldots |0\rangle,$$

or equally well, as any permutation of the above product of operators acting on the vacuum. For example,

$$|2,1,0,0,\ldots\rangle = a_1^\dagger a_1^\dagger a_2^\dagger|0\rangle = a_1^\dagger a_2^\dagger a_1^\dagger|0\rangle = a_2^\dagger a_1^\dagger a_1^\dagger|0\rangle.$$

The fermionic case is a little trickier than the bosonic one because we have to enforce antisymmetry under all possible pairwise interchanges. We define the fermionic creation operator $c^\dagger_\alpha$ by

$$\begin{aligned} c_\alpha^\dagger|n_1, n_2, \ldots, n_{\alpha-1}, 0_\alpha, n_{\alpha+1}, \ldots\rangle &= (-1)^{\nu_\alpha}|n_1, n_2, \ldots, n_{\alpha-1}, 1_\alpha, n_{\alpha+1}, \ldots\rangle, \\ c_\alpha^\dagger|n_1, n_2, \ldots, n_{\alpha-1}, 1_\alpha, n_{\alpha+1}, \ldots\rangle &= 0, \end{aligned}$$

and the annihilation operator c_α by

$$\begin{aligned} c_\alpha|n_1, n_2, \ldots, n_{\alpha-1}, 1_\alpha, n_{\alpha+1}, \ldots\rangle &= (-1)^{\nu_\alpha}|n_1, n_2, \ldots, n_{\alpha-1}, 0_\alpha, n_{\alpha+1}, \ldots\rangle, \\ c_\alpha|n_1, n_2, \ldots, n_{\alpha-1}, 0_\alpha, n_{\alpha+1}, \ldots\rangle &= 0. \end{aligned}$$

where

$$\nu_\alpha = \sum_{\beta<\alpha} N_\beta, \quad \text{where } N_\beta = c_\beta^\dagger c_\beta,$$

measures the total number of particles in single-particle states having an index β < α.

Therefore, in Fermionic system, the particle number operator has

$$N_\alpha|n_1, n_2, \ldots, n_\alpha, \ldots\rangle = n_\alpha|n_1, n_2, \ldots, n_\alpha, \ldots\rangle \qquad \text{for } n_\alpha = 0 \text{ or } 1.$$

and

$$c_\alpha^\dagger c_\beta^\dagger|\Psi\rangle = -c_\beta^\dagger c_\alpha^\dagger|\Psi\rangle \text{ for } \alpha \neq \beta, \qquad c_\alpha^\dagger c_\alpha^\dagger|\Psi\rangle = 0 = -c_\alpha^\dagger c_\alpha^\dagger|\Psi\rangle.$$

$$c_\alpha c_\beta|\Psi\rangle = -c_\beta c_\alpha|\Psi\rangle \text{ for } \alpha \neq \beta, \text{ and } c_\alpha c_\alpha|\Psi\rangle = 0.$$

$$(c_\alpha c_\alpha^\dagger + c_\alpha^\dagger c_\alpha)|\Psi\rangle = (1 - N_\alpha)|\Psi\rangle + N_\alpha|\Psi\rangle = |\Psi\rangle$$

The properties above can be summarized in the anticommutation relations

$$\{c_\alpha^\dagger, c_\beta^\dagger\} = \{c_\alpha, c_\beta\} = 0, \qquad \{c_\alpha, c_\beta^\dagger\} = \delta_{\alpha,\beta} I,$$

where {A, B} = AB + BA is the anticommutator of A and B. These anticommutation properties fundamentally distinguish the fermionic operators from their commuting bosonic counterparts.

Given the anticommutation relations, any multi-particle basis state can be written

$$|n_1, n_2, \ldots, n_\alpha, \ldots\rangle = \left(c_1^\dagger\right)^{n_1} \left(c_2^\dagger\right)^{n_2} \ldots \left(c_\alpha^\dagger\right)^{n_\alpha} \ldots |0\rangle,$$

or equally well, as any permutation of the above product of creation operators with a sign change for each pairwise interchange of adjacent operators. For example,

$$|1,1,1\rangle = c_1^\dagger c_2^\dagger c_3^\dagger|0\rangle = -c_2^\dagger c_1^\dagger c_3^\dagger|0\rangle = c_2^\dagger c_3^\dagger c_1^\dagger|0\rangle = -c_3^\dagger c_2^\dagger c_1^\dagger|0\rangle = c_3^\dagger c_1^\dagger c_2^\dagger|0\rangle = -c_1^\dagger c_3^\dagger c_2^\dagger|0\rangle$$

The operators which involve sum over only single particles are known as **single-particle operators**

$$\hat{F}_1 = \sum_i \hat{f}_1(\vec{r}_i, \vec{p}_i)$$

In second quantization, this operator can be written as

$$\hat{F}_1 = \sum_{l,l'} \langle l|\hat{f}_1|l'\rangle a_l^\dagger a_{l'}$$

where

$$\langle l|\hat{f}_1|l'\rangle = \int_r \phi_l^*(r)\hat{f}_1(r,p)\phi_{l'}(r)$$

The operators which involve sum over two particles are known as **two particle operators**

$$\hat{F}_2 = \sum_{l_1,l_2,l_3,l_4} \langle l_1 l_2|\hat{f}_2|l_4 l_3\rangle a_{l_1}^\dagger a_{l_2}^\dagger a_{l_3} a_{l_4}$$

$$\langle l_1 l_2|\hat{f}_2|l_4 l_3\rangle = \int_{r_1,r_2} \phi_{l_1}^*(r_1)\phi_{l_2}^*(r_2)\hat{f}_2(r_1,p_1;r_2,p_2)\phi_{l_4}(r_1)\phi_{l_3}(r_2)$$

Exercise

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1. Three spinless non-interacting particles, with respective masses m_1, m_2, and m_3 in the ratio m_1:m_2 :m_3=1:2:3, are subject to a common infinite square well potential of width L in one spatial dimension. Determine the energies and the corresponding wave functions in the three lowest lying states of the system.

Exercise

1. Three spinless non-interacting particles, with respective masses m_1, m_2 , and m_3 in the ratio m_1:m_2 :m_3=1:2:3, are subject to a common infinite square well potential of width L in one spatial dimension. Determine the energies and the corresponding wave functions in the three lowest lying states of the system.

Solution: The corresponding single-particle wave functions and energies are

$$\phi_{n_j}(x_j) = \sqrt{\frac{2}{L}} \sin\left(\frac{n_j\pi}{L}x_j\right), \quad j = 1,2,3,$$

$$E_j = \frac{n_j^2\pi^2\hbar^2}{2m_jL^2}, \quad j = 1,2,3.$$

Exercise

Ground state: For the ground state, we have $n_1 = n_2 = n_3 = 1$, and the energy of the system will be

$$E_{111} = \frac{\pi^2\hbar^2}{2L^2}\left(\frac{1}{m_1}+\frac{1}{m_2}+\frac{1}{m_3}\right) = \frac{11\pi^2\hbar^2}{12m_1L^2}.$$

The corresponding ground state wave function is given by

$$\psi_{111}(x_1,x_2,x_3) = \sqrt{\frac{8}{L^3}}\sin\left(\frac{\pi}{L}x_1\right)\sin\left(\frac{\pi}{L}x_2\right)\sin\left(\frac{\pi}{L}x_3\right).$$

First excited state: Since $m_3 > m_2 > m_1$, the first excited state will correspond to $n_1 = n_2 = 1$ and $n_3 = 2$.

$$E_{112} = \frac{\pi^2\hbar^2}{2L^2}\left(\frac{1}{m_1}+\frac{1}{m_2}+\frac{4}{m_3}\right) = \frac{17\pi^2\hbar^2}{12m_1L^2}.$$

$$\psi_{112}(x_1,x_2,x_3) = \sqrt{\frac{8}{L^3}}\sin\left(\frac{\pi}{L}x_1\right)\sin\left(\frac{\pi}{L}x_2\right)\sin\left(\frac{2\pi}{L}x_3\right).$$

Second excited state: The second excited state corresponds to the case when $n_1 = n_3 = 1$ and $n_2 = 2$. Hence, its energy, E_{121}, equals:

$$E_{121} = \frac{\pi^2\hbar^2}{2L^2}\left(\frac{1}{m_1} + \frac{4}{m_2} + \frac{1}{m_3}\right) = \frac{5\pi^2\hbar^2}{3mL^2}$$

The corresponding wave function is given by

$$\psi_{122}(x_1, x_2, x_3) = \sqrt{\frac{8}{L^3}}\, \sin\left(\frac{\pi}{L}x_1\right) \sin\left(\frac{2\pi}{L}x_2\right) \sin\left(\frac{\pi}{L}x_3\right).$$

Similarly, one can determine the energies and the corresponding wave functions of all other excited states of this three-particle system.

Exercise

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2. Two non-interacting particles, each of mass m, are confined to move in a one-dimensional potential well: $V(x) = 0$, for $0 < x < 2a$ and $V(x) = \infty$ elsewhere, where a is a positive constant. What are the energies and the corresponding degeneracies of the three lowest lying states of the system, if the particles are indistinguishable spin-1/2 fermions?

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2. Two non-interacting particles, each of mass m, are confined to move in a one-dimensional potential well: V (x) = 0, for 0 < x < 2a and V (x) = ∞ elsewhere, where a is a positive constant. What are the energies and the corresponding degeneracies of the three lowest lying states of the system, if the particles are indistinguishable spin-1/2 fermions?

Solution: The single particle wave function and energy are

$$\phi_n(x) = \sqrt{\frac{1}{a}} \sin\left(\frac{n\pi}{2a}x\right) \qquad \mathscr{E}_n = \frac{n^2\pi^2\hbar^2}{8ma^2}$$

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It is obvious that the nth energy state of the system will be characterized by two sets of quantum numbers n_1 and n_2. The corresponding stationary state wave function of the system will be

$$\psi_{n_1 n_2}(\xi_1, \xi_2, t) = \phi_{n_1 n_2}(x_1, x_2)\, \chi(S_1, S_2)\, e^{-\frac{i}{\hbar} E_{n_1 n_2} t},$$

where

$$E_{n_1 n_2} = \mathscr{E}_{n_1} + \mathscr{E}_{n_2} = \left(n_1^2 + n_2^2\right) \frac{\pi^2 \hbar^2}{8ma^2}$$

Since the particles are indistinguishable fermions, the ground state of the system will have both the fermions in the single-particle states with $n_1 = n_2 = 1$ under the condition that they will have opposite spins.

$$\mathscr{E}_1 + \mathscr{E}_1 = \pi^2 \hbar^2 / 4ma^2.$$

Since for a fermionic system the overall wave function must be anti-symmetric, the ground state wave function will be given by

$$\psi_{11}(\xi_1,\xi_2) = \frac{1}{a}\sin\left(\frac{n_1\pi}{2a}x_1\right)\sin\left(\frac{n_2\pi}{2a}x_2\right)\chi_{\text{singlet}}(s_1,s_2),$$

where

$$\chi_{\text{singlet}}(s_1,s_2) = \frac{1}{\sqrt{2}}\left[\chi_1^{(+)}\chi_2^{(-)} - \chi_1^{(-)}\chi_2^{(+)}\right],$$

is anti-symmetric with respect to the interchange of particles. The superscripts '(+)' and '(–)' stand for spin up and spin down, respectively.

The first excited state of the system will correspond to $n_1 = 2, n_2 = 1$ or $n_1 = 1, n_2 = 2$. This state will have energy

Exercise

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$$E_{12} = E_{21} = \frac{5\pi^2\hbar^2}{8ma^2}.$$

The wave function of the system will be given by

$$\psi_a(\xi_1, \xi_2) = \begin{cases} \phi_s(x_1, x_2)\, \chi_{\text{singlet}}(s_1, s_2) \\ \phi_a(x_1, x_2)\, \chi_{\text{triplet}}(s_1, s_2). \end{cases}$$

where

$$\chi_{\text{triplet}}(s_1, s_2) = \begin{cases} \chi_1^{(+)}\chi_2^{(+)}, \\ \frac{1}{\sqrt{2}}\left[\chi_1^{(+)}\chi_2^{(-)} + \chi_1^{(-)}\chi_2^{(+)}\right] \\ \chi_1^{(+)}\chi_2^{(+)}. \end{cases}$$

Exercise

The spatial parts of the wave function are

$$\phi_s(x_1,x_2) = \frac{1}{\sqrt{2}a}\left[\sin\left(\frac{\pi x_1}{2a}\right)\sin\left(\frac{\pi x_2}{a}\right) + \sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{2a}\right)\right],$$

$$\phi_a(x_1,x_2) = \frac{1}{\sqrt{2}a}\left[\sin\left(\frac{\pi x_1}{2a}\right)\sin\left(\frac{\pi x_2}{a}\right) - \sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{2a}\right)\right].$$

Since there are four possible spin configurations, the first excited state of the system is 4-fold degenerate.

The second excited state of the system corresponds to $n_1 = n_2 = 2$ and the energy of the system in this state will be

$$E^{(2)} = E_{22} = \frac{\pi^2\hbar^2}{ma^2}.$$

$$\psi_{22}(\xi_1,\xi_2) = \frac{1}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)\chi_{\text{singlet}}(s_1,s_2).$$

3. Show that operators a and a^+ are not Hermitian while operator a^+a is Hermitian.

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3. Show that operators a and a⁺ are not Hermitian while operator a⁺a is Hermitian.

Solution: The matrix elements of a and a⁺ are:

$$a_{mn} = \langle m|a|n\rangle = \sqrt{n}\langle m|n-1\rangle = \sqrt{n}\delta_{m,n-1} \qquad (a_{nm})^* = \langle n|a|m\rangle^* = \left(\sqrt{m}\langle n|m-1\rangle\right)^* = \sqrt{m}\delta_{n,m-1}$$

$$\left(a^\dagger\right)_{mn} = \langle m|a^\dagger|n\rangle = \sqrt{n+1}\langle m|n+1\rangle = \sqrt{n+1}\delta_{m,n+1},$$

$$\left(a^\dagger_{nm}\right)^* = \langle n|a^\dagger|m\rangle^* = \sqrt{m+1}\langle n|m+1\rangle$$
$$= \sqrt{m+1}\delta_{n,m+1} \neq a^\dagger_{nm}$$

The matrix elements of a⁺a are:

$$\left(a^\dagger a\right)_{mn} = \langle m|a^\dagger a|n\rangle = n\delta_{mn} \qquad \left\{\left(a^\dagger a\right)_{nm}\right\}^* = \langle n|a^\dagger a|m\rangle^* = m\delta_{nm}$$