

V25.0109: General Chemistry I (Honors)

Notes for Lecture 7

I. PARTICLE IN A TWO-DIMENSIONAL BOX

A quantum particle of mass m in a two-dimensional square box by a potential energy $V(x, y)$ that is zero if $x \in [0, L]$ and $y \in [0, L]$ and infinite otherwise. Inside the box, the energy is entirely kinetic because $V(x, y) = 0$, so the classical energy is

$$\frac{p_x^2}{2m} + \frac{p_y^2}{2m} = E$$

where p_x and p_y are the two components of the particle's momentum. We see that the energy naturally is expressible as a sum of kinetic energies associated with motion in the x and y directions:

$$E = \varepsilon_x + \varepsilon_y$$

Because the energy is a simple sum, the solutions of the Schrödinger equation can be expressed as simple products of the solutions of the one-dimensional Schrödinger equation for this problem. Note that it is *only* when the energy is expressible in this way that simple product solutions are rigorously correct. Thus, the wave function $\psi(x, y)$ is of the form

$$\psi(x, y) = A \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}x\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}y\right)$$

which satisfies the boundary conditions at $x = 0$ and $y = 0$, namely $\psi(0, y) = 0$ and $\psi(x, 0) = 0$. In order to satisfy the remaining boundary conditions $\psi(L, y) = 0$ and $\psi(x, L) = 0$, we have two conditions:

$$A \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}L\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}y\right) = 0$$

$$A \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}x\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}L\right) = 0$$

The first one can be satisfied if

$$\sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}L\right) = 0$$

independent of y , while the second can be satisfied if

$$\sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}L\right) = 0$$

independent of x . These are the same conditions that we encountered for the one-dimensional box, hence we already know the sin function in each case can be zero in many places. In fact, these two conditions are satisfied if

$$\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}L = n_x\pi$$

$$\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}L = n_y\pi$$

which yield the allowed values of ε_x and ε_y as

$$\varepsilon_{n_x} = \frac{\hbar^2 \pi^2}{2mL^2} n_x^2 \quad \varepsilon_{n_y} = \frac{\hbar^2 \pi^2}{2mL^2} n_y^2$$

We need two different integers n_x and n_y because the conditions are completely independent and can be satisfied by any two different (or similar) values of these integers. The allowed values of the total energy are now given by

$$E_{n_x n_y} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2)$$

Note that the allowed energies now depend on two integers n_x and n_y rather than one. These arise from the *two* independent boundary conditions in the x and y directions. As in the one-dimensional box, the values of n_x and n_y are both restricted to the natural numbers 1, 2, 3, Note, therefore, that the ground state energy E_{11} is

$$E_{11} = \frac{\hbar^2 \pi^2}{mL^2}$$

is larger than for the one-dimensional box because of the contributions from kinetic energy in the x and y directions.

Once the conditions on ε_{n_x} and ε_{n_y} are substituted in, the wave functions become

$$\psi_{n_x n_y}(x, y) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right)$$

The constant A is now determined by the normalization condition

$$\begin{aligned} \int_0^L \int_0^L |\psi_{n_x n_y}(x, y)|^2 dx dy &= 1 \\ A^2 \int_0^L \sin^2\left(\frac{n_x \pi x}{L}\right) dx \int_0^L \sin^2\left(\frac{n_y \pi y}{L}\right) dy &= 1 \\ A^2 \frac{L}{2} \cdot \frac{L}{2} &= 1 \\ A &= \frac{2}{L} \end{aligned}$$

so that

$$\psi_{n_x n_y}(x, y) = \frac{2}{L} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right)$$

The wave functions are somewhat more difficult to visualize because of they are two dimensional. Nevertheless, we can still visualize them, and the figure below shows the following wave functions: $\psi_{11}(x, y)$, $\psi_{21}(x, y)$ and $\psi_{22}(x, y)$.

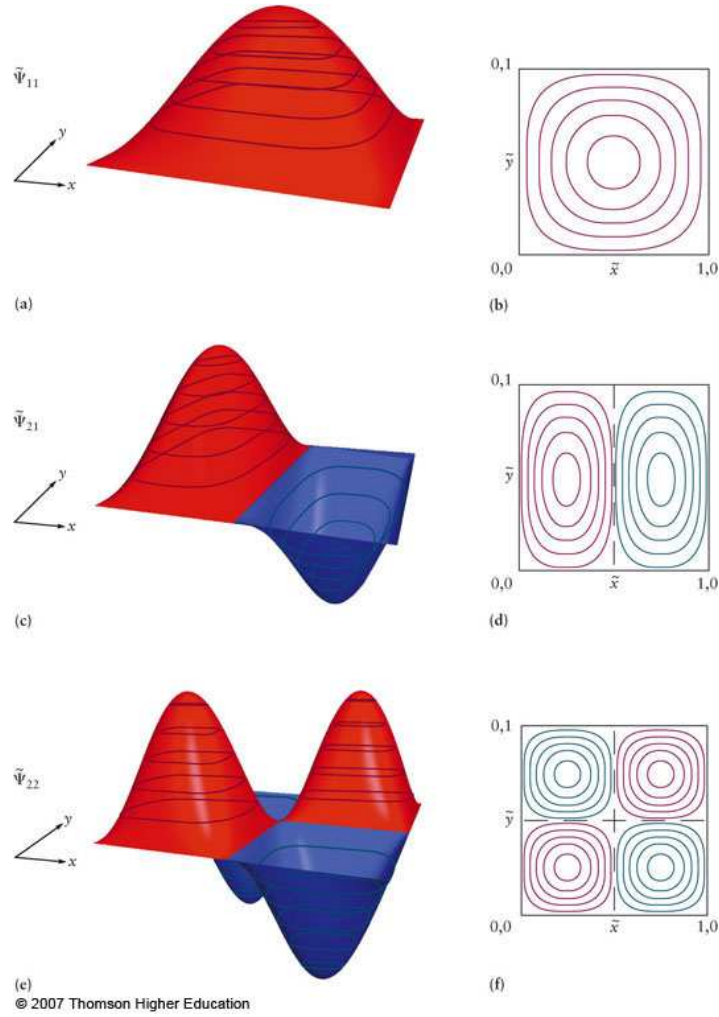


FIG. 1. First few wave functions for a particle in a two-dimensional square box

Note that the figure makes use of what we call *dimensionless* coordinates \bar{x} and \bar{y} , which are defined to be the coordinates of a particle in a *unit box*, i.e. a box with $L = 1$. Thus, the dimensionless coordinates are defined by

$$\bar{x} = \frac{x}{L} \quad \bar{y} = \frac{y}{L}$$

It is important to note that the wave functions can be either positive or negative, even though the associated probability density $p_{n_x n_y}(x, y) = |\psi_{n_x n_y}(x, y)|^2$ is strictly positive. In the figure, the red part of the function is positive, and the blue part is negative. Unlike in the one-dimensional case, where nodes in the wave function are points where $\psi_n(x) = 0$, here entire lines can be nodal. These are called *nodal lines*. For example, in the state $\psi_{21}(x, y)$, there is a nodal line at $\psi_{21}(L/2, y)$. Along the entire line $x = L/2$, the wave function is 0 independent of the value of y . The wave function $\psi_{22}(x, y)$ has two nodal lines when $x = L/2$ and when $y = L/2$. The sign of the wave function and its nodal structure will play central roles later when we consider chemical bonding.

Note that if the box were rectangular rather than square, then instead of having a length of L on both sides, there would be two different lengths L_x and L_y . The formulas for the energies and wave functions become only slightly more complicated:

$$E_{n_x n_y} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

$$\psi_{n_x n_y}(x, y) = \frac{2}{\sqrt{L_x L_y}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right)$$

The definition of the dimensionless variables is also altered slightly

$$\bar{x} = \frac{x}{L_x} \quad \bar{y} = \frac{y}{L_y}$$

The fact that the wave function $\psi_{n_x n_y}(x, y)$ is a product of one-dimensional wave functions:

$$\psi_{n_x n_y}(x, y) = \psi_{n_x}(x)\psi_{n_y}(y)$$

makes the calculation of probabilities rather easy. The probability that a measurement the particle's position will yield a value of $x \in [a, b]$ and $y \in [c, d]$ is

$$\begin{aligned} P(x \in [a, b] \text{ and } y \in [c, d]) &= \int_a^b dx \int_c^d dy |\psi_{n_x n_y}(x, y)|^2 \\ &= \int_a^b dx \int_c^d dy \psi_{n_x}^2(x)\psi_{n_y}^2(y) \\ &= \left[\int_a^b \psi_{n_x}^2(x)dx \right] \left[\int_c^d \psi_{n_y}^2(y)dy \right] \end{aligned}$$

Example: For a particle in a two-dimensional box, if the particle is in the state $\psi_{12}(x, y)$, what is the probability that a measurement of the particle's position will yield $x \in [0, L/2]$ and $y \in [0, L/2]$?

Substituting into the above formula, we have

$$\begin{aligned} P(x \in [0, L/2] \text{ and } y \in [0, L/2]) &= \left[\int_0^{L/2} \psi_1^2(x)dx \right] \left[\int_0^{L/2} \psi_2^2(y)dy \right] \\ &= \left[\frac{2}{L} \int_0^{L/2} \sin^2\left(\frac{\pi x}{L}\right) dx \right] \left[\frac{2}{L} \int_0^{L/2} \sin^2\left(\frac{2\pi y}{L}\right) dy \right] \\ &= \left[\frac{2}{L} \frac{L}{4} \right] \left[\frac{2}{L} \frac{L}{4} \right] \\ &= \frac{1}{4} \end{aligned}$$

II. PARTICLE IN A THREE-DIMENSIONAL BOX

Generalization of the results for a two-dimensional square box to a three-dimensional cubic box is straightforward. Since we live in a three-dimensional world, this generalization is an important one, and we need to be able to think about energy levels and wave functions in three dimensions. The potential energy $V(x, y, z)$ for the cubic box is defined to be 0 if $x \in [0, L]$, $y \in [0, L]$ and $z \in [0, L]$ and infinite otherwise. This means that the wave function $\psi(x, y, z)$ must satisfy six boundary conditions $\psi(0, y, z) = 0$, $\psi(x, 0, z) = 0$, $\psi(x, y, 0) = 0$, $\psi(L, y, z) = 0$, $\psi(x, L, z) = 0$ and $\psi(x, y, L) = 0$.

We first note that the classical energy is the sum of three terms

$$\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} = E$$

where p_x , p_y and p_z are the three components of the particle's momentum vector \mathbf{p} . Thus, we can write the energy as

$$E = \varepsilon_x + \varepsilon_y + \varepsilon_z$$

corresponding to the kinetic energy in the x , y and z directions. Because the energy is a simple sum of energies for the x , y and z directions, the wave function will be a product of wave function forms for the one-dimensional box, and in order to satisfy the first three of the boundary conditions, we can take the sin functions:

$$\psi(x, y, z) = A \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}x\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}y\right) \sin\left(\sqrt{\frac{2m\varepsilon_z}{\hbar^2}}z\right)$$

As in the two-dimensional case, applying second three boundary conditions yields the allowed values of ε_x , ε_y and ε_z , which now require three integers n_x , n_y and n_z :

$$\varepsilon_{n_x} = \frac{\hbar^2 \pi^2}{2mL^2} n_x^2 \quad \varepsilon_{n_y} = \frac{\hbar^2 \pi^2}{2mL^2} n_y^2 \quad \varepsilon_{n_z} = \frac{\hbar^2 \pi^2}{2mL^2} n_z^2$$

so that the allowed values of the total energy are

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

and the wave functions become

$$\psi_{n_x n_y n_z}(x, y, z) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

The constant A is determined from the normalization condition

$$\begin{aligned} \int_0^L \int_0^L \int_0^L |\psi_{n_x n_y n_z}(x, y, z)|^2 dx dy dz &= 1 \\ A^2 \int_0^L \sin^2\left(\frac{n_x \pi x}{L}\right) dx \int_0^L \sin^2\left(\frac{n_y \pi y}{L}\right) dy \int_0^L \sin^2\left(\frac{n_z \pi z}{L}\right) dz &= 1 \\ A^2 \frac{L}{2} \cdot \frac{L}{2} \cdot \frac{L}{2} &= 1 \\ A &= \left(\frac{2}{L}\right)^{3/2} \end{aligned}$$

Thus, the wave functions are

$$\psi_{n_x n_y n_z}(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

As with the two-dimensional box, the three integers n_x , n_y and n_z are restricted to the natural numbers 1,2,3,... Thus, the lowest energy or ground-state energy is

$$E_{111} = \frac{3\hbar^2 \pi^2}{2mL^2}$$

Visualizing the wave functions is tricky because of their high dimensionality. The most common method of visualizing functions of three variables is the use of an *isosurface*. An isosurface of a function $f(x, y, z)$ is the complete set of points x , y , and z for which $f(x, y, z) = C$, where C is a chosen constant. Hence the name *isosurface* – the value of the function $f(x, y, z)$ is the same at all points on the surface.

For wave functions, where the sign can be positive or negative, it is useful to base the value of C not on the wave function value but rather on the probability density $p_{n_x n_y n_z}(x, y, z) = |\psi_{n_x n_y n_z}(x, y, z)|^2$. The figure below shows two isosurfaces of the wave function $\psi_{123}(x, y, z)$. The first occurs at a probability density value of 0.64 and the other occurs at 0.04. These value then imply that the wave function can have a fixed positive or negative value along the surface. In one case, $\psi_{123}(x, y, z) = \pm 0.8$, while in the other, $\psi_{123}(x, y, z) = \pm 0.2$.

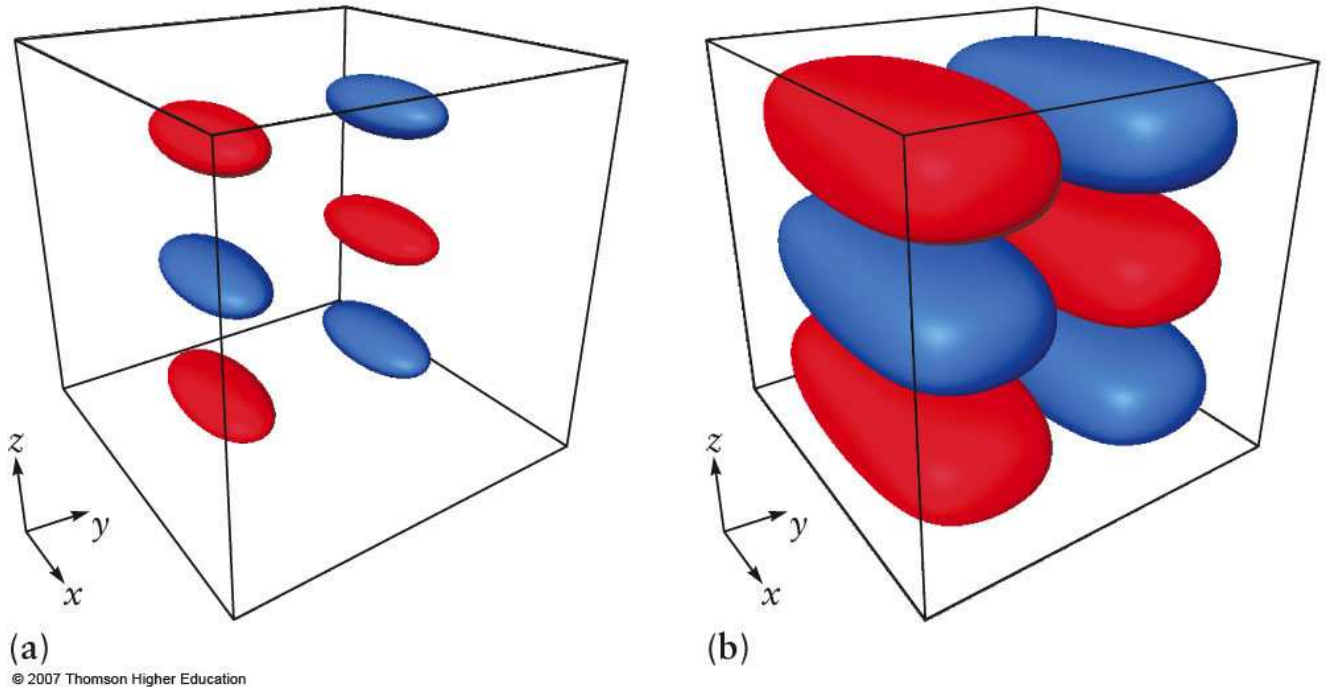


FIG. 2. Isosurfaces of $\psi_{123}(x, y, z)$ at probability density values of 0.64 and 0.04. Red is positive and blue is negative.

As in the two-dimensional case, the fact that the wave function $\psi_{n_x n_y n_z}(x, y, z)$ is a product

$$\psi_{n_x n_y n_z}(x, y, z) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$$

means that the probabilities can be calculated from products of one-dimensional integrals. The probability that a measurement of a particle's position yields a value $x \in [a, b]$, $y \in [c, d]$ and $z \in [f, g]$ is

$$\begin{aligned} P(x \in [a, b] \text{ and } y \in [c, d] \text{ and } z \in [f, g]) &= \int_a^b dx \int_c^d dy \int_f^g dz |\psi_{n_x n_y n_z}(x, y, z)|^2 \\ &= \left[\int_a^b \psi_{n_x}^2(x) dx \right] \left[\int_c^d \psi_{n_y}^2(y) dy \right] \left[\int_f^g \psi_{n_z}^2(z) dz \right] \end{aligned}$$

III. TWO IDENTICAL PARTICLES IN A BOX

Let us return briefly to the particle in a box model and ask what happens if we put two identical particles in the box. If they were classical particles, they would carry an imaginary “label” that would allow us to tell the particles apart. In quantum mechanics, this is no longer possible because all we can predict is the probability that one of the particles is in a region dx_1 about the point x_1 and the other is in a region dx_2 about the point x_2 , but we cannot tell which particle is where. This fact will affect both the allowed energies and the wave functions.

The classical energy inside the box is, in this case

$$\frac{p_1^2}{2m} + \frac{p_2^2}{m} = E$$

where p_1 is the momentum of particle 1, and p_2 is the momentum of particle 2. Because the energy is a sum of independent energies for particles 1 and 2, the energies can also be separated

$$E = \varepsilon_1 + \varepsilon_2$$

The wave function will depend on the positions x_1 and x_2 , $\psi(x_1, x_2)$, and therefore, we have four boundary conditions $\psi(0, x_2) = 0$, $\psi(x_1, 0) = 0$, $\psi(L, x_2) = 0$ and $\psi(x_1, L) = 0$. These give rise to the allowed values of ε_1 and ε_2 in the usual way:

$$\varepsilon_{n_1} = \frac{\hbar^2 \pi^2}{2mL^2} n_1^2 \quad \varepsilon_{n_2} = \frac{\hbar^2 \pi^2}{2mL^2} n_2^2$$

so that the allowed values of the total energy are

$$E_{n_1 n_2} = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2)$$

Here each particle gets an independent integer for enumerating the energy levels n_1 and n_2 .

Just as we did for a single particle in a two-dimensional box, we might expect the wavefunctions to be a simple product

$$\Psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1) \psi_{n_2}(x_2)$$

where $\psi_n(x)$ is just the usual wave function for the particle in a box

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

However, we immediately run into two problems. First, if the particles are truly identical, how do we know whether to assign the energy level n_1 to particle 1 or 2? We could do either, assigning n_2 to the other, and the total energy would not change. However, the simple product wave function above specifies a definite assignment of n_1 to particle 1 and n_2 to particle 2! The second problem is that the simple product form says that there are points at which $\Psi_{n_1 n_2}(x, x) \neq 0$, implying that there is a nonzero probability of finding the two particles at exactly the same point in space, i.e. sitting right on top of each other!

In order to handle the first problem, we simply include two possible product forms, i.e.

$$\psi_{n_1}(x_1) \psi_{n_2}(x_2) \quad \psi_{n_2}(x_1) \psi_{n_1}(x_2)$$

and put them together to form $\Psi_{n_1 n_2}(x_1, x_2)$, which we can do in two ways:

$$\Psi_{n_1 n_2}(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_{n_1}(x_1) \psi_{n_2}(x_2) \pm \psi_{n_2}(x_1) \psi_{n_1}(x_2)]$$

The $1/\sqrt{2}$ is needed for proper normalization. But which combination should be taken? If we take the first one:

$$\Psi_{n_1 n_2}(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_{n_1}(x_1) \psi_{n_2}(x_2) + \psi_{n_2}(x_1) \psi_{n_1}(x_2)]$$

then we have not circumvented the second problem. It will still be possible for the two particles to sit at the same point in space. In fact, there are certain exotic particles in quantum mechanics that can do this (they are called *bosons*), and this possibility is what is responsible for curious phenomena such as superfluidity and superconductivity. However, the more mundane objects we care about, such as protons and electrons, cannot sit on top of each other. Thus, for these particles, we need to take the second form

$$\Psi_{n_1 n_2}(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_{n_1}(x_1) \psi_{n_2}(x_2) - \psi_{n_2}(x_1) \psi_{n_1}(x_2)]$$

This form implies two things. Note first that

$$\Psi_{n_1 n_2}(x, x) = 0$$

which means that for any n_1 and n_2 , there is zero probability to find both particles in small regions near the same point. The other thing we see is that

$$\Psi_{nn}(x_1, x_2) = 0$$

which implies that the two particles cannot be in the same energy level. That this possibility is excluded is known as the *Pauli exclusion principle*, and it plays a key role in both the electronic configurations of atoms and molecules.

Example: Two particles of mass m are in a one-dimensional box of length L . What is the lowest total energy the two particle- system can have?

Since $n_1 = 1, 2, 3, \dots$ and $n_2 = 1, 2, 3, \dots$, if we choose $n_1 = 1$, then, since n_2 cannot be equal to n_1 , the next lowest value we can choose is $n_2 = 2$. Thus, the lowest energy is

$$E_{12} = \frac{\hbar^2 \pi^2}{2mL^2} (1^2 + 2^2) = \frac{5\hbar^2 \pi^2}{2mL^2}$$

Notice that the calculation of probabilities changes a little because of the increased complexity of the wave function. Let us consider the probability that a simultaneous measurement of the position of particle 1 and of particle yields values of x_1 and x_2 , $x_1 \in [a, b]$, $x_2 \in [c, d]$. For electrons, this is given by

$$\begin{aligned} P(x_1 \in [a, b] \text{ and } x_2 \in [c, d]) &= \int_a^b dx_1 \int_c^d dx_2 |\Psi_{n_1 n_2}(x_1, x_2)|^2 \\ &= \frac{1}{2} \int_a^b dx_1 \int_c^d dx_2 [\psi_{n_1}^2(x_1)\psi_{n_2}^2(x_2) - 2\psi_{n_1}(x_1)\psi_{n_2}(x_1)\psi_{n_2}(x_2)\psi_{n_1}(x_2) + \psi_{n_2}^2(x_1)\psi_{n_1}^2(x_2)] \\ &= \frac{1}{2} \left[\int_a^b \psi_{n_1}^2(x_1) dx_1 \right] \left[\int_c^d \psi_{n_2}^2(x_2) dx_2 \right] \\ &\quad - \left[\int_a^b \psi_{n_1}(x_1)\psi_{n_2}(x_1) dx_1 \right] \left[\int_c^d \psi_{n_2}(x_2)\psi_{n_1}(x_2) dx_2 \right] \\ &\quad + \frac{1}{2} \left[\int_a^b \psi_{n_2}^2(x_1) dx_1 \right] \left[\int_c^d \psi_{n_1}^2(x_2) dx_2 \right] \end{aligned}$$