Localization and Spread of the Particle in a Box

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Abstract: The most basic example of a quantum mechanical problem, the one-dimensional particle in a box, is revisited. Three aspects are treated. 1. It is shown that a number of textbooks give an incorrect result for the expectation value of x^2**,** and, therefore, do not obtain the correct spread Δx. Consequently, the verification of the Heisenberg relation is also in error. 2. It is found that textbooks do not mention the origin dependence of expectation values, which is a nuisance, as the problem is evidently treated in the literature with two choices of origin. 3. Superposition of an infinite number of even (cosine) solutions of the one-dimensional particle in the box allows for an analytical demonstration of complete localization of the particle ($\Delta x = 0$).

The particle in the box is the example *par excellence* for the introduction of quantum mechanics in undergraduate programs. The basic ideas of quantization, mean value, uncertainty, et al. can be taught without too much mathematical overload, using the one-dimensional case. The generalization to two and three dimensions demonstrates the connection between quantum numbers and degrees of freedom and is especially useful by virtue of the appearance of degeneracy, both systematic and accidental. In this communication a few aspects of the one-dimensional problem are treated, which have not received the attention they deserve or have been handled maladroitly in the textbooks. In essence three things will be demonstrated:

1. Few textbooks give the correct result for the mean value of x^2, which means that the calculation of the uncertainty (standard deviation) or spread in position as the square root of the variance (see the defining eq 3) is wrong or absent, and the correct verification of the Heisenberg relations consequently is missing.

2. No textbook mentions the fact that the result of the calculation of the mean value of x^2 is origin-dependent. This is important because the calculation may be performed in different ways, namely with the particle moving between boundaries $x = 0$ and $x = \mathrm{a}$, or alternatively between $x = -a/2$ and $x = +a/2$. Of course, the mean value of x is origin-dependent as well, but the result is so obvious, that nobody notices it.

3. It is possible using the cosine solutions (odd quantum numbers) of the particle in the box with $\pm a/2$ as boundaries to demonstrate analytically the complete localization of the particle through superposition of an infinite number of functions, showing the spread going to zero.

The Mean Value of x^2

A one-dimensional box is assumed to have infinite potential energy walls and a width a. The origin will be on the left. The potential energy within the box is zero. The solutions are well known [1]: the energies are $E = k^2h^2/8ma^2$ with quantum number $k = 1, 2, 3, \ldots$ and the wave functions are given by

$$\phi_k = \sqrt{\frac{2}{a}} \sin \frac{k\pi x}{a} \tag{1}$$

The mean value of $\boldsymbol{x}^2$ is defined and calculated (last step integration by parts) as follows:

$$\left\langle x^2 \right\rangle = \int x^2 \phi_k{}^2 dx = \frac{2}{a} \int_0^a x^2 \sin^2 \frac{k\pi x}{a} dx = a^2 \left(\frac{1}{3} - \frac{1}{2k^2\pi^2} \right) \tag{2}$$

This result shows that, whereas $\langle x \rangle$ (= $a/2$), as is shown in all textbooks, is independent of the quantum state that the particle is in, this is not so for $\langle x^2 \rangle$ and consequently also not so for the spread in position. Kauzmann [2] gives the correct expression, but at least two other textbooks [3, 4] are in error. They use the classical limit (= $a^2/3$) instead of the true solution. The spread becomes

$$\begin{aligned} \Delta x &= \sqrt{\left(\left\langle x^2 \right\rangle - \left\langle x \right\rangle^2 \right)} = a \sqrt{\left(\frac{1}{3} - \frac{1}{2k^2\pi^2} - \frac{1}{4} \right)} \\ &= a \sqrt{\left(\frac{1}{12} - \frac{1}{2k^2\pi^2} \right)} \end{aligned} \tag{3}$$

The quantum number dependence of the uncertainty or spread is such that the spread in position is *growing* towards the classical limit with increasing values of k. To obtain the Heisenberg relation, the spread in momentum has to be calculated. Because the particle moves with equal probability to the left and to the right $\langle p \rangle = 0$ and $\Delta p = \sqrt{\langle p^2 \rangle}$. As the particle has only kinetic energy, the energy is equal to $p^2/2m$, rendering $\langle p^2 \rangle = k^2h^2/4a^2$ and from this $\Delta p = kh/2a$. This leads to

$$\Delta p \Delta x = \frac{kh}{2a} . a \sqrt{\left(\frac{1}{12} - \frac{1}{2k^2\pi^2} \right)} = \frac{h}{4\pi} \sqrt{\left(\frac{k^2\pi^2}{3} - 2 \right)} \tag{4}$$

Table 1. The double summation is evaluated explicitly as the sum of 36 terms for the example n = 6

j ⇓ k ⇒	1	2	3	4	5	6
1	–1	1/4 – 1	1/4 – 1/9	1/16 – 1/9	1/16 – 1/25	1/36 – 1/25
2	1/4 – 1	–1/9	1/16 – 1	1/4 – 1/25	1/36 – 1/9	1/16 – 1/49
3	1/4 – 1/9	1/16 – 1	–1/25	1/36 – 1	1/4 – 1/49	1/64 – 1/9
4	1/16 – 1/9	1/4 – 1/25	1/36 – 1	–1/49	1/64 – 1	1/4 – 1/81
5	1/16 – 1/25	1/36 – 1/9	1/4 – 1/49	1/64 – 1	–1/81	1/100 – 1
6	1/36 – 1/25	1/16 – 1/49	1/64 – 1/9	1/4 – 1/81	1/100 – 1	–1/121

Even the minimal value of the expression in the square root ($k = 1$) is larger than one and the Heisenberg relation is verified.

The Origin Dependence

To demonstrate what is involved, a different origin is chosen and the calculation is repeated for a box, situated between $x = -a/2$ and $x = +a/2$. It is found that $\langle x \rangle = 0$, and from the fact that the spread should be independent of the choice of origin, it is to be expected that $\langle x^2 \rangle$ shows origin dependence as well. Because the problem now has symmetry, the solutions of the Schrödinger equation fall into two classes; the symmetric cosine functions for odd quantum numbers and the antisymmetric sine functions for even quantum numbers. The calculation of $\langle x^2 \rangle$ is performed twice:

$$\left\langle x^2 \right\rangle = \frac{2}{a}\int_{-a/2}^{+a/2} x^2 \cos^2 \frac{(2j-1)\pi x}{a} dx = a^2 \left(\frac{1}{12} - \frac{1}{2\left(2j-1\right)^2 \pi^2} \right) \quad (5)$$

$$\left\langle x^2 \right\rangle = \frac{2}{a}\int_{-a/2}^{+a/2} x^2 \sin^2 \frac{2j\pi x}{a} dx = a^2 \left(\frac{1}{12} - \frac{1}{2\left(2j\right)^2 \pi^2} \right) \quad (6)$$

In eqs 5 (odd quantum numbers: symmetric solutions) *and* 6 (even quantum numbers: anti-symmetric solutions) one has j = 1, 2, 3, ... It is clear, that on combining these results with $\langle x \rangle = 0$ and using eq 3, the changes lead to the same origin-independent value of the spread as seen before.

Complete Localization of the Particle in the Box

As is well known [5], superposition of De Broglie waves leads to localization of a quantum particle. This can be shown analytically using the cosine solutions of the one-dimensional particle in the box. The normalized superposition wave function (n mutually orthogonal cosines) is given by:

$$\psi = \sqrt{\frac{2}{na}} \sum_{j=1}^{n} \cos \frac{(2j-1)\pi x}{a} \quad (7)$$

The average value of x^2 now becomes

$$\left\langle x^2 \right\rangle = \frac{2}{na} \sum_{j=1}^{n} \sum_{k=1}^{n} \int_{-a/2}^{+a/2} x^2 \cos \frac{(2j-1)\pi x}{a} \cos \frac{(2k-1)\pi x}{a} dx \quad (8)$$

The integration is performed separately for two cases. In the first case ($j = k$) the calculation is very similar to eq 2 and the result is obtained immediately as

$$a^2 \left\{ \frac{1}{12} - \frac{1}{2n\pi^2} \sum_{i=1}^{n} \frac{1}{(2j-1)^2} \right\} \quad (9)$$

This certainly does not show localization of the particle. In the second case ($j \neq k$) the goniometric formula for the sum of two cosines is used backwards,

$$\frac{1}{na} \sum_{j \neq k}^{n} \left\{ \int_{-a/2}^{+a/2} x^2 \cos \frac{2(j+k-1)\pi x}{a} dx + \int_{-a/2}^{+a/2} x^2 \cos \frac{2(j-k)\pi x}{a} dx \right\} \quad (10)$$

In this expression the cosines can have positive and negative values, depending on their arguments. Consequently interference appears. The result after integration becomes

$$\frac{a^2}{2n\pi^2} \sum_{j \neq k}^{n} \left\{ \frac{(-1)^{j+k-1}}{(j+k-1)^2} + \frac{(-1)^{j-k}}{(j-k)^2} \right\} \quad (11)$$

The first case $j = k$ is included using the Kronecker δ_{jk} (= 1 for $j = k$ and 0 for $j \neq k$) function,

$$\left\langle x^2 \right\rangle = a^2 \left\{ \frac{1}{12} + \frac{1}{2n\pi^2} \sum_{j=1}^{n} \sum_{k=1}^{n} \left[\frac{(-1)^{j+k-1}}{(j+k-1)^2} + (1-\delta_{jk}) \frac{(-1)^{j-k}}{(j-k)^2} \right] \right\} \quad (12)$$

The example given in Table 1 may be continued in rows (j) and columns (k). Any column or row gives:

2[–1 – 1/9 – 1/25 – ...] + 2[1/4 + 1/16 + 1/36 + ...]

These two infinite series, found by Euler, are famous.

$$2[-\pi^2/8] + 2[+\pi^2/24] = -\pi^2/6$$

This occurs n times and thus leads to the final result

$$\left\langle x^2 \right\rangle = a^2 \left\{ \frac{1}{12} + \frac{n}{2n\pi^2} \left(-\frac{\pi^2}{6}\right) \right\} = 0 \quad (13)$$

As $\langle x \rangle = 0$, it follows that $\Delta x = 0$ and complete localization of the particle has been obtained.

References and Notes

1. Atkins, P. W. *Physical Chemistry*, 6th ed.; Oxford University Press: Oxford, 1998; pp 314–321.
2. Kauzmann, W. *Quantum Chemistry;* Academic Press: New York, 1957; p 186.
3. Berry, R. S. ;Rice, A.; Ross, J. *Physical Chemistry;* Wiley & Sons: New York, 1980; p 102. The error has not been corrected in the new 2000 edition.
4. Ratner, M. A.; Schatz, G. C. *Introduction to Quantum Mechanics in Chemistry;* Prentice Hall: Upper Saddle River, NJ, 2001; p 41.
5. Atkins, P. W *Physical Chemistry,* 6th ed.; Oxford University Press: Oxford, 1998; p 307.