PH214C – Pset 7

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Infinite well → positive E

For the infinite square well problem, show that in solving the spatial problem, for the eigenfunctions $U_n(x)$, eigenvalues E_n, that no solutions exist for any $E_n \leq 0$ and show why.

The spatial component $U(x)$ of the wavefunction should satisfy the (one-dimensional) time-invariant Shrödinger equation in the well.

$$-\frac{\hbar^2}{2m}\frac{d^2U}{dx^2} + V(x)U = EU$$

$$V(x) = \begin{cases} \infty & x < 0 \text{ or } x > a \\ 0 & 0 < x < a \end{cases}$$

Since we are looking at the solution to the ODE in the well, where $V = 0$, this reduces to a familiar constant-coefficient second-order homogeneous ODE:

$$\frac{\hbar^2}{2m}\frac{d^2U}{dx^2} + EU = 0$$

The solution will be of the form: $U(x) = Ae^{s_1 x} + Be^{s_2 x}$. Solving normally:

$$\frac{\hbar^2}{2m}s^2 + E = 0 \qquad \text{(auxiliary equation)}$$

$$s = \left(\frac{-2mE}{\hbar^2}\right)^{1/2}$$

$$U(x) = A\exp\left(\frac{\sqrt{-2mE}}{\hbar}x\right) + B\exp\left(-\frac{\sqrt{-2mE}}{\hbar}x\right) \tag{1}$$

With voltage being infinite past the boundaries of the well:

$$\lim_{V\to\infty}\left[-\frac{\hbar^2}{2m}\frac{d^2U}{dx^2} + VU = EU\right]$$

$$\Rightarrow \lim_{V\to\infty}\left[-\frac{\hbar^2}{2mV}\frac{d^2U}{dx^2} + U = \frac{E}{V}U\right]$$

$$\Rightarrow U = 0 \qquad (x < 0 \text{ or } x > a)$$

we obtain the following boundary conditions for the region in the square well:

$$U(0) = 0$$
$$U(a) = 0$$

Looking back at the form of U, we see that it is the sum of two exponentials. If the exponents are real (if $E \leq 0$), then neither exponential will ever be zero (and neither will their sum), so the wavefunction will never satisfy the boundary conditions. Thus, $E > 0$ for any particular solution to the infinite square well. More generally, the set of all particular solutions (eigenfunctions) $\{U_n\}$ will have corresponding energies (eigenvalues) $\{E_n\}$, where $E_i > 0$. This will still be true for any infinite square well problem, including shifted ones (e.g., the next problem).

Shifted well

Repeat the infinite square well problem, finding solutions (eigenvalues and eigenfunctions), but for a well in the interval $-a/2 < x < a/2$. Explain how your results relate to the original well.

The only change this makes to solving the problem is the boundary conditions. The solution in the square well is still of the same form as (1), but we have to match the shifted boundary conditions:

$$U\left(-\frac{a}{2}\right) = 0$$
$$U\left(\frac{a}{2}\right) = 0$$

The general form of $U(x)$ is given by (1). Reexpressing it with $E > 0$ (which must be true according to question 1), expanding using Euler's formula, simplifying, and letting $k = \sqrt{2mE}/\hbar$:

$$U(x) = C\cos kx + D\sin kx$$

Plugging in the boundary conditions, we obtain:

$$C\cos\left(-\frac{ak}{2}x\right) + D\sin\left(-\frac{ak}{2}x\right) = 0$$
$$C\cos\left(\frac{ak}{2}x\right) - D\sin\left(\frac{ak}{2}x\right) = 0 \quad (2)$$
$$C\cos\left(\frac{ak}{2}x\right) + D\sin\left(\frac{ak}{2}x\right) = 0 \quad (3)$$
$$2C\cos\left(\frac{ak}{2}x\right) = 0 \quad ((2)+(3))$$
$$2D\sin\left(\frac{ak}{2}x\right) = 0 \quad ((3)-(2))$$

From the latter two equations, we see that we can cosine functions in the solution if $k = (2n+1)\pi/a$, or sine functions in the solution if $k = 2n\pi/a$, where $n \in \mathbb{Z}$. Note that, since sine and cosine have different zeros, and therefore C and D cannot be simultaneously nonzero. Thus U_n (at a certain energy) must be a pure cosine or sine function. Normalizing (assuming pure cosine):

$$\begin{aligned}
1 &= \int_{-a/2}^{a/2} P(x)\,dx \\
&= \int_{-a/2}^{a/2} U^*(x)U(x)\,dx \\
&= \int_{-a/2}^{a/2} C^2 \cos^2\left(\frac{(2n+1)\pi}{a}x\right)\,dx \\
&= \frac{C^2}{2}\int_{-a/2}^{a/2} 1 + \cos\left(\frac{(2n+1)\pi}{a}x\right)\,dx \\
&= \frac{C^2}{2}(a+0)
\end{aligned}$$

Thus $C = \sqrt{2/a}$. Similarly, for pure sines, we get the same result: $D = \sqrt{2/a}$. Thus, the eigenfunctions and eigenvalues of this shifted infinite square well are:

$$U_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{2n\pi}{a}x\right) \qquad E_n = \frac{(2n+1)^2\pi^2\hbar^2}{2ma^2}$$

or

$$U_n(x) = \sqrt{\frac{2}{a}}\cos\left(\frac{(2n+1)\pi}{a}x\right) \qquad E_n = \frac{2n^2\pi^2\hbar^2}{ma^2}$$

These are similar to the particular solutions of the infinite square well from $0 < x < a$ in that their amplitudes are the same and they are all pure sinusoids. However, we also allow cosine functions because these new boundary conditions allow for it. However, since the discrete sine and cosine are now spaced at with wave numbers $2n\pi/a$ apart, it looks the same as the infinite square well for $0 < x < a$ with sine waves with wave numbers spaced $n\pi/a$ apart. (I.e., The introduction of cosines is simply an artifact of the parity of sine and cosine and doesn't reflect a change in the shape of the solutions.)

Well expectations

Compute $\langle x\rangle$, $\langle x^2\rangle$, $\langle p\rangle$, $\langle p^2\rangle$, σ_x and σ_p for the n-th state of the infinite square well. Do these states satisfy the uncertainty principle? For what n is the product of uncertainties smallest?

$$\psi_n(x,t) = \frac{\sqrt{2}}{a}\sin\left(\frac{n\pi}{a}x\right)e^{-iEt/\hbar}$$

$$
\begin{aligned}
\langle f(x) \rangle &= \int_{-\infty}^{\infty} dx\, \psi^*(x,t)\, f(x)\, \psi(x,t) \\
&= \int_0^a dx\, \psi^* f \psi \qquad\qquad \text{(infinite square well case)}
\end{aligned}
$$

Position expectations

$$
\begin{aligned}
\langle x \rangle_n &= \int_0^a dx, \psi^* x \psi \\
&= \frac{2}{a} \int_0^a dx\, x \sin^2\left(\frac{n\pi}{a} x\right) e^0 \\
&= \frac{2a}{n^2\pi^2} \int_0^{n\pi} du\, u \sin^2 u \qquad\qquad (u = \tfrac{n\pi}{a} x) \\
&= \frac{a}{n^2\pi^2} \int_0^{n\pi} du\, u(1 - \cos(2u)) \\
&= \frac{a}{n^2\pi^2} \left[\frac{u^2}{2} \bigg|_0^{n\pi} - \int_0^{n\pi} du\, u \cos(2u) \right] \\
&= \frac{a}{n^2\pi^2} \left[\frac{n^2\pi^2}{2} - 0 \right] \qquad\qquad \text{(integration by parts)} \\
&= \frac{a}{2}
\end{aligned}
$$

$$
\begin{aligned}
\langle x^2 \rangle_n &= \int_0^a dx, \psi^* x^2 \psi \\
&= \frac{2}{a} \int_0^a dx\, x^2 \sin^2\left(\frac{n\pi}{a} x\right) e^0 \\
&= \frac{2a^2}{n^3\pi^3} \int_0^{n\pi} du\, u^2 \sin^2 u \qquad\qquad (u = \tfrac{n\pi}{a} x) \\
&= \frac{a^2}{n^3\pi^3} \int_0^{n\pi} du\, u^2 (1 - \cos(2u)) \\
&= \frac{a^2}{n^3\pi^3} \left[\frac{u^3}{3} \bigg|_0^{n\pi} - \int_0^{n\pi} du\, u^2 \cos(2u) \right] \\
&= \frac{a^2}{n^3\pi^3} \left[\frac{n^3\pi^3}{3} - \left[\frac{x^2}{2} \sin 2x + \frac{x}{2} \cos 2x - \frac{1}{4} \sin 2x \bigg|_0^{n\pi} \right] \right. \\
&= \frac{a^2}{n^3\pi^3} \left[\frac{n^3\pi^3}{2} - \frac{n\pi}{2} \right] \\
&= a^2 \left(\frac{1}{3} - \frac{1}{2n^2\pi^2} \right)
\end{aligned}
$$

$$
\begin{aligned}
\sigma_{x_n}^2 &= \langle x^2\rangle_n - \langle x\rangle_n^2 \\
&= a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2} - \left(\frac{a}{2}\right)^2\right) \\
&= a^2\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)
\end{aligned}
$$

Momentum expectations

$$
\hat{p} = -i\hbar\frac{\partial\psi}{\partial x}
$$

$$
\begin{aligned}
\langle p\rangle_n &= \int_0^a dx\,\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\left[-i\hbar\left(-\frac{n\pi}{a}\right)\sqrt{\frac{2}{a}}\cos\left(\frac{n\pi}{a}x\right)\right] \\
&= \frac{2i\hbar}{a}\int_0^a dx\,\frac{n\pi}{a}\sin\left(\frac{n\pi}{a}x\right)\cos\left(\frac{n\pi}{a}x\right) \\
&= \frac{2i\hbar}{a}\int_0^a d\left(\sin\left(\frac{n\pi}{a}x\right)\right)\,\sin\left(\frac{n\pi}{a}x\right) \\
&= \frac{2i\hbar}{a}\left[\frac{1}{2}\sin^2\left(\frac{n\pi}{a}x\right)\right|_0^a \\
&= 0
\end{aligned}
$$

$$
\begin{aligned}
\langle p^2\rangle_n &= \int_0^a dx\,\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\left[-\hbar^2\left(-\frac{n^2\pi^2}{a^2}\right)\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\right] \\
&= \frac{2}{a}\left(\frac{\hbar n\pi}{a}\right)^2\int_0^a dx\,\sin^2\left(\frac{n\pi}{a}x\right) \\
&= \frac{1}{a}\left(\frac{\hbar n\pi}{a}\right)^2\int_0^a dx\,1-\cos\left(\frac{n\pi}{a}x\right) \\
&= \frac{1}{a}\left(\frac{\hbar n\pi}{a}\right)^2(a-0) \\
&= \left(\frac{\hbar n\pi}{a}\right)^2
\end{aligned}
$$

$$
\sigma_{p_n}^2 = \langle p^2\rangle_n - \langle p\rangle_n^2 = \left(\frac{\hbar n\pi}{a}\right)^2
$$

Uncertainty

$$\begin{aligned}\sigma_{x_n}\sigma_{p_n} &= \sqrt{a^2\left(\frac{1}{12}-\frac{1}{2n^2\pi^2}\right)}\sqrt{\left(\frac{\hbar n\pi}{a}\right)^2} \\ &= \hbar n\pi\sqrt{\frac{1}{12}-\frac{1}{2n^2\pi^2}}\end{aligned}$$

This has the same uncertainty characteristic: the product of uncertainties of position and momentum is a fixed number. (In other words, decreasing uncertainty for either position or momentum will increase uncertainty of the other.) We can see that this is strictly monotonically increasing w.r.t. n, so the minimum uncertainty is at $n = 1$, which gives the value:

$$\sigma_{x_1}\sigma_{p_1} = \hbar\pi\sqrt{\frac{1}{12}-\frac{1}{2\pi^2}} = 0.568\hbar = 5.99\times10^{-35}\text{ J s}$$

Mixed well

A particle in an infinite square well has the initial wave function

$$\psi(x,0) = A[U_1(x) + U_2(x)]$$

Normalize ψ

Normalize ψ to find A. Will $\psi = \psi(x,0)$ remain normalized for $t > 0$?

Since ψ is real, we can simply square it to get its magnitude. We also know that $\{U_n(x)\}$ is an orthonormal set, so $\int_{-\infty}^{\infty} dx\, U_n U_m = \delta_{nm}$.

$$\begin{aligned}1 &= \int_0^a dx\,\psi^2(x,0) \\ &= A^2\int_0^a dx\,\left[U_1^2 + 2U_1U_2 + U_2^2\right] \\ &= A^2\left[\int_0^a dx\,U_1^2 + 2\int_0^a dx\,U_1U_2 + \int_0^a dx\,U_2^2\right] \\ &= A^2\left[1 + 2(0) + 1\right] \\ A &= \frac{1}{\sqrt{2}}\end{aligned}$$

(Intuitively, this makes sense: since U_1 and U_2 are normalized, the integral of their PDFs [the PDF of ψ] should sum to 2. Thus $A = 1/\sqrt{2}$.) The wavefunction will remain normalized for $t > 0$. Multiplying in the time-dependent part, the full wavefunction is of the form:

$$\psi(x,t) = \frac{1}{\sqrt{2}} \left[U_1(x) + U_2(x)\right] e^{iEt/\hbar}$$

So

$$\begin{aligned}
&\int_0^a dx\, \psi^* \psi \\
&= \int_0^a dx\, \left[A\left[U_1 + U_2\right] e^{-iEt/\hbar}\right] \left[A\left[U_1 + U_2\right] e^{iEt/\hbar}\right] \\
&= \int_0^a dx\, A^2 \left[U_1 + U_2\right]^2 \\
&= \int_0^a dx\, \psi^2(x,0) \\
&= 1
\end{aligned}$$

PDF

Find $\psi(x,t)$ and $|\psi(x,t)|^2$.

As stated above, the wavefunction as a function of position and time can be obtained by multiplying in the time-dependent part (since we solved the wavefunction PDE using separation of variables):

$$\psi(x,t) = \frac{1}{\sqrt{2}} \left[U_1(x) + U_2(x)\right] e^{iEt/\hbar}$$

Finding the PDF (magnitude-squared distribution) is straightforward:

$$\begin{aligned}
|\psi(x,t)|^2 &= \psi^* \psi \\
&= \left[\frac{1}{\sqrt{2}} \left[U_1 + U_2\right] e^{-iEt/\hbar}\right] \left[\frac{1}{\sqrt{2}} \left[U_1 + U_2\right] e^{iEt/\hbar}\right] \\
&= \frac{1}{2} \left[U_1(x) + U_2(x)\right]
\end{aligned}$$

Momentum and position

Find $\langle x \rangle$ and $\langle p \rangle$.

Position

$$\begin{aligned}
\langle x\rangle &= \int_0^a dx\,\psi^*(x,t)\,x\,\psi(x,t) \\
&= \int_0^a dx\,A^2x\left[U_1e^{-iE_1t/\hbar}+U_2e^{-iE_2t/\hbar}\right]\left[U_1e^{iE_1t/\hbar}+U_2e^{iE_2t/\hbar}\right] \\
&= A^2\left[\int_0^a dx\,xU_1^2+\int_0^a dx\,xU_1U_2\left[e^{i(E_1-E_2)t/\hbar}+e^{i(E_2-E_1)t/\hbar}\right]+\int_0^a dx\,xU_2^2\right] \\
&= A^2[I_1+I_2+I_3] \\
I_1 &= \int_0^a dx\,xU_1^2 \\
&= \frac{2}{a}\int_0^a dx\,x\sin^2\left(\frac{\pi}{a}x\right) \\
&= \frac{1}{a}\left[\int_0^a dx\,x-\int_0^a dx\,\cos\left(\frac{2\pi}{a}x\right)\right] \\
&= \frac{1}{a}\left[\left.\frac{x^2}{2}\right|_0^a-0\right] && \text{(integration by parts)} \\
&= \frac{a}{2} \\
I_3 &= \frac{a}{2} && \text{(works out same as } I_1\text{)} \\
I_2 &= 2\int_0^a dx\,xU_1U_2\left[e^{i(E_1-E_2)t/\hbar}+e^{i(E_2-E_1)t/\hbar}\right] \\
&= \frac{4}{a}\int_0^a dx\,x\sin\left(\frac{\pi}{a}x\right)\sin\left(\frac{2\pi}{a}x\right)\left[2\cos\left(\frac{E_2-E_1}{\hbar}t\right)\right] \\
&= \frac{4}{a}\cos\left(\frac{E_2-E_1}{\hbar}t\right)\int_0^a dx\,x\left[\cos\left(\frac{\pi}{a}x\right)-\cos\left(\frac{3\pi}{a}x\right)\right] \\
&= \frac{4}{a}\cos\left(\frac{E_2-E_1}{\hbar}t\right)\left[-\frac{2a^2}{\pi^2}+\frac{2a^2}{9\pi^2}\right] && \text{(integration by parts)} \\
&= -\frac{64a}{9\pi^2}\cos\left(\frac{E_2-E_1}{\hbar}t\right) \\
\langle x\rangle &= A^2[I_1+I_3+I_2] \\
&= \frac{1}{2}\left[a-\frac{64a}{9\pi^2}\cos\left(\frac{E_2-E_1}{\hbar}t\right)\right] \\
&= a\left(\frac{1}{2}-\frac{32}{9\pi^2}\cos\left(\frac{E_2-E_1}{\hbar}t\right)\right) \\
&= a\left(\frac{1}{2}-\frac{32}{9\pi^2}\cos\left(\frac{3\hbar^2\pi^2}{2ma^2}t\right)\right)
\end{aligned}$$

Momentum

$$\begin{aligned}
\langle p\rangle &= \int_0^a dx\ \left[A\left[U_1e^{-iE_1t/\hbar}+U_2e^{-iE_2t/\hbar}\right]\right] \\
&\quad\times\left[\left(-i\hbar\frac{\partial}{\partial x}\right)\left(A\left[U_1e^{iE_1t/\hbar}+U_2e^{iE_2t/\hbar}\right]\right)\right] \\
&= -i\hbar A^2\int_0^a dx\ \left[\sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right)e^{-iE_1t/\hbar}+\sqrt{\frac{2}{a}}\sin\left(\frac{2\pi}{a}x\right)e^{-iE_2t/\hbar}\right] \\
&\quad\times\left[\frac{\pi}{a}\sqrt{\frac{2}{a}}\cos\left(\frac{\pi}{a}x\right)e^{iE_1t/\hbar}+\frac{2\pi}{a}\sqrt{\frac{2}{a}}\cos\left(\frac{2\pi}{a}x\right)e^{iE_2t/\hbar}\right] \\
&= -\frac{i\hbar}{a}\left[\int_0^a dx\,\frac{\pi}{a}\sin\left(\frac{\pi}{a}x\right)\cos\left(\frac{\pi}{a}x\right)\right. \\
&\qquad+\int_0^a dx\,\frac{2\pi}{a}\sin\left(\frac{\pi}{a}x\right)\cos\left(\frac{2\pi}{a}x\right)e^{i(E_1-E_2)t/\hbar} \\
&\qquad+\int_0^a dx\,\frac{\pi}{a}\sin\left(\frac{2\pi}{a}x\right)\cos\left(\frac{\pi}{a}x\right)e^{i(E_2-E_1)t/\hbar} \\
&\qquad\left.+\int_0^a\frac{2\pi}{a}\sin\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}x\right)\right] \\
&= -i\hbar A^2[I_1+I_2+I_3+I_4] \\
I_1 &= \int_0^a dx\,\frac{\pi}{a}\sin\left(\frac{\pi}{a}x\right)\cos\left(\frac{\pi}{a}x\right) \\
&= \int_0^\pi d\left(\sin\left(\frac{\pi}{a}\right)\right)\ \sin\left(\frac{\pi}{a}x\right) \\
&= \frac{1}{2}\left[\sin\left(\frac{\pi}{a}x\right)\right|_0^\pi \\
&= 0 \\
I_4 &= 0\text{ (by analogous calculation)} \\
I_2 &= \frac{2\pi}{a}\int_0^a dx\ \sin\left(\frac{\pi}{a}x\right)\cos\left(\frac{2\pi}{a}x\right)e^{i(E_1-E_2)t/\hbar} \\
&= \frac{\pi}{a}e^{i(E_1-E_2)t/\hbar}\int_0^a dx\ \sin\left(\frac{3\pi}{a}x\right)-\sin\left(\frac{\pi}{a}x\right) \\
&= \frac{\pi}{a}e^{i(E_1-E_2)t/\hbar}\left[-\frac{a}{3\pi}\cos\left(\frac{3\pi}{a}x\right)+\frac{a}{\pi}\cos\left(\frac{\pi}{a}x\right)\right|_0^a \\
&= -\frac{2}{3}e^{i(E_1-E_2)t/\hbar} \\
I_3 &= \frac{2}{3}e^{i(E_2-E_1)t/\hbar}\text{ (by similar calculation)}
\end{aligned}$$

$$
\begin{aligned}
\langle p\rangle &= -i\hbar A^2[I_1+I_2+I_3+I_4] \\
&= -i\hbar A^2\left[0-\frac{2}{3}e^{i(E_1-E_2)t/\hbar}+\frac{2}{3}e^{i(E_2-E_1)t/\hbar}+0\right] \\
&= \hbar A^2\left[\frac{4}{3}\left(\frac{e^{i(E_2-E_1)t/\hbar}-e^{-i(E_2-E_1)t/\hbar}}{2i}\right)\right] \\
&= \frac{4\hbar A^2}{3}\sin\left(\frac{E_2-E_1}{\hbar}t\right) \\
&= \frac{4\hbar A^2}{3}\sin\left(\frac{3\hbar^2\pi^2}{2ma^2}t\right)
\end{aligned}
$$

Expectation of H

Find the expectation value of H and compare it to E_1 and E_2.

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$
\begin{aligned}
\langle H\rangle &= \int_0^a dx\,\left[\frac{1}{\sqrt{2}}\left[U_1+U_2\right]e^{-iEt/\hbar}\right]\left[\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\left(\frac{1}{\sqrt{2}}[U_1+U_2]e^{iEt/\hbar}\right)\right] \\
&= \frac{\hbar^2}{4m}\int_0^a dx\,[U_1+U_2]\left[\left(\frac{\pi}{a}\right)^2 U_1+\left(\frac{2\pi}{a}\right)^2 U_2\right] \\
&= \frac{\hbar^2}{4m}\int_0^a dx\,\left[\left(\frac{\pi}{a}\right)^2 U_1^2+\left(\frac{\sqrt{5}\pi}{a}\right)^2 U_1U_2+\left(\frac{2\pi}{a}\right)^2 U_2^2\right] \\
&= \frac{\hbar^2}{4m}\left[\left(\frac{\pi}{a}\right)^2\int_0^a dx\,U_1^2+\left(\frac{\sqrt{5}\pi}{a}\right)^2\int_0^a dx\,U_1U_2+\left(\frac{2\pi}{a}\right)^2\int_0^a dx\,U_2^2\right] \\
&= \frac{\hbar^2}{4m}\left[\left(\frac{\pi}{a}\right)^2(1)+\left(\frac{\sqrt{5}\pi}{a}\right)^2(0)+\left(\frac{2\pi}{a}\right)^2(1)\right] \\
&= \frac{5\pi^2\hbar^2}{4ma^2}
\end{aligned}
$$

We know that the energies of a given particular solution are:

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

so

$$
\begin{aligned}
\langle H \rangle &= \frac{5\pi^2\hbar^2}{4ma^2} \\
&= \frac{1}{2}\left[\frac{1^2\pi^2\hbar^2}{2ma^2} + \frac{2^2\pi^2\hbar^2}{2ma^2}\right] \\
&= A^2\left[E_1 + E_2\right] \\
&= A^2\left[\langle H \rangle_1 + \langle H \rangle_2\right]
\end{aligned}
$$

as expected.