THE TIME-DEPENDENT WAVEPACKET APPROACH, OBTAINING SCATTERING INFORMATION
Homework 8

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EXERCISE 1

1.a: Explain the meaning of $|\psi(x)|^2 dx$ in Quantum Mechanics

In quantum mechanics, the modulus square of the wave function $|\psi(x)|^2 dx$ represents the probability density function that describes the probability of a particle described by a wave function $\psi(x)$ being in an interval dx around x.

Subsequently, this function should result in 1 after integration, according to the features of a probability density function:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

1.b: Write down the mathematical relation which allows to calculate $\psi(x)$ starting from $\widehat{\psi(p)}$

The inverse Fourier transform:

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \widehat{\psi(p)} \exp\left(\frac{ipx}{\hbar}\right) dp = FT^{-1}(\widehat{\psi(p)})$$

$\widehat{\psi(p)}$ – the wavefunction in the momentum representation; $\psi(x)$ – the wavefunction in the position representation; The exponential term $\exp\left(\frac{ipx}{\hbar}\right)$ is a complex exponential function that acts as the kernel of the inverse Fourier transform.

1.c: Explain the precise meaning of $\Delta_\psi P_x$ in Quantum Mechanics and give a mathematical expression to calculate it

$\Delta_\psi P_x$ represents the uncertainty in the measurement of the momentum along the x-axis for a quantum state described by the wave function ψ. This arises from the Heisenberg Uncertainty Principle,

$$\Delta_\psi X \cdot \Delta_\psi P_x \geqslant \frac{\hbar}{2}$$

which states that certain pairs of physical properties, like position and momentum, cannot be simultaneously measured with arbitrary precision.

$\Delta_\psi P_x$ is defined as the standard deviation of the momentum in the state ψ. The expression for $\Delta_\psi P_x$ is given by:

$$\Delta_\psi P_x = \sqrt{\langle P_x^2 \rangle - \langle P_x \rangle^2}$$

where:

- $\langle P_x \rangle$ is the expectation value (average value) of the momentum in the x-direction.
- $\langle P_x^2 \rangle$ is the expectation value of the square of the momentum in the x-direction.

$$\langle P_x \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(-i\hbar \frac{d}{dx} \right) \psi(x) dx$$

$$\langle P_x^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(-i\hbar \frac{d}{dx} \right)^2 \psi(x) dx$$

1.d: How do you calculate $\langle X \rangle_\psi$ using the function $\psi(x)$?

To calculate the expectation value of position $\langle X \rangle_\psi$ using the wave function $\psi(x)$, one uses the formula below:

$$\langle X \rangle_\psi = \int_{-\infty}^{\infty} x |\psi(x)|^2 dx$$

In this equation, x is the position, and $|\psi(x)|^2$ is the probability density, obtained from $\psi(x)$.

1.e

Considering the gaussian which is programmed in the code,

$$\psi(x) = \left(\frac{2}{\pi \Gamma^2} \right)^{1/4} e^{-\frac{(x-X_0)^2}{\Gamma^2}} e^{ik_0(x-X_0)}$$

obtain analitically $\widehat{\psi(p)}$. HINT: the following integral might be useful:

$$\int_{-\infty}^{+\infty} e^{-a^2u^2/2} e^{ibu} du = \frac{\sqrt{2\pi}}{a} e^{-\frac{b^2}{2a^2}} \left(\text{ with } \operatorname{Re}\left(a^2\right) > 0\right)$$

The Fourier transform is defined as:

$$\widehat{\psi(p)} = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \psi(x) e^{-\frac{ipx}{\hbar}} dx$$

Plugging in the expression for $\psi(x)$:

$$\widehat{\psi(p)} = \frac{1}{\sqrt{2\pi\hbar}} \left(\frac{2}{\pi\Gamma^2}\right)^{1/4} \int_{-\infty}^{+\infty} e^{-\frac{(x-X_0)^2}{\Gamma^2}} e^{ik_0(x-X_0)} e^{-\frac{ipx}{\hbar}} dx$$

Let's work a bit with the integral part of the expression above. We could decompose it into an integral of four exponent functions:

$$\int_{-\infty}^{+\infty} e^{-\frac{(x-X_0)^2}{\Gamma^2}} e^{ik_0(x-X_0)} e^{-\frac{ipx}{\hbar}} dx = \int_{-\infty}^{+\infty} e^{-\frac{(x-X_0)^2}{\Gamma^2}} \cdot e^{ik_0(x-X_0)} \cdot e^{-\frac{ip(x-X_0)}{\hbar}} \cdot e^{-\frac{ipX_0}{\hbar}} dx$$

$e^{-\frac{ipX_0}{\hbar}}$ is not dependent on x, so we can put it outside of the integral. So after simplification, we get:

$$e^{-\frac{ipX_0}{\hbar}} \int_{-\infty}^{+\infty} e^{-\frac{(x-X_0)^2}{\Gamma^2}} \cdot e^{i(x-X_0)(k_0-\frac{p}{\hbar})} dx$$

It is the right time to recall the hint provided:

$$\int_{-\infty}^{+\infty} e^{-a^2u^2/2} e^{ibu} du = \frac{\sqrt{2\pi}}{a} e^{-\frac{b^2}{2a^2}} \left(\text{ with } \operatorname{Re}\left(a^2\right) > 0\right)$$

$$u = (x - X_0)$$
$$b = (k_0 - \frac{p}{\hbar})$$

$$a = \sqrt{\frac{2}{\Gamma^2}}$$

$$du = d(x - X_0) = dx$$

$$\int_{-\infty}^{+\infty} e^{-\frac{(x-X_0)^2}{\Gamma^2}} \cdot e^{i(x-X_0)(k_0 - \frac{p}{\hbar})}\, dx = \frac{\sqrt{2\pi}}{\sqrt{\frac{2}{\Gamma^2}}} e^{-\frac{(k_0-\frac{p}{\hbar})^2}{2(\sqrt{\frac{2}{\Gamma^2}})^2}}$$

By now, we just need to simplify this expression:

$$\widehat{\psi(p)} = \frac{1}{\sqrt{2\pi\hbar}} \left(\frac{2}{\pi\Gamma^2}\right)^{1/4} e^{-\frac{ipX_0}{\hbar}} \frac{\sqrt{2\pi}}{\sqrt{\frac{2}{\Gamma^2}}} e^{-\frac{(k_0-\frac{p}{\hbar})^2}{2(\sqrt{\frac{2}{\Gamma^2}})^2}}$$

After arithmetical magic, we get:

$$\widehat{\psi(p)} = \left(\frac{\Gamma^2}{2\pi\hbar^2}\right)^{1/4} \cdot e^{-\frac{ipX_0}{\hbar}} \cdot e^{-\frac{\Gamma^2\left(k_0-\frac{p}{\hbar}\right)^2}{4}}$$

And finally, $k_0 = \frac{p_0}{\hbar}$:

$$\widehat{\psi(p)} = \left(\frac{\Gamma^2}{2\pi\hbar^2}\right)^{1/4} \cdot e^{-\frac{ipX_0}{\hbar}} \cdot e^{-\frac{\Gamma^2(p_0-p)^2}{4\hbar^2}}$$

1.f: Remember that, using the code, you can generate the momentum representation of different gaussians. Show, by plotting the position representation and the momentum representation associated to different gaussian functions, that the uncertainty relation ($\Delta_\psi X \cdot \Delta_\psi P_x \geqslant \hbar/2$) holds, explaining its meaning. If you change any parameters in the code, please indicate which. (NOTE: you could also build these functions by yourself, without using the code; however, the code is ready to do that)

I decided to plot the functions via using my code. To make it easier to see that the uncertainty principle holds in all cases, I plotted the dependencies of $\Delta_\psi X \cdot \Delta_\psi P_x$ and a line corresponding to $\hbar/2$ (see Figure 4). In all cases, the product is higher than $\hbar/2$. I have included the chosen parameters in the plot captions.

Heisenberg principle highlights a fundamental property of quantum systems: the more precisely we know the position of a particle, the less precisely we can know its momentum, and vice versa.

The uncertainty in position and momentum of gaussian wavepackets is represented by their respective widths in position and momentum representations. If the gaussian is narrow in position space (indicating a small $\Delta_\psi X$), it will be wide in momentum space (indicating a large $\Delta_\psi P_x$), and vice versa.

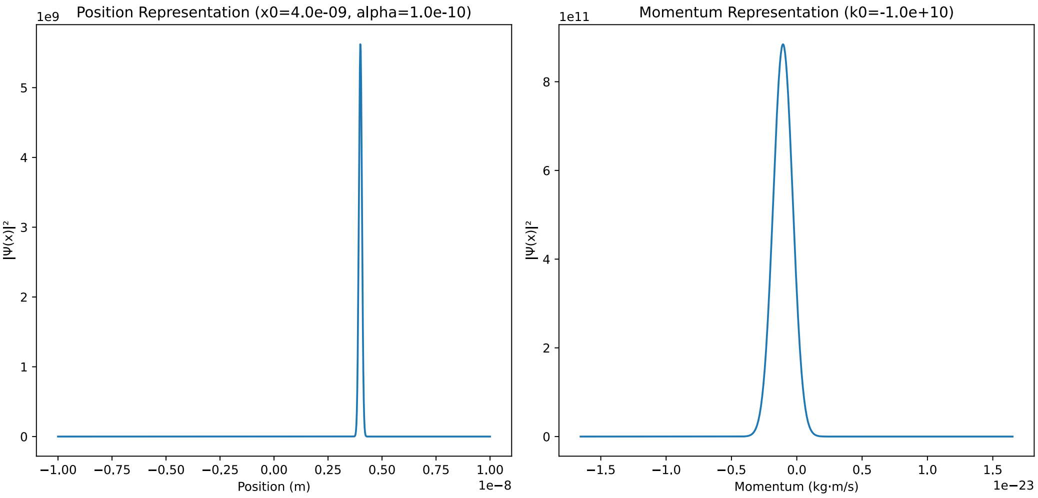

Figure 1: For $x_0 = 4.0 \times 10^{-9}$ m, $\alpha = 1.0 \times 10^{-10}$ m, $k_0 = -1.0 \times 10^{10}$ m^{-1}: $\Delta x = 7.07 \times 10^{-11}$ m, $\Delta p = 1.60 \times 10^{-15}$ kg·m/s Uncertainty product = 1.13×10^{-25} J·s $\frac{\hbar}{2} = 5.27 \times 10^{-35}$ J·s ; Uncertainty Principle Verified: True

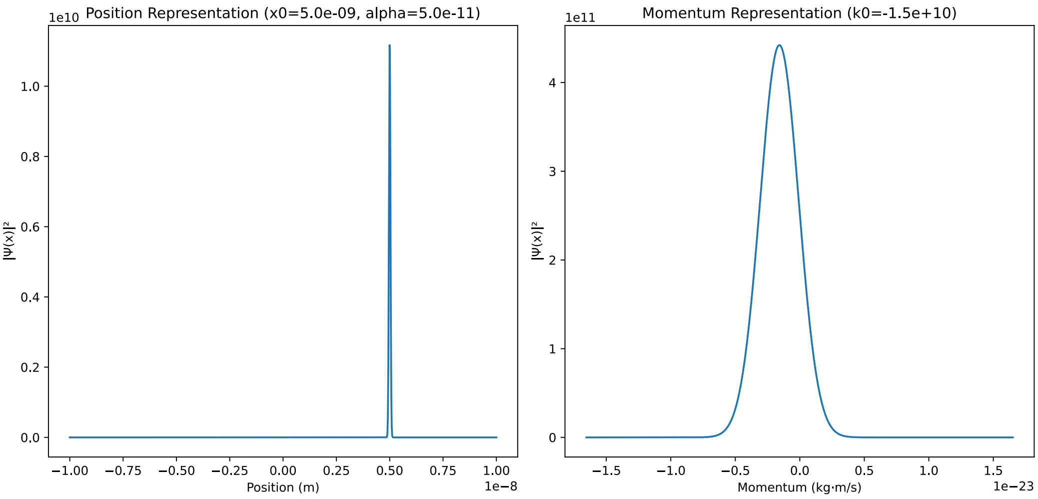

Figure 2: For $x_0 = 5.0 \times 10^{-9}$ m, $\alpha = 5.0 \times 10^{-11}$ m, $k_0 = -1.5 \times 10^{10}$ m^{-1}: $\Delta x = 3.54 \times 10^{-11}$ m, $\Delta p = 4.38 \times 10^{-15}$ kg·m/s Uncertainty product = 1.55×10^{-25} J·s $\frac{\hbar}{2} = 5.27 \times 10^{-35}$ J·s ; Uncertainty Principle Verified: True

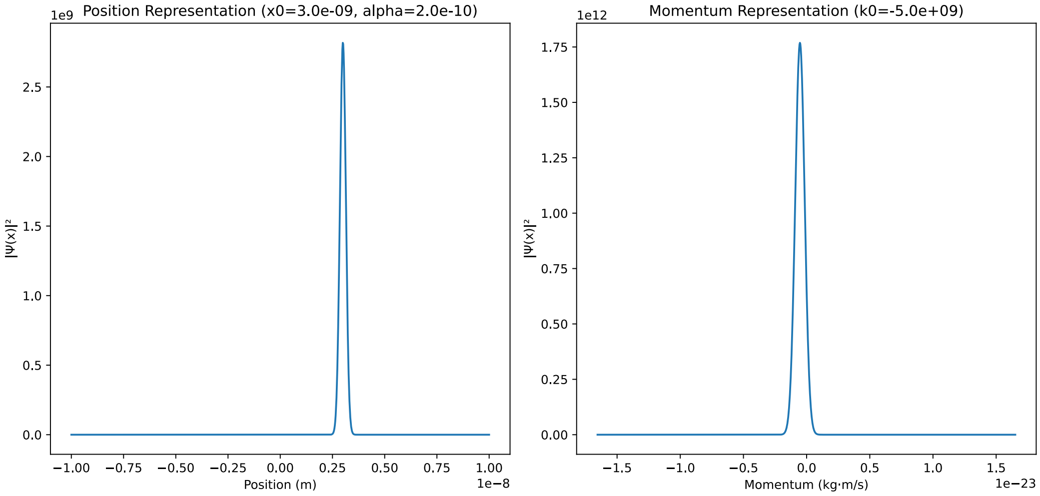

Figure 3: For $x_0 = 3.0 \times 10^{-9}$ m, $\alpha = 2.0 \times 10^{-10}$ m, $k_0 = -5.0 \times 10^{9}$ m^{-1}: $\Delta x = 1.41 \times 10^{-10}$ m, $\Delta p = 4.10 \times 10^{-16}$ kg·m/s Uncertainty product = 5.80×10^{-26} J·s $\frac{\hbar}{2} = 5.27 \times 10^{-35}$ J·s ; Uncertainty Principle Verified: True

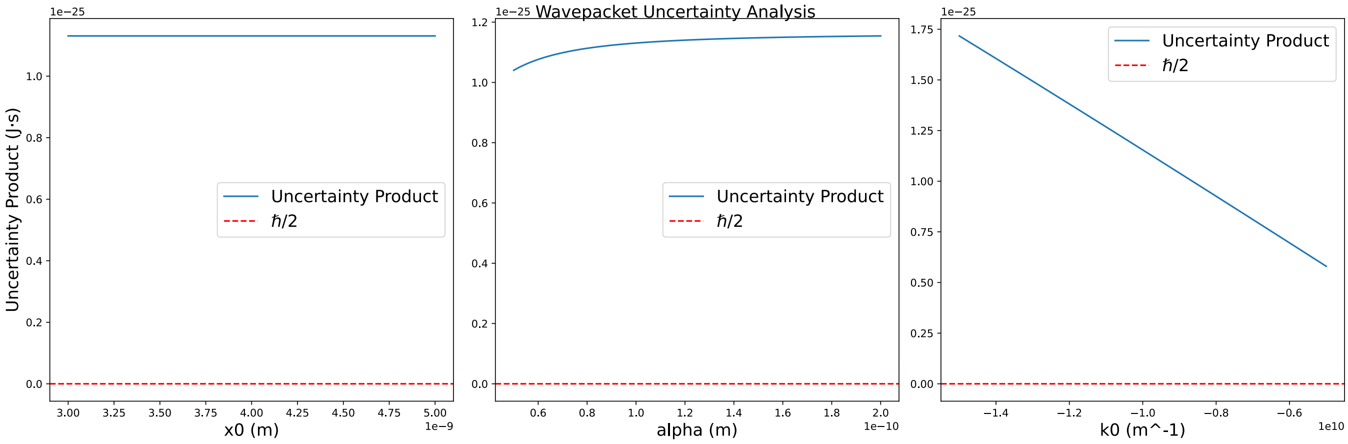

Figure 4: Plots for uncertanity products dependent on different parameters

EXERCISE 2

2.i: Imagine that the mass of the particle is 80u **and we want to explore energies in the range** $\left(700\ \mathrm{cm}^{-1}, 900\ \mathrm{cm}^{-1}\right)$**. Assuming that the TD method only provides accurate results for those energies in the gaussian within the range** $\langle T\rangle_\psi \pm \Delta_\psi T$**, which numerical values of** k_0 **and** Γ **would you use (include units)? Use the code to generate this function and plot its modulus square.**

We are given an energy range $\left(700\,\mathrm{cm}^{-1}, 900\,\mathrm{cm}^{-1}\right)$. To find the central energy value ($E_{\mathrm{mean}} = ecol$) and the energy width ($\Delta E = deltae$), we calculate the average(800) and the difference of the maximum and minimum energies with this average(100), respectively. The wavevector k_0 is calculated using the equation:

$$k_0 = -\sqrt{\frac{2\mu E_{\mathrm{mean}}}{\hbar^2}}$$

where μ is the mass of the particle, E_{mean} is the mean energy, and $\hbar$ is the reduced Planck constant. The negative sign indicates the wavepacket propagate to the left. The width Γ is calculated using the equation:

$$\Gamma = \sqrt{\frac{2E_{\mathrm{mean}}}{\mu}}\frac{\hbar}{\Delta E}$$

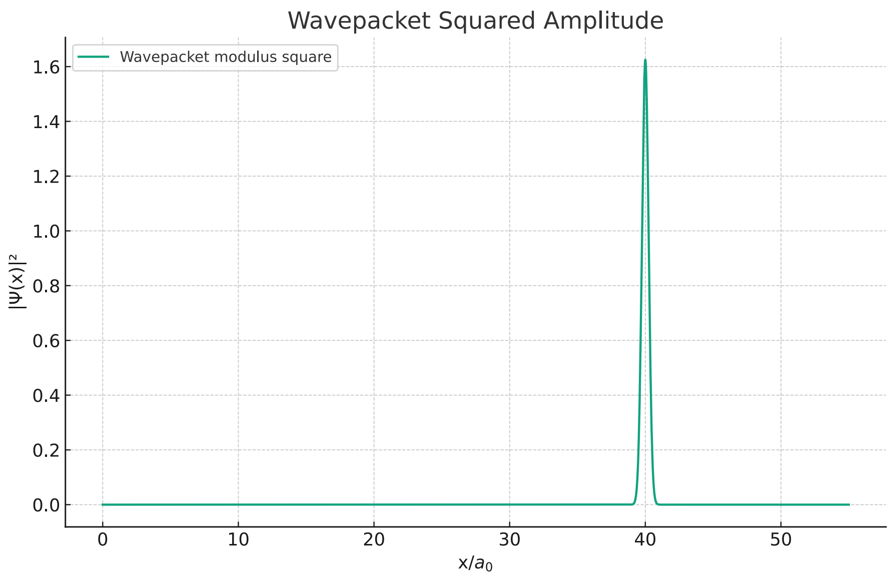

Figure 5: Modulus square; Answer: k_0 = -61.62 a_0^{-1} and $\Gamma = 0.26\,a_0$

2.ii: ii) As we discussed, the mean value of the kinetic energy of this gaussian is approximately given by $\langle T \rangle_\psi \approx \frac{\hbar^2 k_0^2}{2\mu}$ (accurate enough for our purposes). Obtain analytically (by integration) the exact expression of $\langle T \rangle_\psi$ as a function of μ, Γ, k_0.

$$\langle T \rangle_\psi = \int_{-\infty}^{+\infty} \frac{\hbar^2 k^2}{2\mu} |\psi(k)|^2 \, dk$$

$$\psi(x) = \left(\frac{2}{\pi \Gamma^2} \right)^{1/4} e^{-\frac{(x-X_0)^2}{\Gamma^2}} e^{ik_0(x-X_0)}$$

$$\widehat{\psi(p)} = \left(\frac{\Gamma^2}{2\pi\hbar^2} \right)^{1/4} \cdot e^{-\frac{ipX_0}{\hbar}} \cdot e^{-\frac{\Gamma^2\left(k_0 - \frac{p}{\hbar}\right)^2}{4}}$$

Since $\widehat{\psi(p)} = \widehat{\psi}\left(k = \frac{p}{\hbar}\right) / \sqrt{\hbar}$, we can switch to k-representation:

$$\widehat{\psi(k)} = \sqrt{\hbar} \left(\frac{\Gamma^2}{2\pi\hbar^2} \right)^{1/4} \cdot e^{-ikX_0} \cdot e^{-\frac{\Gamma^2(k_0-k)^2}{4}}$$

$$|\widehat{\psi(k)}|^2 = \frac{\hbar\Gamma}{\sqrt{2\pi}} \cdot e^{-\frac{\Gamma^2(k_0-k)^2}{2}}$$

$$\langle T \rangle_\psi = \underbrace{\frac{\hbar^2 \Gamma}{2\mu\sqrt{2\pi}}}_{=A} \int_{-\infty}^{+\infty} k^2 \cdot e^{-\frac{\Gamma^2(k-k_0)^2}{2}} \, dk$$

Substitution:

$$u = k - k_0 \qquad k = u + k_0 \qquad du = d(k-k_0) = dk$$

$$\langle T \rangle_\psi = A \int_{-\infty}^{+\infty} (u + k_0)^2 \cdot e^{-\frac{\Gamma^2 u^2}{2}} \, du$$

$$\langle T \rangle_\psi = A \int_{-\infty}^{+\infty} (u^2 + 2uk_0 + k_0^2) \cdot e^{-\frac{\Gamma^2 u^2}{2}} \, du$$

$$\langle T\rangle_\psi = A\left(\int\limits_{-\infty}^{+\infty} u^2\cdot e^{-\frac{\Gamma^2u^2}{2}}\,du + \int\limits_{-\infty}^{+\infty} 2uk_0\cdot e^{-\frac{\Gamma^2u^2}{2}}\,du + \int\limits_{-\infty}^{+\infty} k_0^2\cdot e^{-\frac{\Gamma^2u^2}{2}}\,du\right)$$

The integral $\int\limits_{-\infty}^{+\infty} 2uk_0\cdot e^{-\frac{\Gamma^2u^2}{2}}\,du$ has an odd integrand. According to the hint provided, it is equal to zero:

$$\int\limits_{-\infty}^{+\infty} x^{2n+1}e^{-ax^2}dx = 0(\text{odd integrand}),\text{ with } a\in\mathbb{R}, a>0, n\geq 0)$$

$$\int\limits_{-\infty}^{+\infty} x^{2n}e^{-ax^2}dx = \frac{1\cdot 3\cdot 5\cdot\ldots\cdot(2n-1)}{2^n a^n}\sqrt{\frac{\pi}{a}}$$

(even integrand), with $a\in\mathbb{R}, a>0, n\geq 1$

$$\int\limits_{-\infty}^{+\infty} u^2\cdot e^{-\frac{\Gamma^2u^2}{2}}\,du = \frac{1}{2a}\sqrt{\frac{\pi}{a}} = \frac{1}{\Gamma^2}\sqrt{\frac{2\pi}{\Gamma^2}} = \frac{\sqrt{2\pi}}{\Gamma^3}$$

$$\int\limits_{-\infty}^{+\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}},\text{ with } a\in\mathbb{R}, a>0$$

$$\int\limits_{-\infty}^{+\infty} k_0^2\cdot e^{-\frac{\Gamma^2u^2}{2}}\,du = k_0^2\frac{\sqrt{2\pi}}{\Gamma}$$

$$\langle T\rangle_\psi = A\left(\frac{\sqrt{2\pi}}{\Gamma^3} + k_0^2\frac{\sqrt{2\pi}}{\Gamma}\right)$$

$$\langle T\rangle_\psi = \frac{\hbar^2\Gamma}{2\mu\sqrt{2\pi}}\cdot\frac{\sqrt{2\pi}}{\Gamma}\left(\frac{1}{\Gamma^2}+k_0^2\right) = \frac{\hbar^2}{2\mu}\left(\frac{1}{\Gamma^2}+k_0^2\right) \approx \frac{\hbar^2k_0^2}{2\mu}$$

2.iii:

Using a gaussian with parameters $e_{\mathbf{col}} = 500.0d_0 \times$ conve1 and $deltae = e_{\mathbf{col}}/3.2d_0$, and the same mass that was initially in the program, generate using the code, the wavepackets $\psi(x)$ corresponding to various times of propagation, t_i. Compare them by plotting $|\psi(x)|^2$. From the graphs, and analyzing the change of the position of the center of the gaussian with time, extract an approximate velocity for the wavepacket; relate it numerically to the mean momentum of the initial gaussian using Ehrenfest theorems (be careful with units).

In fig.6, gaussians for some timesteps are represented. We see that with propagation of the wavepacket to the left, the gaussian width (Γ) increases, whereas the height of the gaussians decreases. If we look at the gaussian for timestep 4000, we can also notice that it becomes slightly asymmetrical (close to the barrier). To be able to calculate the velocity, we need to plot the function

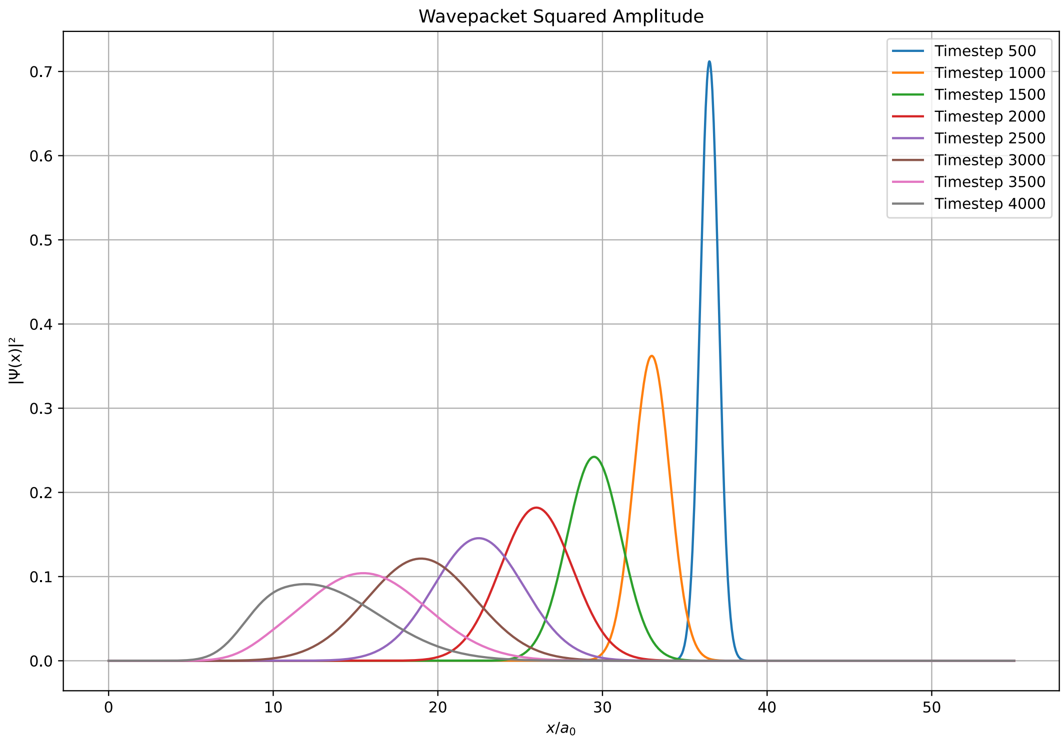

Figure 6: Wavepackets squared amplitude by time

of the coordinates of the gaussian centers over time. In this case, in fig.6, I picked up 8 functions. In fig.7, we got an almost linear function of the center coordinate over time. A linear approximation of this function gives us the slope, which is equal to velocity ($V = \frac{\Delta x}{\Delta t}$). Even though the function looks linear, the velocity value actually is not constant, which could be noticed from fig. 8. The velocity is constant in the range of time 1–3 ps and equal to 6.78 $\alpha_0/ps = 358.66\, m/s$. By multiplying by mass $87u = 87 \cdot 1.660539040 \cdot 10^{-27} kg$, we get momentum $p = 5.18 \cdot 10^{-23}$ kg · m/s.

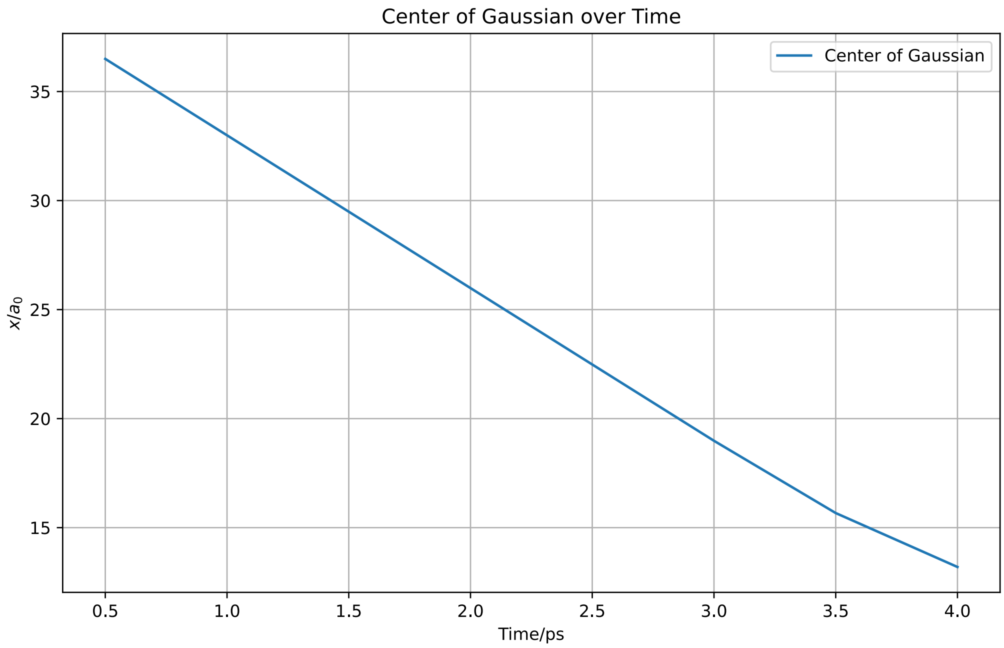

Figure 7: Position of the center of the gaussian over time for chosen timesteps

According to Ehrenfest's theorem, the expectation value of the momentum operator in quantum mechanics corresponds to classical momentum. Therefore, the calculated velocity can be related to the mean momentum p of the gaussian using the relation $p = m \cdot v$, where m is the mass of the particle.

For a gaussian wavepacket, the mean momentum can also be expressed in terms of the wave number k_0 as $p = -\hbar k_0$. From the *sal* output file, $k_0 = -50.79797\alpha_0^{-1}$.

$$\langle V \rangle = -\frac{\hbar k_0}{\mu}$$

$$\langle p \rangle = -\hbar k_0$$

$$\langle p \rangle = -1.054571800 \cdot 10^{--34} J \cdot s \cdot -50.79797\alpha_0 \cdot (0.529 \cdot 10^{-10})^{-1} = 10.01 \cdot 10^{-23}\,\text{kg} \cdot \text{m/s}$$

Generally speaking, the results have the same order of magnitude, but the approximate value is 2x larger.

In the figures 11, I represented the same plots but over 20000 timesteps, so we can notice that the wavepacket propagates backward after 4000 timesteps

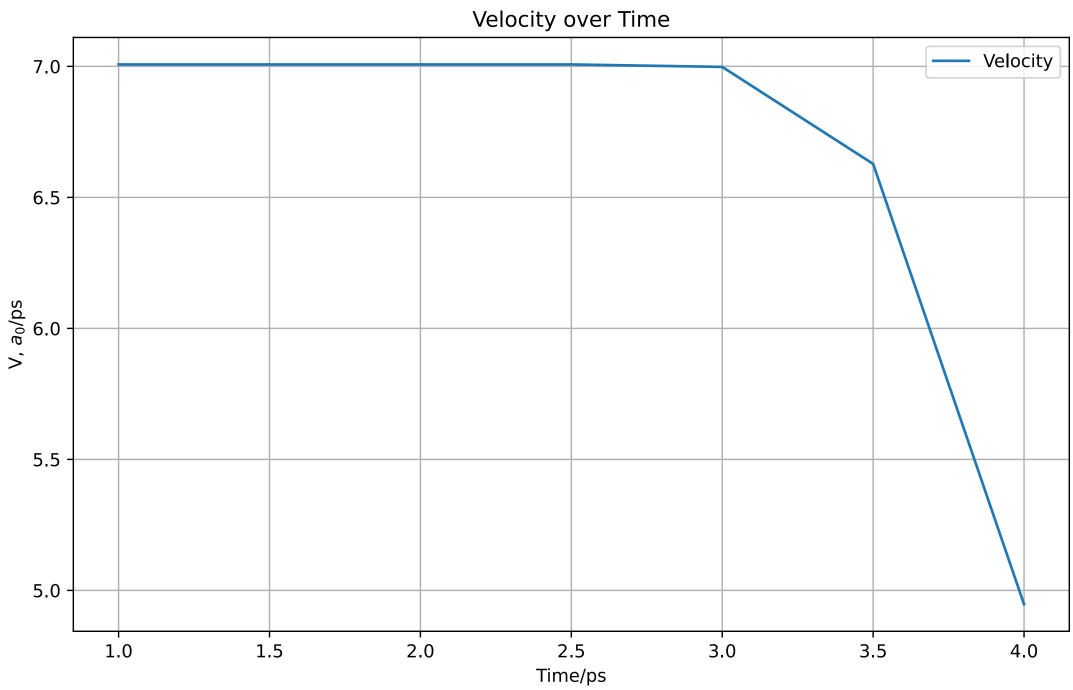

Figure 8: Velocity of the wavepacket over time for chosen timesteps

after absorption. Additionally, we see the changing of the velocity over time before and after reflection.

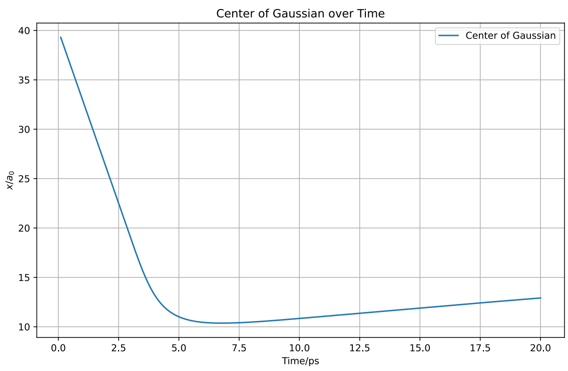

Figure 9: Position of the center

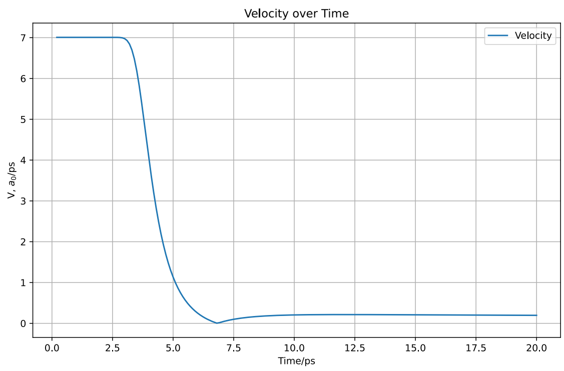

Figure 10: Velocity of the gaussian

Figure 11: Position of the center and velocity of the gaussian over time