Homework 1

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1 Problem 4.2

Use separation of variable in *cartesian* coordinates to solve the infinite *cubical* well (or particle in a box):

$$V(x,y,z) = \begin{cases} 0, & \forall x,y,z \in [0,a] \\ \infty, & \forall x,y,z \notin [0,a] \end{cases}$$

1. Find the stationary states, and the corresponding energies.
2. Call the distinct energies $E_1, E_2, \ldots$ in order of increasing energy. Find E_1, E_2, E_3, E_4, E_5 and E_6. Determine their degeneracies (that is, the number of different states that share the same energy).
3. What is the degeneracy of E_{14}, and why is this case interesting?

Solution 1: Stationary states

To find the stationary states of the infinite cubical well, we are going to solve the time independent Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla\psi = E\psi,\ \forall x,y,z \in [0,a],$$

with the following boundary conditions $\psi(0,0,0) = \psi(a,a,a) = 0$. To solve the equation we are going to use the method of separation of variables, that is, that we assume that the solution of the differential equation has the following form $\psi(x,y,z) = X(x)Y(y)Z(z)$. Substituting this solution to the differential equation, we can perfom some algebraic manipulation,

$$-\frac{\hbar^2}{2m}\nabla\psi = E\psi$$
$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)X(x)Y(y)Z(z) = -\frac{2m}{\hbar^2}EX(x)Y(y)Z(z)$$
$$Y(y)Z(z)\frac{\partial^2}{\partial x^2}X(x)+X(x)Z(z)\frac{\partial^2}{\partial y^2}Y(y)+X(x)Y(y)\frac{\partial^2}{\partial z^2}Z(z) = -\frac{2m}{\hbar^2}EX(x)Y(y)Z(z)$$
$$\frac{1}{X(x)}\frac{\partial^2}{\partial x^2}X(x)+\frac{1}{Y(y)}\frac{\partial^2}{\partial y^2}Y(y)+\frac{1}{Z(z)}\frac{\partial^2}{\partial z^2}Z(z) = -\frac{2m}{\hbar^2}E.$$

Now we can re-write this partial differential equation into three diferential equations assumming that $E=\frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)$,

$$\frac{\mathrm{d}^2X(x)}{\mathrm{d}x^2} = -k_x^2X(x) \to X(x) = A_x\sin[k_xx]+B_x\cos[k_xx],$$
$$\frac{\mathrm{d}^2Y(y)}{\mathrm{d}y^2} = -k_y^2Y(y) \to Y(y) = A_y\sin[k_yy]+B_y\cos[k_yy],$$
$$\frac{\mathrm{d}^2Z(z)}{\mathrm{d}z^2} = -k_z^2Z(z) \to Z(z) = A_z\sin[k_zz]+B_z\cos[k_zz].$$

In order to find the expression for the coefficients $A_n,\ B_n$ and k_n, we start by applying the boundary conditions. Since sin and cos are periodic functions, they satisfy $f(0)=f(a)$, however only the sin function satisfy the condition $f(0)=f(a)=0$, hence, we set $B_x=B_y=B_z=0$ leading to,

$$X(x) = A_x\sin[k_xx],\quad Y(y) = A_y\sin[k_yy],\quad Z(z) = A_z\sin[k_zz].$$

Now we recall the fact that x, y and z have units of distance and that the argument of the sin function must be dimensonless, combining this restriction with the property of periodicity we can define the constants k_n as, $k_x = n_x\pi/a,\ k_y = n_y\pi/a,\ k_z = n_z\pi/a$, where $(n_x, n_y, n_z)\in\mathbb{Z}^+$. With this information we can re-write the solution as,

$$\psi(x,y,z) = A_xA_yA_z\sin\left[\frac{n_x\pi}{a}x\right]\sin\left[\frac{n_y\pi}{a}y\right]\sin\left[\frac{n_z\pi}{a}z\right],$$

with

$$E = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2+n_y^2+n_z^2\right),\quad (n_x,n_y,n_z)\in\mathbb{Z}^+.$$

Finally, in order to get the expression for A_x, A_y and A_z we apply the normalization restiction to each spatial dimension,

$$\int_0^a A_l^2\sin^2\left[\frac{n_l\pi}{a}s\right]ds = A_l^2\frac{a}{4}\left(2-\frac{1}{\pi n}\sin[2\pi n]\right) = 1,$$

since $n\in\mathbb{Z}^+$ we get that $A_l=\sqrt{2/a}$, therefore,

$$\boxed{\psi(x,y,z) = \sqrt{\frac{8}{a^3}}\sin\left[\frac{n_x\pi}{a}x\right]\sin\left[\frac{n_y\pi}{a}y\right]\sin\left[\frac{n_z\pi}{a}z\right],\quad (n_x,n_y,n_z)\in\mathbb{Z}^+}$$

Solution 2: Energy analysis

To find the values of the energy we recall the following expression,

$$E = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right), \quad (n_x, n_y, n_z) \in \mathbb{Z}^+.$$

Since the energy is determine by $\left(n_x^2 + n_y^2 + n_z^2\right)$ we can focus our analysis in that value. On the other hand, to find the degeneracies of the states, we can study the possible permutation of the tuples form by (n_x, n_y, n_z) with a maximum value of m, and compute the sum of the squares to get the associate energy to each tuple.

As a heads up, we can expect degeneracies the following degeneracies: $1, 3, 6$. If all the values are equal, the we can only form one unique tuple (a, a, a), hence, degeneracy 1. For the case in which we have two distinct values, then we can form 3 unique tuples, (a, b, b), (a, b, b) and (b, b, a), hence, degeneracy 3. Finally, for the case in which all the values are different we can get 6 unique tuples,(a, b, c), (a, c, b), $\ldots$, (c, a, b), hence degeneracy 6. In order to facilitate the numeric computation, the following julia script was implmented,

```julia
# Posible values for nx, ny and nz
n_max=3;
n = (1:1:n_max);

# Energy function
function getEnergy(nx,ny,nz)
    return nx.^2 .+ ny.^2 .+ nz.^2
end

# Create the tuples/states
tuples=Iterators.product(n,n,n);

# Get the energy of each state an array with that
states = reshape([ [getEnergy(it...),it] for it in tuples],prod(size(
    tuples)),1);

# Get the states and degeneracy
sort_states=sort(states,dims=1);

# Take the unique energies
energies = unique(first.(sort_states));

# Get the states and compute the degeneracy
index=map(s-> searchsorted(reduce(vcat,first.(sort_states)),s),
    energies);
degeneracy=length.(index);
```

which results in the following values,

Energy	Degeneracy
$E_1 = \frac{\pi^2\hbar^2}{2ma^2}3$	1
$E_2 = \frac{\pi^2\hbar^2}{2ma^2}6$	3
$E_3 = \frac{\pi^2\hbar^2}{2ma^2}9$	3
$E_4 = \frac{\pi^2\hbar^2}{2ma^2}11$	3
$E_5 = \frac{\pi^2\hbar^2}{2ma^2}12$	1
$E_6 = \frac{\pi^2\hbar^2}{2ma^2}14$	6

Solution 3: E_14

For this case, we use the same script as before, but we need to increase the value m at least to 4 to get 20 values of unique energies. When the maximum value of $n_x,\ n_y$ or n_z is 4, we only get one state for $E_{14} = 27$, $(3, 3, 3)$. However, when we increase the maximum value to $m = 5$, we get 32 values of unique energies and a degeneracy of 4 for E_{14},

$$(3, 3, 3) \quad , (1, 1, 5), \quad (1, 5, 1), \quad (5, 1, 1).$$

Here we can see that this case is interesting, because it can not be well describe using combinatorics. As we can see from the tuples, the total degeneracy of E_{14} is the sum of the case when the parameters $n_x,\ n_y$ and n_z are equal (degeneracy of 1), and when two of the parameters are equal (degeneracy of 3). Another curiosity is that each case is associated with two distinct maximum values of the parameters, where the case of all parameters are equal, the maximum value is 3, and when we have two parameters equal, the maximum value is 5.

2 Problem 4.3

Use

$$P_l^m(x) \equiv \left(1 - x^2\right)^{|m|/2} \left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^{|m|} P_l(x)$$

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^l \left(x^2 - 1\right)^l$$

$$Y_l^m(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\cos[\theta])$$

to construct Y_0^0 and Y_2^1. Check that they are normalized and orthogonal.

Solution 4: Spherical harmonic

We start with $Y_0^0(\theta,\phi)$, $m=l=0$ subsistuting those values into the associate Legendre prolynomials,

$$P_0(x) \equiv \frac{1}{2^0 0!}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^0 \left(x^2-1\right)^0 = 1,$$

and

$$P_0^0(x) \equiv \left(1-x^2\right)^{|0|/2}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^{|0|} P_0(x) = 1,$$

hence,

$$Y_0^0(\theta,\phi) = \frac{1}{\sqrt{4\pi}}.$$

Now, to check if it is normalize we integrate in spherical coordinates from $\theta \in (0,\pi)$ and $\phi \in (0,2\pi)$,

$$\begin{aligned}
\int_0^\pi \int_0^{2\pi} \left|Y_0^0(\theta,\phi)\right|^2 \sin\theta d\theta d\phi &= \int_0^\pi \int_0^{2\pi} \frac{1}{4\pi} \sin\theta d\theta d\phi \\
&= \frac{1}{4\pi}\left[\int_0^\pi \sin\theta d\theta\right]\left[\int_0^{2\pi} d\phi\right] \\
&= \frac{1}{4\pi}[2][2\pi] \\
&= 1
\end{aligned}$$

$$\boxed{\int_0^\pi \int_0^{2\pi} \left|Y_0^0(\theta,\phi)\right|^2 \sin\theta d\theta d\phi = 1}$$

Now we do the same procedure with Y_2^1, $m=1$ and $l=2$, which gives that $P_2^1(x) = \sqrt{1-x^2}\frac{\mathrm{d}}{\mathrm{d}x}P_2(x)$ and $P_2(x) = 1/2(3x^2-1)$, hence,

$$P_2(x) \equiv \frac{1}{2^2 2!}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 \left(x^2-1\right)^2 = \frac{1}{2}\left(3x^2-1\right)$$

and

$$P_2^1(x) \equiv \left(1-x^2\right)^{|1|/2}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^{|1|} P_2^1(x) = 3x\sqrt{1-x^2}$$

$$\begin{aligned}
Y_2^1(\theta,\phi) &= -\sqrt{\frac{(2(2)+1)}{4\pi}\frac{(2-|1|)!}{(2+|1|)!}} e^{im\phi} P_2^1(\cos[\theta]) \\
&= -\sqrt{\frac{5}{4\pi}\frac{1}{6}} e^{i\phi} 3\cos[\theta]\sqrt{1-\cos^2[\theta]} = -\sqrt{\frac{5}{24\pi}} e^{i\phi}\sqrt{9}\cos[\theta]\sin[\theta] \\
&= -\sqrt{\frac{15}{8\pi}} e^{i\phi}\cos[\theta]\sin[\theta]
\end{aligned}$$

Now we check if the function is normalize,

$$\begin{aligned}
\int_0^{\pi}\int_0^{2\pi}\left|Y_2^1(\theta,\phi)\right|^2\sin\theta d\theta d\phi &= \int_0^{\pi}\int_0^{2\pi}\frac{15}{8\pi}\cos^2[\theta]\sin^2[\theta]\sin\theta d\theta d\phi \\
&= \frac{15}{8\pi}\left[\int_0^{\pi}\cos^2[\theta]\sin^2[\theta]\sin\theta d\theta\right]\left[\int_0^{2\pi}d\phi\right] \\
&= \frac{15}{8\pi}\left[\frac{4}{15}\right][2\pi] \\
&= 1
\end{aligned}$$

$$\boxed{\int_0^{\pi}\int_0^{2\pi}\left|Y_2^1(\theta,\phi)\right|^2\sin\theta d\theta d\phi = 1}$$

Finally, to check orthogonality we perform th following procedure,

$$\begin{aligned}
\int_0^{\pi}\int_0^{2\pi}\left[Y_0^0(\theta,\phi)\right]^*Y_2^1(\theta,\phi)\sin\theta d\theta d\phi &= \int_0^{\pi}\int_0^{2\pi}\left[\frac{1}{\sqrt{4\pi}}\right]\left[-\sqrt{\frac{15}{8\pi}}e^{i\phi}\cos[\theta]\sin[\theta]\right]\sin\theta d\theta d\phi \\
&= -\frac{1}{\sqrt{4\pi}}\sqrt{\frac{15}{8\pi}}\left[\int_0^{\pi}\cos[\theta]\sin[\theta]\sin\theta d\theta\right]\left[\int_0^{2\pi}e^{i\phi}d\phi\right] \\
&= -\sqrt{\frac{15}{32\pi^2}}[0][0] \\
&= 0
\end{aligned}$$

$$\boxed{\int_0^{\pi}\int_0^{2\pi}\left[Y_0^0(\theta,\phi)\right]^*Y_2^1(\theta,\phi)\sin\theta d\theta d\phi = 0}$$

3 Problem 4.13

- Find $\langle r\rangle$ and $\langle r^2\rangle$ for an electron in the ground state of hydrogen. Express your answers in terms of the Bohr radius (ρ).
- Find $\langle x\rangle$ and $\langle x^2\rangle$ for an electron in the ground state of hydrogen. *Hint:* this requires no new integration-note that $r^2 = x^2 + y^2 + z^2$, and exploit the symmetry of the ground state.
- Find $\langle x^2\rangle$ in the state $n = 2, l = 1, m = 1$. *Warning:* This state is not symmetrical in x, y, z. Use $x = r\sin\theta\cos\phi$.

Solution 5: Expected value of position.

By solving the Schrodinger equation in spherical coordinates with the Coulomb's law as the potential energy, the stationary states are in terms of the Bohr's radius,

$$\psi_{(n,m,l)}(r,\theta,\phi) = \frac{1}{r}\rho^{l+1}e^{-\rho}\upsilon(\rho)Y_l^m(\theta,\phi),$$

with $\upsilon(\rho)$ being a polynimial of degree $j_{\max} = n - l - 1$ with coefficients,

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)}c_j.$$

For the ground state of the Hydrogen atom we set the parameters to $(n = 1, l = 0, m = 0)$, which gives,

$$\psi_{1,0,0}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}.$$

To compute the expected value we perform the following operation,

$$\begin{aligned}
\langle r \rangle &= \int_V r|\psi_{1,0,0}(r,\theta,\phi)|^2 dV \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} r\frac{1}{\pi a^3}e^{-2r/a}r^2 \sin\theta d\theta d\phi dr \\
&= \frac{1}{\pi a^3}\int_0^\infty e^{-2r/a}r^3 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \\
&= \frac{1}{\pi a^3}\left(\frac{3}{8}a^4\right)(2)(2\pi) \\
&= \frac{3}{2}a.
\end{aligned}$$

Now, for $\langle r^2 \rangle$,

$$\begin{aligned}
\left\langle r^2 \right\rangle &= \int_V r^2|\psi_{1,0,0}(r,\theta,\phi)|^2 dV \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2\frac{1}{\pi a^3}e^{-2r/a}r^2 \sin\theta d\theta d\phi dr \\
&= \frac{1}{\pi a^3}\int_0^\infty e^{-2r/a}r^4 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \\
&= \frac{1}{\pi a^3}\left(\frac{3}{4}a^5\right)(2)(2\pi) \\
&= 3a^2.
\end{aligned}$$

Therefore,

$$\boxed{\langle r \rangle = \frac{3}{2}a, \quad \left\langle r^2 \right\rangle = 3a^2}$$

Solution 6: Expected values and standard deviation of the x component.

Recalling the hint, $r^2 = x^2 + y^2 + z^2$ and using the symmetry of the ground state we can conclude that,

$$\begin{aligned}\left\langle x^2\right\rangle &= \frac{1}{3}\left\langle r^2\right\rangle \\ &= a^2.\end{aligned}$$

On the other hand, for $\langle x\rangle$ we can write the integrals considering that $x = r\sin\theta\cos\phi$,

$$\begin{aligned}\langle x\rangle &= \int_0^\infty\int_0^\pi\int_0^{2\pi}(r\sin\theta\cos\phi)\frac{1}{\pi a^3}e^{-2r/a}r^2\sin\theta d\theta d\phi dr \\ &= \frac{1}{\pi a^3}\int_0^\infty e^{-2r/a}r^3 dr\int_0^\pi\sin^2\theta d\theta\int_0^{2\pi}\cos\phi d\phi \\ &= \frac{1}{\pi a^3}\left(\frac{3}{8}a^4\right)\left(\frac{\pi}{2}\right)(0) \\ &= 0\end{aligned}$$

Hence,

$$\boxed{\langle x\rangle = 0, \quad \left\langle x^2\right\rangle = a^2}$$

Solution 7: Stationary state $(n = 2, l = 1, m = 1)$

For this case we recall the stationay state of the hydrogen atom,

$$\psi_{(n,m,l)}(r,\theta,\phi) = \frac{1}{r}\rho^{l+1}e^{-\rho}\upsilon(\rho)Y_l^m(\theta,\phi),$$

with $\upsilon(\rho)$ being a polynimial of degree $j_{\max} = n - l - 1$ with coefficients,

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)}c_j.$$

Applying the values of the parameters,

$$\psi_{(2,1,1)}(r,\theta,\phi) = -\frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}re^{-r/2a}e^{i\phi}\sin\theta.$$

Now we can perform the previous procedures to compute $\langle x^2 \rangle$,

$$\begin{aligned}
\left\langle x^2 \right\rangle &= \int_V r^2 |\psi_{1,0,0}(r,\theta,\phi)|^2 dV \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} (r\sin\theta\cos\phi)^2 \frac{1}{64\pi a^5} r^2 e^{-r/a} \sin^2\theta r^2 \sin\theta d\theta d\phi dr \\
&= \frac{1}{64\pi a^5} \int_0^\infty r^6 e^{-r/a} dr \int_0^\pi \sin^5\theta d\theta \int_0^{2\pi} \cos^2\phi d\phi \\
&= \frac{1}{64\pi a^5} \left(720a^7\right)\left(\frac{16}{15}\right)(\pi) \\
&= 12a^2
\end{aligned}$$

Therefore,

$$\boxed{\left\langle x^2 \right\rangle = 12a^2}$$

4 Problem 4.14

What is the *most probable* value of r, in the ground state of hydrogen? (The answer is not zero!) *Hint:* First you must figure out the probability that the electron would be found between r and $r + dr$.

Solution 8: Most probable value of the position in the ground state.

To compute the most probable value of r we need to compute the maximum value of the probability density function associate with the ground state. In order to get the probability density function we formulate the following integral,

$$P = \int_0^r \int_0^\pi \int_0^{2\pi} |\psi_{1,0,0}(r,\theta,\phi)|^2 r^2 \sin\theta d\theta d\phi dr,$$

since the angular symmetry is a guaranteed feature of the ground state, we can simplify the expression to,

$$P = \int_0^r 4\pi |\psi_{1,0,0}(r,\theta,\phi)|^2 r^2 dr.$$

Now, from the context of probability, we known that the probability density function is the integran,

$$p(r) = 4\pi r^2 |\psi_{1,0,0}(r,\theta,\phi)|^2.$$

Now we can get the most probable value of r,

$$\begin{aligned}\frac{\mathrm{d}p(r)}{\mathrm{d}x} &= \frac{\mathrm{d}}{\mathrm{d}x}4\pi r^2|\psi_{1,0,0}(r,\theta,\phi)|^2 \\ &= \frac{\mathrm{d}}{\mathrm{d}x}4\pi r^2\frac{1}{\pi a^3}e^{-2r/a} \\ &= \frac{1}{a^3}\left(\frac{2}{a}(a-r)re^{-2r/a}\right),\end{aligned}$$

finally, $\frac{\mathrm{d}}{\mathrm{d}x}p(r) = 0$,

$$\begin{aligned}\frac{1}{a^3}\left(\frac{2}{a}(a-r)re^{-2r/a}\right) &= 0 \\ are^{-2r/a} &= r^2e^{-2r/a} \\ a &= r.\end{aligned}$$

$$\boxed{\frac{\mathrm{d}p(r)}{\mathrm{d}x} = 0 \to r = a}$$

5 Problem 4.23

In problem 4.3 you showed that

$$Y_2^1(\theta,\phi) = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\phi}.$$

Apply the raising operator to find $Y_2^2(\theta,\phi)$. Use equation $A_l^m = \hbar\sqrt{l(l+1)-m(m\pm 1)} = \hbar\sqrt{(l\mp m)(l\pm m+1)}$ to get the normalization.

Solution 9: Raising operator of angular momentum.

Recalling the raising operator,

$$L_+ = \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cos[\theta]\frac{\partial}{\partial\theta}\right).$$

Applying the operator into Y_2^1,

$$\begin{aligned}
L_+Y_2^1 &= \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cos\left[\theta\right]\frac{\partial}{\partial\theta}\right)\left[-\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\phi}\right] \\
&= -\sqrt{\frac{15}{8\pi}}\hbar e^{i\phi}\left(\frac{\partial}{\partial\theta}\left[\sin\theta\cos\theta e^{i\phi}\right] + i\cos\left[\theta\right]\frac{\partial}{\partial\theta}\left[\sin\theta\cos\theta e^{i\phi}\right]\right) \\
&= -\sqrt{\frac{15}{8\pi}}\hbar e^{i2\phi}\left(\cos^2\left[\theta\right] - \sin^2\left[\theta\right] - \cos^2\left[\theta\right]\right) \\
&= \sqrt{\frac{15}{8\pi}}\hbar\left(e^{i\phi}\sin\left[\theta\right]\right)^2,
\end{aligned}$$

due to future convinience, we can re-write the expression as follows,

$$L_+Y_2^1 = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\hbar\left(e^{i\phi}\sin\left[\theta\right]\right)^2.$$

Finally, we apply the normalization constant A_2^1,

$$\begin{aligned}
\frac{1}{A_2^1}\left(L_+Y_2^1\right) &= \frac{1}{\hbar\sqrt{2\cdot 3 - 1\cdot 2}}\left(\frac{1}{2}\sqrt{\frac{15}{2\pi}}\hbar\left(e^{i\phi}\sin\left[\theta\right]\right)^2\right) \\
&= \frac{1}{4}\sqrt{\frac{15}{2\pi}}\left(e^{i\phi}\sin\left[\theta\right]\right)^2
\end{aligned}$$

$$\boxed{Y_2^2(\theta,\phi) = \frac{1}{A_2^1}\left(L_+Y_2^1\right) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\left(e^{i\phi}\sin\left[\theta\right]\right)^2}$$