1. Welcome back 2-D SHO!

Using non-degenerate perturbation theory, we worked out a few problems for the 1-D SHO. In two dimensions, however, we encounter a system where most excited states are degenerate in energy, so more sophisticated techniques are needed. With this as a warning: Consider a 2-D isotropic SHO, which in Cartesian coordinates has the Hamiltonian

$$\hat{H}^0 = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right] + \frac{1}{2} m\omega^2 (x^2 + y^2)$$

where $\omega = (\kappa/m)^{1/2}$ with $\kappa =$ spring constant. The eigenvalues of this Hamiltonian are

$$E_n^{(0)} = \hbar \omega (n + 1)$$

with $n = n_x + n_y$, and $n_x, n_y = 0, 1, 2, \ldots$.

Now turn on an external potential of the form $\hat{H}' = \varepsilon xy$. Treating this as a small quantity, calculate the first-order energy shift of the ground state and show that it vanishes.

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SOLUTION

As is often the case in physics, the ease or complexity of solving this problem depends a lot on how we attack it. We are dealing with a two-dimensional, isotropic SHO, that is perturbed by a weak interaction of the form $H' \propto xy$. Given this potential, it should seem clear that we want to work in Cartesian coordinates. At some point we will also need to evaluate some matrix elements, and there are several techniques for doing this, e.g., using raising and lowering operators on abstract eigenstates, or using coordinate representations of the operators and wave functions to carry out integrals. In most cases, the former technique is easier, but we can see how things play out.

With the above ideas as guidelines, we turn first to the unperturbed Hamiltonian. In this case, separation of variables is trivial, and we have

$$\hat{H}^0 = \hat{H}^0(x) + \hat{H}^0(y)$$

with

$$\hat{H}^0(z) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + \frac{1}{2} m\omega^2 z^2 \quad z = x \text{ or } y$$
Thus, the solutions of Schrödinger’s Equation will be of the form
\[
\psi(x, y) = X(x) Y(y)
\]
where \( X \) and \( Y \) are solutions of the one-dimensional SHO problem in \( x \) or \( y \), respectively. Each 1-D solution is characterized by a single quantum number, \( n_x \) or \( n_y \), with energies
\[
E_{n_z} = (n_z + 1/2) \hbar \omega \quad n_z = 0, 1, 2, \ldots
\]
As before, \( z \) is either \( x \) or \( y \). The total energy of the 2-D system is therefore
\[
E_n = E_{n_x} + E_{n_y} = (n_x + n_y + 1) \hbar \omega = (n + 1) \hbar \omega
\]
where we have defined the total energy quantum number \( n \equiv n_x + n_y \).

Given this separation into \( x \) and \( y \) relations, it is fairly easy to work with raising and lowering operators, noting that we have separate (independent) operators in each dimension. For any particular eigenstate, we just need to specify our two quantum numbers, so we use the notation \(|n_x, n_y\rangle\) for our state vectors. If we wanted to use a coordinate representation, then \(|n_x, n_y\rangle \rightarrow \psi_{n_x}(x) \psi_{n_y}(y)\), where a wave function of a single variable is understood to mean a solution of the 1-D SHO problem in that coordinate.

Before evaluating the effects of the perturbation, it is also useful to recall a few key features of the raising and lowering operators. For each coordinate \( z \) (= \( x \) or \( y \)), we can write
\[
z = \left( \frac{\hbar}{2m\omega} \right)^{1/2} [a_+^{(z)} + a_-^{(z)}] = \beta [a_+^{(z)} + a_-^{(z)}]
\]
with \( \beta \equiv \sqrt{\hbar/2m\omega} \). Note that these operators only affect the quantum number of the corresponding coordinate so, for example, we find that
\[
a_+^{(x)} |n_x, n_y\rangle = \sqrt{n_x + 1} |n_x + 1, n_y\rangle \quad a_-^{(y)} |n_x, n_y\rangle = \sqrt{n_y} |n_x, n_y - 1\rangle
\]
We now have all the pieces in place to solve this problem. Consider first the ground state, with \( n = 0 \). This means that \( n_x = 0 \) and \( n_y = 0 \), so there is no degeneracy! The \( n = 0 \) energy level consists of the single state \(|0, 0\rangle\), and so we can calculate the first-order effect of our perturbation immediately, using
\[
E_0^{(1)} = \langle \psi_0^{(0)} | \hat{H}' | \psi_0^{(0)} \rangle = \varepsilon \langle 0, 0 | xy | 0, 0 \rangle
\]
Now we see the full power of using the raising and lowering operators. Rather than writing our wave functions in terms of Hermite polynomials and exponentials of \( x^2 \) and \( y^2 \), then doing messy integrals, we just manipulate quantum numbers. For example:
\[
y |0, 0\rangle = \beta [a_+^{(y)} + a_-^{(y)}] |0, 0\rangle = \beta |0, 1\rangle
\]
and so
\[
xy |0, 0\rangle = \beta^2 [a_+^{(x)} + a_-^{(x)}] |0, 1\rangle = \beta^2 |1, 1\rangle
\]
Because all the unperturbed wave functions are orthogonal to each other, the inner product of $|0, 0\rangle$ with $|1, 1\rangle$ is exactly zero. More explicitly, we use the above to see:

$$E_0^{(1)} = \varepsilon \langle 0, 0 | xy | 0, 0 \rangle = \varepsilon \beta^2 \langle 0, 0 | 1, 1 \rangle = 0$$

The ground state energy of the 2-D SHO is indeed unaffected by this perturbation, at least to first order, as we wanted to show.

2. The (2-D) SHO Must Go On!

Continuing the above: solve for the first-order energy shift of the first excited state(s).

_SOLUTION_

We now turn to the first excited state, when $n = 1$. There are two ways to attain this: either $n_x = 1$ and $n_y = 0$, or $n_x = 0$ and $n_y = 1$. These means that the first excited level of the 2-D SHO is doubly degenerate ($d = 2$), and so we must use the techniques of degenerate perturbation theory. We have two unperturbed states, described in our compact notation as $|1, 0\rangle$ and $|0, 1\rangle$, and we must find the right linear combinations of these that diagonalize $\hat{H}'$. Thus, following the procedures discussed in class, we start by evaluating the elements of the $2 \times 2$ matrix that represents $\hat{H}'$ in this basis. Our first element is

$$H'_{11} = \varepsilon \langle 1, 0 | xy | 1, 0 \rangle = 0$$

This vanishes by inspection, _i.e._, with a little bit of thinking. The operators $x$ and $y$ can move the quantum numbers $n_x$ and $n_y$ up and down by 1, but they _always_ change them, so we never regain the state we started with. This means that the expectation value of $xy$ in _any_ state will always be zero (see previous problem for another example!). In particular,

$$H'_{22} = \varepsilon \langle 0, 1 | xy | 0, 1 \rangle = 0$$

So, all that’s left is the off-diagonal element. This takes only slightly more work. We have

$$H'_{12} = \varepsilon \langle 1, 0 | xy | 0, 1 \rangle$$

Proceeding as before, we see _make sure these make sense to you!_

$$y |0, 1\rangle = \beta \left[ \sqrt{2} |0, 2\rangle + |0, 0\rangle \right]$$

and then

$$xy |0, 1\rangle = \beta^2 \left[ \sqrt{2} |1, 2\rangle + |1, 0\rangle \right]$$
Using orthogonality again, we get the nice result

\[ H'_{12} = \varepsilon \langle 1, 0 | xy | 0, 1 \rangle = \varepsilon \beta^2 \langle 1, 0 | [\sqrt{2} | 1, 2 \rangle + | 1, 0 \rangle \rangle = \varepsilon \beta^2 (0 + 1) = \frac{\varepsilon \hbar}{2m\omega} \]

Because the \( \hat{x} \) operators have no effect on \( n_y \), etc., we could also have just broken this up into its \( x \) and \( y \) pieces, and solved for the product of the 1-D matrix elements

\[ H'_{12} = \varepsilon \langle 1 | x | 0 \rangle \langle 0 | y | 1 \rangle \]

which yields the same result. Either way, we obtain our final (and more intuitive) form for \( H'_{12} \) by multiplying top and bottom by \( \omega \), which gives us

\[ H'_{12} = \frac{\varepsilon}{2\kappa} \hbar \omega \]

Noting that the energy level spacing of the unperturbed system is just \( \hbar \omega \), we see that \( \varepsilon \) being “small” means it should be small relative to the spring constant \( \kappa \), such that

\[ \varepsilon \ll 2\kappa \]

Finally, because \( \hat{H}' \) is hermitian, we also know that \( H'_{21} = (H'_{12})^* \), and so the matrix \( H' \) is completely known. Defining \( A \equiv \varepsilon \hbar \omega / 2\kappa \), we now have to solve the secular equation

\[
\begin{vmatrix}
H'_{11} - E^{(1)}_\mu & H'_{12} \\
H'_{21} & H'_{22} - E^{(1)}_\mu
\end{vmatrix} = \begin{vmatrix}
-E^{(1)}_\mu & A \\
A^* & -E^{(1)}_\mu
\end{vmatrix} = 0
\]

From the properties of a determinant, we obtain our (almost) final result

\[ (E^{(1)}_\mu)^2 - |A|^2 = 0 \]

We can easily read off our two eigenvalues, \( E^{(1)}_\mu = \pm A \), and see that our perturbation does indeed break the degeneracy, with energy shifts

\[ E^{(1)}_+ = \frac{\varepsilon}{2\kappa} \hbar \omega \quad \text{and} \quad E^{(1)}_- = -\frac{\varepsilon}{2\kappa} \hbar \omega \]

This is a curious result. Because the operator \( xy \) changes both quantum numbers of the state, its expectation value always vanishes. Hence, the first-order energy shift will be zero for any non-degenerate level. This also means that, for degenerate levels, the diagonal elements of \( H'_{mn} \) will vanish, and the only effect will be due to the fact that \( xy \) mixes different states. Put another way, our two first excited states \( |1, 0 \rangle \) and \( |0, 1 \rangle \) are exactly the wrong choices for the “correct” unperturbed wave functions \( \psi^0 \). The “right” choices are the two orthogonal combinations formed by taking the sum and the difference of these two states, that is, \( \psi^0_\pm = (1/\sqrt{2}) [|1, 0 \rangle \pm |0, 1 \rangle] \).
3. Relatively Easy, Relativistically

When examining the first-order corrections to the hydrogen atomic energy levels due to relativistic effects, we found a term proportional to \( p^4 \), where \( p \) is the electron’s momentum. We attributed this to higher-order terms in the kinetic energy \( T \) when expanded in powers of \( p^2 \). What is the next term in this expansion, \( i.e., \) what is the third term in \( T(p) \) when \( pc/(mc^2) \) is a small quantity? Rewrite your answer in terms of \( T_0 \equiv p^2/2m \), and estimate its magnitude in eV.

**SOLUTION**

This problem is relatively easy \( \ldots \) since it has nothing to do with quantum mechanics! We just want to do a non-relativistic reduction of the fully relativistic relation between kinetic energy \( T \) and linear momentum \( p \) for a particle of mass \( m \), working to one higher order than we did in class.

We start by expressing the total energy \( E \) of a particle of mass \( m \) in terms of either \( m \) and \( T \), or \( m \) and \( p \). We know

\[
E = mc^2 + T
\]

but also

\[
E = [(mc^2)^2 + (pc)^2]^{1/2} = mc^2 \left[ 1 + \left( \frac{pc}{mc^2} \right)^2 \right]^{1/2}
\]

Equating these, we obtain the exact result

\[
T = mc^2 \left\{ \left[ 1 + \left( \frac{p}{mc} \right)^2 \right]^{1/2} - 1 \right\}
\]

We now want to carry out a expansion of the term in square brackets, treating \( p/mc \) as a small quantity. Thus, we need to work out the expansion for \( (1 + \varepsilon)^{1/2} \) to third-order, taking \( \varepsilon \) to be small. Using a standard Taylor Series, we get

\[
(1 + \varepsilon)^{1/2} = \sum_{n=0}^{\infty} \frac{\varepsilon^n}{n!} \left[ \frac{d^n}{d\varepsilon^n} (1 + \varepsilon)^{1/2} \right]_{\varepsilon=0}
\]

\[
= 1 + \frac{\varepsilon}{1!} \cdot \frac{1}{2} + \frac{\varepsilon^2}{2!} \cdot \frac{1}{2} \cdot \frac{-1}{2} + \frac{\varepsilon^3}{3!} \cdot \frac{1}{2} \cdot \frac{-1}{2} \cdot \frac{-3}{2} + \ldots
\]

\[
= 1 + \frac{\varepsilon}{2} - \frac{\varepsilon^2}{8} + \frac{\varepsilon^3}{16} + \ldots
\]
Using this in our equation for $T$ yields

$$T = mc^2 \left\{ 1 + \frac{1}{2} \left( \frac{p}{mc} \right)^2 - \frac{1}{8} \left( \frac{p}{mc} \right)^4 + \frac{1}{16} \left( \frac{p}{mc} \right)^6 + \ldots \right\} - 1$$

$$= mc^2 \left[ \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} + \frac{p^6}{16m^6c^6} + \ldots \right]$$

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \frac{p^6}{16m^5c^4} + \ldots$$

This is a nice result. To first order we regain the classical Newtonian result $T = p^2/2m$. The next-order term is also the same as we assumed in lecture, so we have confirmed that as well. Finally, this tells us that the third-order term (or second-order correction) to $T$ is

$$T^{(2)} = \frac{p^6}{16m^5c^4}$$

Just to tidy things up, it is sometimes more useful to express the above expansion in terms of the non-relativistic kinetic energy, which I will call $T_0$, i.e., $T_0 \equiv p^2/2m$. Written this way, we have

$$T = T_0 - \frac{1}{2mc^2} (T_0)^2 + \frac{1}{2(mc^2)^2} (T_0)^3 + \ldots$$

$$= T_0 \left[ 1 - \frac{1}{2} \left( \frac{T_0}{mc^2} \right) + \frac{1}{2} \left( \frac{T_0}{mc^2} \right)^2 + \ldots \right]$$

Expressed in this form, it becomes very clear that we are dealing with a non-relativistic expansion, because with each additional power of $T_0$, we also have an additional factor of $1/(mc^2)$ to suppress it. Thus, we can now just read off that $T_0/(mc^2)$ is our small quantity in this expansion.

We can also get a rough idea of the size of the second-order correction by noting that we expect $T_0 \sim 10$ eV, while $2mc^2 \sim 10^6$ eV, and so

$$T^{(2)} \sim \frac{(10)^3}{(10^6)^2} = 10^{-9} \text{ eV}$$

As expected, this is about five orders of magnitude smaller than the first-order correction, which we showed was of order $10^{-4}$ eV, which in turn is about five orders of magnitude smaller than $T_0$. 
4. Angular Anguish

Please do problem 6.16, found on page 276 in the text. Pay attention to the hint, or your ‘anguish’ will grow exponentially!

SOLUTION

For this problem, we work out a series of commutation relations involving the orbital, spin, and total angular momentum vectors $\mathbf{L}$, $\mathbf{S}$, and $\mathbf{J}$, respectively. This is pretty much brute force stuff, but it helps to keep in mind a few key rules:

1) $\mathbf{L}$ and $\mathbf{S}$ operate in different spaces, so they always commute with each other.
2) $L^2$ commutes with each of the $L_i$ $(i = x, y, z)$; same for $S^2$ and $S_i$.
3) The components of $\mathbf{L}$ obey $[L_i, L_j] = i\varepsilon_{ijk}\hbar L_k$. Similar for $\mathbf{S}$.

Armed with these relations, we just grind ’em out.

(a) $[\mathbf{L} \cdot \mathbf{S}, \mathbf{L}]$ Expanding the dot product, we note

$$[\mathbf{L} \cdot \mathbf{S}, L_x] = [L_x S_x + L_y S_y + L_z S_z, L_x]$$

$$= S_x[L_x, L_x] + S_y[L_y, L_x] + S_z[L_z, L_x]$$

$$= S_x(0) + S_y(-i\hbar L_z) + S_z(i\hbar L_y)$$

$$= i\hbar (L_y S_z - L_z S_y) = i\hbar (L \times S)_x$$

We get similar results for the other components, and so we recast this in vector form as

$$[\mathbf{L} \cdot \mathbf{S}, \mathbf{L}] = i\hbar (\mathbf{L} \times \mathbf{S})$$

(b) $[\mathbf{L} \cdot \mathbf{S}, \mathbf{S}]$ This is identical to part a, except we simply reverse the roles of $\mathbf{L}$ and $\mathbf{S}$. So, without any work at all we find

$$[\mathbf{L} \cdot \mathbf{S}, \mathbf{S}] = i\hbar (\mathbf{S} \times \mathbf{L})$$

(c) $[\mathbf{L} \cdot \mathbf{S}, \mathbf{J}]$ Using our results from a and b, we get directly

$$[\mathbf{L} \cdot \mathbf{S}, \mathbf{J}] = [\mathbf{L} \cdot \mathbf{S}, \mathbf{L}] + [\mathbf{L} \cdot \mathbf{S}, \mathbf{S}] = i\hbar (\mathbf{L} \times \mathbf{S} + \mathbf{S} \times \mathbf{L}) = 0$$

(d) $[\mathbf{L} \cdot \mathbf{S}, L^2]$ As noted above, $L^2$ commutes with all components of both $\mathbf{L}$ and $\mathbf{S}$, so

$$[\mathbf{L} \cdot \mathbf{S}, L^2] = 0$$

(e) $[\mathbf{L} \cdot \mathbf{S}, S^2]$ $S^2$ also commutes with $\mathbf{L}$ and $\mathbf{S}$, so it vanishes for the same reason as (d)

(f) $[\mathbf{L} \cdot \mathbf{S}, J^2]$ Knowing that $\mathbf{J} = \mathbf{L} + \mathbf{S}$, we square this and find

$$[\mathbf{L} \cdot \mathbf{S}, J^2] = [\mathbf{L} \cdot \mathbf{S}, L^2] + [\mathbf{L} \cdot \mathbf{S}, S^2] + 2[\mathbf{L} \cdot \mathbf{S}, \mathbf{L} \cdot \mathbf{S}] = 0 + 0 + 0 = 0$$
5. Fine By Me

The final expression we obtained for the fine structure of the hydrogen atom had two contributions that just ‘happened’ to be of the same size: a relativistic correction, and the effects of spin-orbit coupling. Combining these two pieces, though, takes a bit of algebra. Supply that algebra here, and show explicitly that the relativistic term (Eq. 6.57) and the spin-orbit term (Eq. 6.65) can be added to yield the fine-structure term given in Eq. 6.66. Rewrite this last expression to obtain the result for the hydrogen energy levels given in Eq. 6.67. **Hint:** This is mostly just messy algebra. One suggestion is to realize that for a given $\ell$, the quantum number $j$ can have only one of two values, so treat the two cases separately and show that they each yield the same result.

**SOLUTION**

As indicated, our job here is to “supply that algebra” needed to combine the relativistic and spin-orbit contributions to the hydrogen atom energy levels into a single expression that we observe in nature as fine structure. In this case, the algebra is very easy once we develop a strategy, but there is still a lot of it.

To start, let’s collect our two contributions. From Eq. 6.57, we have (with $E_n \equiv E_n^{(0)}$)

$$E_{1\text{rel}} = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{\ell+1/2} \right]$$

For the spin-orbit piece, Eq. 6.65 gives us

$$E_{1\text{s.o.}} = \frac{(E_n)^2}{2mc^2} \left[ \frac{2n [j(j+1) - \ell(\ell+1) - 3/4]}{\ell(\ell+1/2)(\ell+1)} \right]$$

The only real trick here is to figure out how to add these two terms in such a way that the quantum number $\ell$ no longer appears in the sum. The easiest approach is to realize that there are only two possibilities – either $j = \ell + 1/2$ or $j = \ell - 1/2$ – and we just need to work out each case separately. If we start with the first case, $j = \ell + 1/2$, then $\ell = j - 1/2$. Using this substitution, the two expressions above become

$$E_{1\text{rel}} = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j} \right]$$

and

$$E_{1\text{s.o.}} = \frac{(E_n)^2}{2mc^2} \left[ \frac{2n [j(j+1) - (j-1/2)(j+1/2) - 3/4]}{(j-1/2)(j)(j+1/2)} \right]$$

$$= \frac{(E_n)^2}{2mc^2} \left[ \frac{2n [j^2 + j - j^2 + 1/4 - 3/4]}{(j-1/2)(j)(j+1/2)} \right]$$
Doing some housecleaning inside the square brackets in the numerator, we see that this reduces to just $2n(j - 1/2)$, and so we get the much more compact result

$$E_{s.o.}^1 = \frac{(E_n)^2}{2mc^2} \left[ \frac{2n}{j(j+1/2)} \right]$$

Adding these two contributions together, we find that for $j = \ell + 1/2$:

$$E_{fs}^1 = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j} + \frac{2n}{j(j+1/2)} \right]$$

$$= \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n(j+1/2)}{j(j+1/2)} + \frac{2n}{j(j+1/2)} \right]$$

$$= \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j+1/2} \right]$$

So at least for this case, we have confirmed Eq. 6.66 in the text.

We now consider the other possibility, that $j = \ell - 1/2$, and so $\ell = j + 1/2$. As before, we first write down our two contributions for this case, giving us

$$E_{rel}^1 = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j+1} \right]$$

and

$$E_{s.o.}^1 = \frac{(E_n)^2}{2mc^2} \left[ \frac{2n[j(j+1) - (j+1/2)(j+3/2) - 3/4]}{(j+1/2)(j+1)(j+3/2)} \right]$$

$$= \frac{(E_n)^2}{2mc^2} \left[ \frac{2n[j^2 + j - j^2 - 2j - 3/4 - 3/4]}{(j+1/2)(j+1)(j+3/2)} \right]$$

$$= \frac{(E_n)^2}{2mc^2} \left[ \frac{-2n}{(j+1)(j+1/2)} \right]$$

Adding these together, we find that for $j = \ell - 1/2$:

$$E_{fs}^1 = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j+1} - \frac{2n}{(j+1)(j+1/2)} \right]$$

$$= \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n(j+1/2)}{(j+1)(j+1/2)} - \frac{2n}{(j+1)(j+1/2)} \right]$$

$$= \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j+1/2} \right]$$

So we confirm Eq. 6.66 for this case as well, and hence conclude that this equation is valid under all conditions.
Our last step is to use this result to derive a complete expression for the hydrogen energy levels, at least to this level of accuracy. Recalling that for the unperturbed solutions we have \( E_n = E_1/n^2 \), we find

\[
E_{nj} = \frac{E_1}{n^2} + \frac{(E_1)^2}{(n^4)2mc^2} \left[ 3 - \frac{4n}{j + 1/2} \right]
\]

\[
= \frac{E_1}{n^2} \left\{ 1 + \frac{(E_1)}{(n^2)2mc^2} \left[ 3 - \frac{4n}{j + 1/2} \right] \right\}
\]

Defining the fine structure constant \( \alpha \equiv ke^2/(\hbar c) \), we can express \( E_1 \) as

\[
E_1 = -mc^2 \frac{(ke^2)^2}{2\hbar^2 c^2} = -\frac{1}{2}mc^2 \alpha^2
\]

and then rewrite the previous expression in the form

\[
E_{nj} = E_1 \left\{ 1 - \frac{\alpha^2}{4n^2} \left[ 3 - \frac{4n}{j + 1/2} \right] \right\}
\]

Just to set the scale, we can replace \( E_1 \) by its approximate value of \(-13.6 \text{ eV}\), and arrive at our final result:

\[
E_{nj} = -\frac{13.6 \text{ eV}}{n^2} \left\{ 1 + \frac{\alpha^2}{n^2} \left[ \frac{n}{j + 1/2} - \frac{3}{4} \right] \right\}
\]