Time-Dependent Perturbation Theory: Solved Problems

1. Consider a hydrogen atom in a time-dependent electric field $\mathbf{E} = E(t)\ \mathbf{k}$. Calculate all ten of the dipole matrix elements between the $n = 1$ ground state and the four $n = 2$ excited states. Also calculate the five expectation values of the dipole operator for these five states. Note that "calculate" here means show that fourteen out of the fifteen are zero with a clever argument, so that you only need to do one integral!

First, do the calculation using the even-odd symmetry with respect to z of the three ingredients, namely: (1) the wavefunctions, (2) the dipole term, and (3) the limits of integration. Show which matrix elements must vanish and which ones can survive:

(a) Write down the $n = 1$ ground state wavefunction, and the four $n = 2$ excited state wavefunctions in spherical coordinates:

$$\psi_{nlm}(\mathbf{r}) =< r, \theta, \phi \mid n, l, m >= R_{nl}(r)\ Y_{lm}(\theta, \phi).$$

(b) Show that these five wavefunctions squared $\mid \psi_{nlm}(x, y, z) \mid^2$ are all even functions of z.

(c) Use your result from part b to show that the matrix elements

$$< n, l, m \mid z \mid n, l, m >= \int_{-\infty}^{\infty} z\ \mid \psi(x, y, z) \mid^2\ dx\ dy\ dz = 0.$$

(d) Show that four of these five states are even functions of z, namely that ψ_{100}, ψ_{200}, ψ_{211} and ψ_{21-1} are all even functions of z, and that ψ_{210} is an odd function of z.

(e) Use your result from part d to show that all the following dipole matrix elements between pairs of the even states are zero, *i.e.,* show that

$$< 1, 0, 0 \mid z \mid 2, 0, 0 > = < 1, 0, 0 \mid z \mid 2, 1, 1 > = < 1, 0, 0 \mid z \mid 2, 1, -1 > = 0,$$

$$< 1, 0, 0 \mid z \mid 2, 1, 0 > = < 2, 1, 1 \mid z \mid 2, 1, 0 > = < 2, 1, -1 \mid z \mid 2, 1, 0 > = 0,$$

$$< 2, 0, 0 \mid z \mid 2, 1, 1 > = < 2, 0, 0 \mid z \mid 2, 1, -1 > = < 2, 1, 1 \mid z \mid 2, 1, -1 > = 0.$$

(f) Use the even and odd argument in z to explain why the only non-zero matrix elements are

$$< 1, 0, 0 \mid z \mid 2, 1, 0 > = \int_{-\infty}^{\infty} \psi^*_{200}(x, y, z)\ z\ \psi_{210}(x, y, z)\ dx\ dy\ dz,$$

and

$$< 2, 0, 0 \mid z \mid 2, 1, 0 > = \int_{-\infty}^{\infty} \psi^*_{100}(x, y, z)\ z\ \psi_{210}(x, y, z)\ dx\ dy\ dz.$$

(g) Put in the wavefunctions and calculate the two non-zero $H_1 = -eEz$ integrals from part f, *i.e.,* do the integrals. For example, calculate

$$< 1,0,0 \mid H_1 \mid 2,1,0 >= -eE \ \frac{1}{\sqrt{\pi a^3}} \ \frac{1}{\sqrt{32\pi a^3}} \ \frac{1}{a} \int_{-\infty}^{\infty} \ e^{-r/a} \ e^{-r/2a} \ z \ d^3r$$

or

$$< 1,0,0 \mid z \mid 2,1,0 >= -eE \ \frac{1}{\sqrt{\pi a^3}} \ \frac{1}{\sqrt{32\pi a^3}} \ \frac{1}{a} \int_{-\infty}^{\infty} \ e^{-r/a} \ e^{-r/2a} \ (r\cos\theta) \ \sin\theta \ d\theta \ d\phi \ r^2 \ dr.$$

You should find that

$$< 1,0,0 \mid H_1 \mid 2,1,0 >= -(2^8/3^5\sqrt{2}) \ eEa \ \simeq \ -0.7449 \ eEa,$$

and that

$$< 2,0,0 \mid z \mid 2,1,0 >= -3 \ eEa.$$

Second, do the calculation using the orthonormality of the spherical harmonics and the addition rules for angular momentum:

(h) First show that $z = r\cos\theta \simeq Y_{10}(\theta,\phi)$. Then use the angular momentum addition rules to add Y_{10} to one (or the other) Y_{lm} under the integral. Finally, use the orthonormality of the Y_{lm}'s to show that all the matrix elements except $< 1,0,0 \mid z \mid 2,1,0 >$ must vanish.

(i) Which method do you prefer? Explain why you prefer it! It is very important that you fully understand both methods: they are both extremely powerful and extremely useful!!!

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1. The wave function expressed in spherical coordinates is given by

$$\psi_{nlm}(\vec{r}) = <r,\theta,\phi\big|n,l,m> \ R_{nl}(r)Y_{lm}(\theta,\phi).$$

Using the functional forms of the $R_{nl}s$ and of the spherical harmonics, we find

$$\boxed{\psi_{100} = R_{10}Y_{00} = 2a^{-3/2}e^{-r/a}\left(\frac{1}{4\pi}\right)^{1/2} = \frac{1}{\sqrt{\pi}}a^{-3/2}e^{-r/a},}$$

$$\boxed{\psi_{200} = R_{20}Y_{00} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1-\frac{r}{2a}\right)e^{-r/2a}\left(\frac{1}{4\pi}\right)^{1/2} = \frac{1}{2\sqrt{2\pi}}a^{-3/2}\left(1-\frac{r}{2a}\right)e^{-r/2a},}$$

$$\psi_{210} = R_{21}Y_{10} = \frac{1}{\sqrt{24}} a^{-3/2} \left(\frac{r}{a}\right) e^{-r/2a} \left(\frac{3}{4\pi}\right)^{1/2} \cos(\theta) = \frac{1}{4\sqrt{2\pi}} a^{-3/2} \left(\frac{r}{a}\right) e^{-r/2a} \cos(\theta),$$

$$\psi_{211} = R_{21}Y_{11} = \frac{1}{\sqrt{24}} a^{-3/2} \left(\frac{r}{a}\right) e^{-r/2a} \left[-\left(\frac{3}{8\pi}\right)^{1/2} \sin(\theta) e^{i\phi}\right] = -\frac{1}{8\sqrt{\pi}} a^{-3/2} \left(\frac{r}{a}\right) e^{-r/2a} \sin(\theta) e^{i\phi},$$

$$\psi_{21,-1} = R_{21}Y_{1,-1} = \frac{1}{\sqrt{24}} a^{-3/2} \left(\frac{r}{a}\right) e^{-r/2a} \left(\frac{3}{8\pi}\right)^{1/2} \sin(\theta) e^{-i\phi} = \frac{1}{8\sqrt{\pi}} a^{-3/2} \left(\frac{r}{a}\right) e^{-r/2a} \sin(\theta) e^{-i\phi}.$$

1.(b) Remember, an even function is one for which $f(-x) = f(x)$. If there is more than one independent variable, as we have here, the function may be even with respect to one or more of the variables. Even with respect to z for the function $f(x, y, z)$ means that $f(x, y, -z) = f(x, y, z)$. The wave functions are currently in spherical coordinates $\psi(r, \theta, \phi)$. We need to find their symmetries in Cartesian coordinates

$$r = \left(x^2 + y^2 + z^2\right)^{1/2}, \quad \cos\theta = \frac{z}{\left(x^2 + y^2 + z^2\right)^{1/2}}, \quad \sin\theta = \frac{\left(x^2 + y^2\right)^{1/2}}{\left(x^2 + y^2 + z^2\right)^{1/2}}, \quad \text{and} \quad \phi = \tan^{-1}\left(\frac{y}{x}\right).$$

We actually only need to do enough examination to determine the symmetry with respect to z and not a complete change of variables. Using the ψ_{nlm}'s from part a, we find

$$\left|\psi_{100}(x, y, z)\right|^2 = \frac{1}{\pi} a^{-3} e^{-2\left(x^2+y^2+z^2\right)^{1/2}/a}, \qquad \text{where} \qquad (-z)^2 = z^2$$

$$\Rightarrow \quad \left|\psi_{100}(x, y, -z)\right|^2 = \left|\psi_{100}(x, y, z)\right|^2 \quad \text{so} \quad \left|\psi_{100}\right|^2 \quad \text{is even wrt } z.$$

$$\left|\psi_{200}(x, y, z)\right|^2 = \frac{1}{8\pi} a^{-3} \left(1 - \frac{\left(x^2 + y^2 + z^2\right)^{1/2}}{2a}\right)^2 e^{-\left(x^2+y^2+z^2\right)^{1/2}/a} \quad \text{and} \quad (-z)^2 = z^2 \qquad \text{in both places}$$

$$\Rightarrow \quad \left|\psi_{200}(x, y, -z)\right|^2 = \left|\psi_{200}(x, y, z)\right|^2 \quad \text{so} \quad \left|\psi_{200}\right|^2 \quad \text{is even wrt } z.$$

$$\left|\psi_{210}(x, y, z)\right|^2 = \frac{1}{32\pi} a^{-3} \left(\frac{\left(x^2 + y^2 + z^2\right)}{a^2}\right) e^{-\left(x^2+y^2+z^2\right)^{1/2}/a} \frac{z^2}{\left(x^2 + y^2 + z^2\right)}$$

and $(-z)^2 = z^2$ in all four places

$$\Rightarrow \quad \left|\psi_{210}(x,y,-z)\right|^2 = \left|\psi_{210}(x,y,z)\right|^2 \quad \text{so} \quad \left|\psi_{210}\right|^2 \quad \text{is even wrt } z.$$

$$\left|\psi_{211}(x,y,z)\right|^2 = \frac{1}{64\pi} a^{-3} \left(\frac{(x^2+y^2+z^2)}{a^2} \right) e^{-\left(x^2+y^2+z^2\right)^{1/2}/a} \frac{x^2+y^2}{(x^2+y^2+z^2)} e^{i\phi(x,y)}$$

and $(-z)^2 = z^2$ in all three places

$$\Rightarrow \quad \left|\psi_{211}(x,y,-z)\right|^2 = \left|\psi_{211}(x,y,z)\right|^2 \quad \text{so} \quad \left|\psi_{211}\right|^2 \quad \text{is even wrt } z.$$

$$\left|\psi_{21,-1}(x,y,z)\right|^2 = \frac{1}{64\pi} a^{-3} \left(\frac{(x^2+y^2+z^2)}{a^2} \right) e^{-\left(x^2+y^2+z^2\right)^{1/2}/a} \frac{x^2+y^2}{(x^2+y^2+z^2)} e^{-i\phi(x,y)}$$

and $(-z)^2 = z^2$ in all three places

$$\Rightarrow \quad \left|\psi_{211}(x,y,-z)\right|^2 = \left|\psi_{211}(x,y,z)\right|^2 \quad \text{so} \quad \left|\psi_{211}\right|^2 \quad \text{is even wrt } z.$$

1.(c) Here we use the facts that the product of an even function is an odd function, and that an odd function integrated between symmetric limits is zero. The expectation values of z are given by

$$<n,l,m|z|n,l,m> = \int_{-\infty}^{\infty} z\left|\psi(x,y,z)\right|^2 dx\,dy\,dz = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} z\left|\psi(x,y,z)\right|^2 dz,$$

but z is an odd function, and all of the $\left|\psi_{nlm}(x,y,z)\right|^2$ are even functions, so all of the $z\left|\psi_{nlm}(x,y,z)\right|^2$ are odd functions. The integral with respect to z is between symmetric limits. Therefore

$$<n,l,m|z|n,l,m> = \left(\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \right) \cdot 0 = 0.$$

1.(d) Referring to wave functions of part (a) and the Cartesian/spherical relations of part (b),

$$\psi_{100} = \frac{1}{\sqrt{\pi}} a^{-3/2} e^{-\left(x^2+y^2+z^2\right)^{1/2}/a}, \qquad \text{and} \quad (-z)^2 = z^2$$

$$\Rightarrow \quad \psi_{100}(x, y, -z) = \psi_{100}(x, y, z) \quad \text{so} \quad \psi_{100} \quad \text{is even wrt } z.$$

$$\psi_{200}(x, y, z) = \frac{1}{2\sqrt{2\pi}} a^{-3/2} \left(1 - \frac{\left(x^2 + y^2 + z^2\right)^{1/2}}{2a} \right) e^{-\left(x^2+y^2+z^2\right)^{1/2}/2a},$$

and $(-z)^2 = z^2$ in both places

$$\Rightarrow \quad \psi_{200}(x, y, -z) = \psi_{200}(x, y, z) \quad \text{so} \quad \psi_{200} \quad \text{is even wrt } z.$$

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}} a^{-3/2} \left(\frac{\left(x^2 + y^2 + z^2\right)^{1/2}}{a} \right) e^{-\left(x^2+y^2+z^2\right)^{1/2}/2a} \frac{z}{\left(x^2 + y^2 + z^2\right)^{1/2}},$$

This is an odd function. In the three places where $\left(x^2 + y^2 + z^2\right)^{1/2}$ is substituted for r, $(-z)^2 = z^2$. This portion of the wave function is even. The remaining factor is z, which is an odd function. The product of an even and an odd function is an odd function

$$\Rightarrow \quad \psi_{210}(x, y, -z) = -\psi_{210}(x, y, z) \quad \text{so} \quad \psi_{210} \quad \text{is odd wrt } z.$$

$$\psi_{211} = -\frac{1}{8\sqrt{\pi}} a^{-3/2} \left(\frac{\left(x^2 + y^2 + z^2\right)^{1/2}}{a} \right) e^{-\left(x^2+y^2+z^2\right)^{1/2}/2a} \frac{\left(x^2 + y^2\right)^{1/2}}{\left(x^2 + y^2 + z^2\right)^{1/2}} e^{i\phi(x,y)},$$

where $(-z)^2 = z^2$ in all three places, and $\phi = \phi(x, y)$ is independent of z,

$$\Rightarrow \quad \psi_{211}(x, y, -z) = \psi_{211}(x, y, z) \quad \text{so} \quad \psi_{211} \quad \text{is even wrt } z.$$

$$\psi_{21,-1} = -\frac{1}{8\sqrt{\pi}} a^{-3/2} \left(\frac{\left(x^2 + y^2 + z^2\right)^{1/2}}{a} \right) e^{-\left(x^2+y^2+z^2\right)^{1/2}/2a} \frac{\left(x^2 + y^2\right)^{1/2}}{\left(x^2 + y^2 + z^2\right)^{1/2}} e^{-i\phi(x,y)},$$

where $(-z)^2 = z^2$ in all three places, and $\phi = \phi(x, y)$ is again independent of z,

$$\Rightarrow \quad \psi_{21,-1}(x, y, -z) = \psi_{21,-1}(x, y, z) \quad \text{so} \quad \psi_{21,-1} \quad \text{is even wrt } z.$$

1.(e) From part (d), ψ_{100}, ψ_{200}, ψ_{211}, and $\psi_{21,-1}$ are even functions with respect to z. Using the same argument as in part (c),

$$< \psi_{\text{even wrt } z} \big| z \big| \psi_{\text{even wrt } z} > = \int_{-\infty}^{\infty} \left(\psi_{\text{even wrt } z} \right)^* z \left(\psi_{\text{even wrt } z} \right) \, dx \, dy \, dz$$
$$= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} \left(\psi_{\text{even wrt } z} \right)^* z \left(\psi_{\text{even wrt } z} \right) \, dz.$$

Again, z is an odd function. The product of an even and odd function is odd; this odd function multiplied by another even function yields an odd function overall. The integral with respect to z is between symmetric limits, and an integral of an odd function between symmetric limits is zero. Therefore

$$< 1,0,0 \big| z \big| 2,0,0 > = < 1,0,0 \big| z \big| 2,1,1 > = < 1,0,0 \big| z \big| 2,1,-1 > = 0$$
$$< 2,0,0 \big| z \big| 2,1,1 > = < 2,0,0 \big| z \big| 2,1,-1 > = < 2,1,1 \big| z \big| 2,1,-1 > = 0.$$

1.(f) The remaining matrix elements are given by

$$< 1,0,0 \big| z \big| 2,1,0 >, \quad < 2,0,0 \big| z \big| 2,1,0 >, \quad < 2,1,1 \big| z \big| 2,1,0 > \quad \text{and} \quad < 2,1,-1 \big| z \big| 2,1,0 > .$$

These integrals all have the form $\int_{-\infty}^{\infty}$ (even function) (odd function) (odd function) with respect to z, which we would expect to be non-zero. We can examine two at once, using $z = r\cos\theta$, and the volume element in spherical coordinates which is $dv = r^2 \sin\theta dr d\theta d\phi$,

$$< 2,1,\pm 1 \big| z \big| 2,1,0 > = \int_{-\infty}^{\infty} \left(\frac{\mp 1}{8\sqrt{\pi}} a^{-3/2} \left(\frac{r}{a} \right) e^{-r/2a} \sin(\theta) e^{\pm i\phi} \right)^* r\cos\theta \, \frac{1}{4\sqrt{2\pi}} a^{-3/2} \left(\frac{r}{a} \right) e^{-r/2a} \cos(\theta) \, dV$$
$$= \frac{\mp 1}{32\pi\sqrt{2}} \frac{1}{a^5} \int_0^{\infty} dr \, r^5 e^{-r/a} \int_0^{\pi} d\theta \, \sin^2\theta \cos^2\theta \int_0^{2\pi} d\phi \, e^{\mp i\phi}$$

Examining just the azimuthal integral, we find

$$\int_0^{2\pi} d\phi \, e^{\mp i\phi} = \int_0^{2\pi} d\phi \, \cos\phi \mp i \sin\phi$$
$$= \int_0^{2\pi} d\phi \, \cos\phi \mp i \int_0^{2\pi} d\phi \, \sin\phi$$
$$= \sin\phi \Big|_0^{2\pi} \pm i\cos\phi \Big|_0^{2\pi}$$
$$= (0-0) \pm i\,(1-1) = 0,$$

therefore, the integral over all space will be zero regardless of the values of the radial and polar integrals, *i.e.*,

$$< 2,1,1 \big| z \big| 2,1,0 > = < 2,1,-1 \big| z \big| 2,1,0 > = 0.$$

1.(g) We have been examining expectation values of z because $H_1 = -eEz$, where $-eE$ is a constant. If the expectation value is non-zero, the value of the integral multiplied by $-eE$ will express the result in energy units.

There are two remaining integrals. Using $z = r\cos\theta$ and $dV = r^2 \sin\theta dr d\theta d\phi$, the integral

$$
\begin{aligned}
<2,0,0\big|z\big|2,1,0> &= \int_{-\infty}^{\infty} \left(\frac{1}{2\sqrt{2\pi}} a^{-3/2} \left(1 - \frac{r}{2a}\right) e^{-r/2a} \right)^* r\cos\theta \, \frac{1}{4\sqrt{2\pi}} a^{-3/2} \left(\frac{r}{a}\right) e^{-r/2a} \cos(\theta)\, dV \\
&= \frac{1}{16\pi a^4} \int_0^{\infty} dr \, \left(1 - \frac{r}{2a}\right) r^4 e^{-r/a} \int_0^{\pi} d\theta \, \cos^2\theta \sin\theta \int_0^{2\pi} d\phi \\
&= \frac{1}{16\pi a^4} \int_0^{\infty} dr \, \left(1 - \frac{r}{2a}\right) r^4 e^{-r/a} \int_0^{\pi} d\theta \, \cos^2\theta \sin\theta \, [2\pi] \\
&= \frac{1}{8a^4} \int_0^{\infty} dr \, \left(1 - \frac{r}{2a}\right) r^4 e^{-r/a} \left[-\frac{\cos^3\theta}{3} \right]_0^{\pi} \\
&= \frac{1}{8a^4} \int_0^{\infty} dr \, \left(1 - \frac{r}{2a}\right) r^4 e^{-r/a} \left[\frac{2}{3} \right] \\
&= \frac{1}{12a^4} \int_0^{\infty} dr \, \left(1 - \frac{r}{2a}\right) r^4 e^{-r/a} \\
&= \frac{1}{12a^4} \left[\int_0^{\infty} dr \, r^4 e^{-r/a} - \frac{1}{2a} \int_0^{\infty} dr \, r^5 e^{-r/a} \right].
\end{aligned}
$$

These integrals are evaluated using

$$
\int_0^{\infty} x^n e^{-\mu x} \, dx = n! \, \mu^{-n-1}, \qquad \mathrm{Re}\, \mu > 0,
$$

with $\mu = 1/a$ for both, and with $n = 4$ and 5 respectively, so we find

$$
\begin{aligned}
<2,0,0\big|z\big|2,1,0> &= \frac{1}{12a^4} \left[4! \left(\frac{1}{a}\right)^{-4-1} - \frac{1}{2a} 5! \left(\frac{1}{a}\right)^{-5-1} \right] \\
&= \frac{1}{12a^4} \left[\frac{4 \cdot 3 \cdot 2}{(1/a)^5} - \frac{1}{2a} \left(\frac{5 \cdot 4 \cdot 3 \cdot 2}{(1/a)^6} \right) \right] \\
&= \frac{1}{12a^4} \left[24a^5 - \frac{1}{2a} 120 a^6 \right] = \frac{1}{12a^4} \left[24a^5 - 60a^5 \right] \\
&= \frac{1}{12a^4} \left(-36a^5 \right) = -3a.
\end{aligned}
$$

Since $H_1 = -eEz$, we find

$$
\boxed{\Rightarrow \quad <2,0,0\big|z\big|2,1,0> = 3eEa.}
$$

The last integral is $<1,0,0|z|2,1,0>$ which in energy units is given by

$$
\begin{aligned}
<1,0,0\big|H_1\big|2,1,0> &= <1,0,0\big| -eEz\big|2,1,0> \\
&= -eE <1,0,0\big|z\big|2,1,0> \\
&= -eE\int_{-\infty}^{\infty} (\psi_{100})^* \; z\,\psi_{210}\,dV \\
&= -eE\int_{-\infty}^{\infty} \frac{1}{\sqrt{\pi}}a^{-3/2}e^{-r/a}\; z\, \frac{1}{4\sqrt{2\pi}}a^{-3/2}\left(\frac{r}{a}\right)e^{-r/2a}\cos(\theta)\,dV \\
&= -\frac{eE}{4\pi\sqrt{2}a^4}\int_{-\infty}^{\infty} re^{-3r/2a}\; z\,\cos(\theta)\,dV.
\end{aligned}
$$

Using $z = r\cos\theta$ and $dV = r^2\sin\theta dr d\theta d\phi$, we find

$$
\begin{aligned}
<1,0,0\big|H_1\big|2,1,0> &= -\frac{eE}{4\pi\sqrt{2}a^4}\int_{-\infty}^{\infty} r^4e^{-3r/2a}\cos^2\theta\sin\theta\,dr\,d\theta\,d\phi \\
&= -\frac{eE}{4\pi\sqrt{2}a^4}\int_0^{\infty} dr\, r^4e^{-3r/2a}\int_0^{\pi} d\theta\,\cos^2\theta\sin\theta\int_0^{2\pi} d\phi \\
&= -\frac{eE}{4\pi\sqrt{2}a^4}\int_0^{\infty} dr\, r^4e^{-3r/2a}\int_0^{\pi} d\theta\,\cos^2\theta\sin\theta(2\pi) \\
&= -\frac{eE}{2\sqrt{2}a^4}\int_0^{\infty} dr\, r^4e^{-3r/2a}\left[-\frac{\cos^3\theta}{3}\right]_0^{\pi} \\
&= -\frac{eE}{2\sqrt{2}a^4}\int_0^{\infty} dr\, r^4e^{-3r/2a}\left[-\frac{-1-1}{3}\right]_0^{\pi} \\
&= -\frac{eE}{3\sqrt{2}a^4}\int_0^{\infty} dr\, r^4e^{-3r/2a}.
\end{aligned}
$$

As before, using

$$
\int_0^{\infty} x^n e^{-\mu x}\,dx = n!\mu^{-n-1}, \qquad \mathrm{Re}\,\mu > 0,
$$

with $\mu = 3/2a$ and $n = 4$ we find

$$
\begin{aligned}
<1,0,0\big|H_1\big|2,1,0> &= -\frac{eE}{3\sqrt{2}a^4}\,4!\left(\frac{3}{2a}\right)^{-5} \\
&= -\frac{eE}{3\sqrt{2}a^4}\,\frac{4\cdot 3\cdot 2(2a)^5}{3^5} \\
&= -\frac{eE}{3\sqrt{2}a^4}\,\frac{3\cdot 2^3\cdot 2^5\cdot a^5}{3^5}
\end{aligned}
$$

$$
\boxed{\Rightarrow \quad <1,0,0\big|H_1\big|2,1,0> = -\frac{eE}{\sqrt{2}}\,\frac{2^8\cdot a}{3^5} = -0.7449eEa.}
$$

1.(h) The wave functions under consideration are $\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi)$, which are explicitly

$$\psi_{100} = R_{10}Y_{00}, \quad \psi_{200} = R_{20}Y_{00}, \quad \psi_{210} = R_{21}Y_{10}, \quad \psi_{211} = R_{21}Y_{11}, \quad \psi_{21,-1} = R_{21}Y_{1,-1}.$$

The integrals for the expectation values of z are given by

$$\begin{aligned} <n,l,m\big|z\big|n',l',m'> &= <n,l,m\big|r\cos\theta\big|n',l',m'> \\ &= \int_{-\infty}^{\infty} \psi^*_{nlm}\, r\cos\theta\, \psi_{n'l'm'}\, dV \\ &= \int_{-\infty}^{\infty} R^*_{nl}Y^*_{lm}\, r\cos\theta\, R_{n'l'}Y_{l'm'}\, dV \\ &= \int_0^{\infty} R^*_{nl}R_{n'l'}\, r^3\, dr \int Y^*_{lm}\cos\theta\, Y_{l'm'}\, d\Omega, \end{aligned}$$

where the factor of r^2 in the radial integral comes from the volume element. The angular momentum addition rules and the integration can be summarized by

$$\int Y^*_{lm}\cos\theta\, Y_{l'm'}\, d\Omega, = \left[\frac{(l'-m'+1)(l'+m'+1)}{(2l'+1)(2l'+3)}\right]^{1/2} \delta_{mm'}\delta_{l,l'+1} + \left[\frac{l'-m')(l'+m')}{(2l'-1)(2l'+1)}\right]^{1/2} \delta_{mm'}\delta_{l,l'-1}.$$

For this integral to be non-zero, l' must differ from l by ± 1. This means that

$$<1,0,0\big|z\big|1,0,0> = <2,0,0\big|z\big|2,0,0> = <2,1,0\big|z\big|2,1,0> = <2,1,1\big|z\big|2,1,1> = <2,1,-1\big|z\big|2,1,-1>$$

$$= <1,0,0\big|z\big|2,0,0> = <2,1,0\big|z\big|2,1,1> = <2,1,0\big|z\big|2,1,-1> = <2,1,1\big|z\big|2,1,-1> = 0.$$

Also, m must equal m' for the integral to be non-zero, so

$$<1,0,0\big|z\big|2,1,1> = <1,0,0\big|z\big|2,1,-1> = <2,0,0\big|z\big|2,1,1> = <2,0,0\big|z\big|2,1,-1> = 0.$$

Only $< 1,0,0\big|z\big|2,1,0 >$ and $< 2,0,0\big|z\big|2,1,0 >$ remain as non-zero possibilities. Knowing that $z = r\cos\theta \sim Y_{10}$, we can see that these two integrals have the form

$$\int Y_{00}Y_{10}Y_{10}\, d\Omega.$$

Parity conservation in angle space can be summarized by $l_1+l_2+l_3+m_1+m_2+m_3 =$ even integer. For our two integrals, this condition is satisfied for the integer 2. For both $<1,0,0\big|z\big|2,1,0>$ and $<2,0,0\big|z\big|2,1,0>$, the integral over solid angle can now be evaluated using

$$\int Y^*_{00}\cos\theta\, Y_{10}\, d\Omega, = \left[\frac{(1-0+1)(1+0+1)}{(2\cdot 1+1)(2\cdot 1+3)}\right]^{1/2} \delta_{00}\delta_{0,1+1} + \left[\frac{(1-0)(1+0)}{(2\cdot 1-1)(2\cdot 1+1)}\right]^{1/2} \delta_{00}\delta_{0,1-1}.$$

Here, the first expression on the right side of the equation will be zero because the indices on the second Kronecker δ are not identical. Both sets of indices on the Kronecker δ of second expression on the right are identical, so we find

$$\int Y^*_{00}\cos\theta\, Y_{10}\, d\Omega, = \frac{1}{\sqrt{3}}.$$

Next, we will evaluate the radial integrals using this angular factor. We find

$$\begin{aligned}
<1,0,0|z|2,1,0> &= \frac{1}{\sqrt{3}}\int_0^\infty R_{10}\, r\, R_{21}\, r^2\, dr \\
&= \frac{1}{\sqrt{3}}\int_0^\infty \left(2a^{-3/2}e^{-r/a}\right)\left(\frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}e^{-r/2a}\right) r^3\, dr \\
&= \frac{1}{3\sqrt{2}a^4}\int_0^\infty r^4 e^{-3r/2a} dr
\end{aligned}$$

This integral can be evaluated using

$$\int_0^\infty x^n e^{-\mu x}\, dx = n!\ \mu^{-n-1}, \qquad \mathrm{Re}\,\mu > 0,$$

with $\mu = 3/2a$ and $n = 4$, so we find

$$\begin{aligned}
<1,0,0|z|2,1,0> &= \frac{1}{3\sqrt{2}a^4} 4\cdot 3\cdot 2\left(\frac{3}{2a}\right)^{-5} \\
&= \frac{1}{3\sqrt{2}a^4}\frac{3\cdot 2^3\cdot 2^5\cdot a^5}{3^5}
\end{aligned}$$

$$\Rightarrow \quad <1,0,0|z|2,1,0> = \frac{2^8}{\sqrt{2}\cdot 3^5}a$$

$$\Rightarrow \quad <1,0,0|H_1|2,1,0> = -eE\frac{2^8}{\sqrt{2}\cdot 3^5}a = -0.7449eEa, \quad \text{which is the same as part (g).}$$

The other integral is given by

$$\begin{aligned}
<2,0,0|z|2,1,0> &= \frac{1}{\sqrt{3}}\int_0^\infty R_{20}\, r\, R_{21}\, r^2\, dr \\
&= \frac{1}{\sqrt{3}}\int_0^\infty \left(\frac{1}{\sqrt{2}}a^{-3/2}\left(1-\frac{r}{2a}\right)e^{-r/2a}\right)\left(\frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}e^{-r/2a}\right) r^3\, dr \\
&= \frac{1}{\sqrt{3}\sqrt{2}\sqrt{24}a^4}\int_0^\infty \left(1-\frac{r}{2a}\right) r^4 e^{-r/a}\, dr \\
&= \frac{1}{12a^4}\int_0^\infty r^4 e^{-r/a}\, dr - \frac{1}{24a^5}\int_0^\infty r^5 e^{-r/a}\, dr.
\end{aligned}$$

We can evaluate this integral using the same procedure, with $\mu = 1/a$ and $n = 4$ and 5 respectively. We find

$$\begin{aligned}
<2,0,0|z|2,1,0> &= \frac{1}{12a^4}\frac{4\cdot 3\cdot 2}{(1/a)^5} - \frac{1}{24a^5}\frac{5\cdot 4\cdot 3\cdot 2}{(1/a)^6} \\
&= \frac{24a^5}{12a^4} - \frac{120a^6}{24a^4}
\end{aligned}$$

$$\Rightarrow \quad <2,0,0\big|z\big|2,1,0> = 2a - 5a = -3a, \quad \text{which is the same as part (g)}$$

$$\text{and} \quad <2,0,0\big|H_1\big|2,1,0> = 3eEa.$$

1.(i) …Wow! That spherical harmonic stuff does seem to be a lot less work….

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2. Find the exact solution to the two coupled differential equations that describe the time evolution of the two-state system

$$\frac{dc_a(t)}{dt} = (i\hbar)^{-1} < a \mid H_1 \mid b > \; e^{-i\omega_0 t} \; c_b(t)$$
$$\frac{dc_b(t)}{dt} = (i\hbar)^{-1} < b \mid H_1 \mid a > \; e^{+i\omega_0 t} \; c_a(t),$$

i.e., find the exact time-dependent probability amplitudes for the two states $c_a(t)$ and $c_b(t)$.

(a) Calculate the time derivative of the second differential equation, *i.e.,* calculate the time derivative of the equation for $dc_b(t)/dt$. Note that your new equation relates the second derivative $d^2c_b(t)/dt^2$ on the left hand side to $c_a(t)$ and to the first derivative $dc_a(t)/dt$ on the right hand side.

(b) The next step is to eliminate the dependence on $c_a(t)$ and $dc_a(t)/dt$. Substitute the first equation for $dc_a(t)/dt$ into the right hand side of your second order equation to eliminate the dependence on dc_a/dt. Then solve the second first-order equation for $c_a(t)$ in terms of $dc_b(t)/dt$ and use it to eliminate the dependence on $c_a(t)$. You should have obtained the following differential equation for $c_b(t)$

$$\frac{d^2c_b(t)}{dt^2} = (i\omega_0)\,\frac{dc_b(t)}{dt} \;-\; \frac{1}{\hbar^2} \mid < a \mid H_1 \mid b > \mid^2 c_b(t).$$

Let $\alpha^2 \; = \mid < a \mid H_1 \mid b > \mid^2 / \hbar^2$ to obtain

$$\frac{d^2c_b(t)}{dt^2} \;-\; (i\omega_0)\,\frac{dc_b(t)}{dt} \;+\; \alpha^2 \, c_b(t) = 0.$$

(c) This is an ordinary linear second-order differential equation with constant coefficients, so it can be solved with a solution of the form $g(t) = exp(-\lambda t)$. Substitute $g(t)$ into the differential equation, do the time derivatives, and divide out the common factor of $exp(-\lambda t)$ that remains in each term after doing the time derivatives to obtain the characteristic equation that λ must obey. You should obtain the quadratic equation $\lambda^2 \; + \; (i\omega_0)\,\lambda \; + \; \alpha^2 \; = \; 0.$

(d) Solve this quadratic equation to find the characteristic values of λ. You should find that $\lambda \; = \; \frac{1}{2}[\; -i\omega \;\; \pm \;\; \sqrt{-\,\omega_0^2 \; - \; 4\alpha^2} \;]$. It will save a lot of writing below to define $(i\omega) \;\; = \sqrt{-\,\omega_0^2 \; - \; 4\alpha^2}$ since then $\lambda = (i/2)[-\omega_0 \pm \omega]$.

(e) Put the characteristic values of λ into the general solution to obtain the general form of the solution $c_b(t) \; = \; g(t) \; = \; A \; \exp(\; i\,(\omega_0 + \omega)t/2) \; + \; B \; \exp(\; i\,(\omega_0 - \omega)t/2)$. Show that this can be rewritten as

$$c_b(t) = [\; C \; \cos(\frac{\omega t}{2}) \; + \; D \; \sin(\frac{\omega t}{2})\;] \; \exp(\frac{i\omega_0 t}{2}).$$

(f) Use the initial condition $c_b(0) = 0$ to show that the coefficient of the cosine term $C = 0$ so that

$$c_b(t) \;=\; D\,\sin{(\frac{\omega t}{2})}\,\exp{(\frac{i\omega_0 t}{2})}.$$

We still need to find $c_a(t)$ and D. So, substitute your result for $c_b(t)$ back into the first-order differential equation that relates $dc_b(t)/dt$ to $c_a(t)$:

$$\frac{dc_b(t)}{dt} \;=\; (i\hbar)^{-1}\; < b \mid H_1 \mid a > \;\exp{(i\omega_0 t)}\; c_a(t).$$

(g) Show that this substitution leads to

$$c_a(t) = \frac{i\hbar}{< b \mid H_1 \mid a >}\,\frac{\omega}{2}\,\exp{(\frac{-i\omega_0 t}{2})}\,D\,\left[\cos{(\frac{\omega t}{2})} \;+\; i\,\left(\frac{\omega_0}{\omega}\right)\,\sin{(\frac{\omega t}{2})}\right].$$

(h) Now use initial condition for $c_a(t)$, namely that $c_a(0) \;=\; 1$, to find the value of D. You should find that $D \;=\; 2\;< b \mid H_1 \mid a >\;/\;i\hbar\omega$.

(i) Finally, put it all together to show that the exact time-dependent probability amplitudes are given by

$$c_a(t) = \exp{(\frac{-i\omega_0 t}{2})}\;\left[\cos{(\frac{\omega t}{2})} \;+\; i\,\left(\frac{\omega_0}{\omega}\right)\,\sin{(\frac{\omega t}{2})}\right]$$

$$c_b(t) = \frac{2\;< b \mid H_1 \mid a >}{i\hbar\omega}\;\exp{(\frac{i\omega_0 t}{2})}\;\sin{(\frac{\omega t}{2})}\;.$$

(j) Use the exact results in part i to show that $\mid c_a \mid^2 \;+\; \mid c_b \mid^2 =\; 1$.

2.(a) The two coupled differential equations that describe the two-state system are

$$\frac{dc_a(t)}{dt} = \frac{1}{i\hbar}\,< a\big|H_1\big|b >\, e^{-i\omega_0 t} c_b(t)$$

$$\frac{dc_b(t)}{dt} = \frac{1}{i\hbar}\,< b\big|H_1\big|a >\, e^{+i\omega_0 t} c_a(t).$$

The time derivative of the second differential equation is

$$\frac{d^2 c_b(t)}{dt^2} = \frac{1}{i\hbar}\,< b\big|H_1\big|a >\, e^{i\omega_0 t}(i\omega_0)c_a(t) + \frac{1}{i\hbar}\,< b\big|H_1\big|a >\, e^{i\omega_0 t}\frac{dc_a(t)}{dt},$$

which assumes $H_1 \neq H_1(t)$, *i.e.*, this system oscillates between pure states. In this case

$$\boxed{\frac{d^2 c_b(t)}{dt^2} = \frac{\omega_0}{\hbar}\,< b\big|H_1\big|a >\, e^{i\omega_0 t} c_a(t) + \frac{1}{i\hbar}\,< b\big|H_1\big|a >\, e^{i\omega_0 t}\frac{dc_a(t)}{dt}.}$$

2.(b) To eliminate the first derivative in the last equation, we substitute the first coupled differential equation into the boxed equation,

$$\frac{d^2c_b(t)}{dt^2} = \frac{\omega_0}{\hbar} <b|H_1|a> e^{i\omega_0 t}c_a(t) + \frac{1}{i\hbar} <b|H_1|a> e^{i\omega_0 t}\frac{1}{i\hbar} <a|H_1|b> e^{-i\omega_0 t}c_b(t)$$

$$= \frac{\omega_0}{\hbar} <b|H_1|a> e^{i\omega_0 t}c_a(t) - \frac{1}{\hbar^2} <b|H_1|a><a|H_1|b> c_b(t)$$

$$= \frac{\omega_0}{\hbar} <b|H_1|a> e^{i\omega_0 t}c_a(t) - \frac{1}{\hbar^2}\left| <a|H_1|b> \right|^2 c_b(t). \tag{1}$$

Now

$$\frac{dc_b(t)}{dt} = \frac{1}{i\hbar} <b|H_1|a> e^{i\omega_0 t}c_a(t)$$

$$\Rightarrow \quad c_a(t) = \frac{i\hbar e^{-i\omega_0 t}}{<b|H_1|a>}\frac{dc_b(t)}{dt}.$$

Substituting this into equation (1) yields

$$\frac{d^2c_b(t)}{dt^2} = \frac{\omega_0}{\hbar} <b|H_1|a> e^{i\omega_0 t}\frac{i\hbar e^{-i\omega_0 t}}{<b|H_1|a>}\frac{dc_b(t)}{dt} - \frac{1}{\hbar^2}\left| <a|H_1|b> \right|^2 c_b(t)$$

$$= i\omega_0\frac{dc_b(t)}{dt} - \frac{1}{\hbar^2}\left| <a|H_1|b> \right|^2 c_b(t)$$

Let

$$\alpha^2 = \frac{\left| <a|H_1|b> \right|^2}{\hbar^2}$$

$$\boxed{\Rightarrow \quad \frac{d^2c_b(t)}{dt^2} - i\omega_0\frac{dc_b(t)}{dt} + \alpha^2 c_b(t) = 0.}$$

2.(c) The solution for a second order differential equation with constant coefficients is given by $g(t) = e^{-\lambda t}$, so we find

$$\frac{dg}{dt} = \frac{d}{dt}e^{-\lambda t} = -\lambda e^{-\lambda t}$$

$$\Rightarrow \quad \frac{d^2g}{dt^2} = \frac{d}{dt}\left(-\lambda e^{-\lambda t}\right) = \lambda^2 e^{-\lambda t}.$$

In this case, $g(t) = c_b(t)$. Substituting this into the last boxed equation,

$$\lambda^2 e^{-\lambda t} + i\omega_0\lambda e^{-\lambda t} + \alpha^2 e^{-\lambda t} = 0$$

$$\boxed{\Rightarrow \quad \lambda^2 + i\omega_0\lambda + \alpha^2 = 0.}$$

2.(d) This equation is quadratic in λ, so we can use the quadratic formula to find the values of λ,

$$\lambda = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-i\omega_0 \pm \sqrt{(i\omega_0)^2 - 4(1)\alpha^2}}{2(1)}$$

$$\boxed{\Rightarrow \quad \lambda = \frac{1}{2}\left[-i\omega_0 \pm \sqrt{-\omega_0^2 - 4\alpha^2}\right]}$$

Let $i\omega = \sqrt{-\omega_0^2 - 4\alpha^2}$. Then

$$\lambda = \frac{1}{2}\left[-i\omega_0 \pm i\omega\right] = \frac{i}{2}\left[-\omega_0 \pm \omega\right].$$

2.(e) From part (c), the solution for a second order differential equation with constant coefficients is given by $g(t) = e^{-\lambda t}$, so the general solution will be a linear combination of all such $g(t)s$, that is, the sum of the exponentials with both possible values of λ. There are two values of λ, so we find

$$g(t) = e^{-\lambda t} = e^{-\frac{i}{2}[-\omega_0 \pm \omega]} = e^{\frac{i}{2}[\omega_0 \mp \omega]}$$

$$\Rightarrow \quad g_1(t) = e^{\frac{i}{2}[\omega_0 + \omega]} \qquad g_2(t) = e^{\frac{i}{2}[\omega_0 - \omega]}.$$

The general solution for $g(t) = c_b(t)$ is given by

$$c_b(t) = Ag_1(t) + Bg_2(t)$$

$$\boxed{\begin{aligned} c_b(t) &= Ae^{\frac{i}{2}[\omega_0+\omega]} + Be^{\frac{i}{2}[\omega_0-\omega]} \\ &= Ae^{i\omega_0 t/2}e^{i\omega t/2} + Be^{i\omega_0 t/2}e^{-i\omega t/2}. \end{aligned}}$$

To simplify notation in the reduction to the desired form, let $\beta = \omega/2$, and $\beta_0 = \omega_0/2$. Then

$$\begin{aligned} c_b(t) &= Ae^{i\beta_0 t}e^{i\beta t} + Be^{i\beta_0 t}e^{-i\beta t} \\ &= A\left(\cos\beta_0 t + i\sin\beta_0 t\right)\left(\cos\beta t + i\sin\beta t\right) + B\left(\cos\beta_0 t + i\sin\beta_0 t\right)\left(\cos\beta t - i\sin\beta t\right) \\ &= A\left(\cos\beta_0 t\cos\beta t + i\sin\beta_0 t\cos\beta t + i\cos\beta_0 t\sin\beta t - \sin\beta_0 t\sin\beta t\right) \\ &\qquad + B\left(\cos\beta_0 t\cos\beta t + i\sin\beta_0 t\cos\beta t - i\cos\beta_0 t\sin\beta t + \sin\beta_0 t\sin\beta t\right) \\ &= \big(A+B\big)\cos\beta_0 t\cos\beta t - \big(A-B\big)\sin\beta_0 t\sin\beta t + i\big(A-B\big)\cos\beta_0 t\sin\beta t + i\big(A+B\big)\sin\beta_0 t\cos\beta t \\ &= \big(A+B\big)\cos\beta t\left[\cos\beta_0 t + i\sin\beta_0 t\right] + \big(A-B\big)\sin\beta t\left[-\sin\beta_0 t + i\cos\beta_0 t\right]. \end{aligned}$$

Let $C = \big(A+B\big)$, and $\big(A-B\big) = -iD$. Using these, the previous equation becomes

$$\begin{aligned} c_b(t) &= C\cos\beta t e^{i\beta_0 t} - iD\sin\beta t\left[-\sin\beta_0 t + i\cos\beta_0 t\right] \\ &= C\cos\beta t e^{i\beta_0 t} + D\sin\beta t\left[\cos\beta_0 t + i\sin\beta_0 t\right] \\ &= C\cos\beta t e^{i\beta_0 t} + D\sin\beta t e^{i\beta_0 t}. \end{aligned}$$

Remembering that $\beta = \omega/2$, and that $\beta_0 = \omega_0/2$, we find

$$\boxed{c_b(t) = \left[C\cos\frac{\omega t}{2} + D\sin\frac{\omega t}{2} \right] e^{i\omega_0 t/2}.}$$

2.(f) If $c_b(0) = 0$, then

$$\begin{aligned} c_b(0) &= [C\cos(0) + D\sin(0)]\, e^0 = 0 \\ &\Rightarrow \quad [C \cdot 1 + D \cdot 0] \cdot 1 = 0 \\ &\Rightarrow \quad C = 0 \end{aligned}$$

$$\boxed{\Rightarrow \quad c_b(t) = D\sin\frac{\omega t}{2} e^{i\omega_0 t/2}.}$$

We can differentiate this,

$$\begin{aligned} \frac{d}{dt}c_b(t) &= \frac{d}{dt}\left[D\sin\frac{\omega t}{2} e^{i\omega_0 t/2} \right] \\ &= D\left[\cos\left(\frac{\omega t}{2}\right)\frac{\omega}{2} e^{i\omega_0 t/2} + \sin\frac{\omega t}{2} e^{i\omega_0 t/2}\frac{i\omega_0}{2} \right] \\ &= \frac{D}{2}\left[\omega\cos\left(\frac{\omega t}{2}\right) + i\omega_0\sin\frac{\omega t}{2} \right] e^{i\omega_0 t/2}, \end{aligned}$$

and substitute it into the second of the original coupled differential equations,

$$\frac{dc_b(t)}{dt} = \frac{1}{i\hbar} < b\big|H_1\big|a > e^{+i\omega_0 t} c_a(t).$$

2.(g) This yields

$$\frac{D}{2}\left[\omega\cos\left(\frac{\omega t}{2}\right) + i\omega_0\sin\frac{\omega t}{2} \right] e^{i\omega_0 t/2} = \frac{1}{i\hbar} < b\big|H_1\big|a > e^{+i\omega_0 t} c_a(t)$$

$$\boxed{\begin{aligned} \Rightarrow \quad c_a(t) &= \frac{i\hbar}{< b\big|H_1\big|a >}\frac{D}{2}\left[\omega\cos\left(\frac{\omega t}{2}\right) + i\omega_0\sin\frac{\omega t}{2} \right] e^{-i\omega_0 t/2} \\ &= \frac{i\hbar}{< b\big|H_1\big|a >}\frac{\omega D}{2}\left[\cos\left(\frac{\omega t}{2}\right) + i\left(\frac{\omega_0}{\omega}\right)\sin\frac{\omega t}{2} \right] e^{-i\omega_0 t/2}. \end{aligned}}$$

2.(h) If $c_a(0) = 1$,

$$c_a(0) = \frac{i\hbar}{<b|H_1|a>} \frac{D}{2} \left[\omega \cos(0) + i\omega_0 \sin 0\right] e^0 = 1$$

$$\Rightarrow \quad \frac{i\hbar}{<b|H_1|a>} \frac{D}{2} \left[\omega \cdot 1 + i\omega_0(0)\right] = 1$$

$$\Rightarrow \quad \frac{i\hbar}{<b|H_1|a>} \frac{D}{2} \omega = 1$$

$$\boxed{\Rightarrow \quad D = \frac{2 <b|H_1|a>}{i\hbar\omega}.}$$

2.(i) Using this in the results from parts (g) and (f),

$$c_a(t) = \frac{i\hbar}{2 <b|H_1|a>} \frac{2 <b|H_1|a>}{i\hbar\omega} \left[\omega \cos\left(\frac{\omega t}{2}\right) + i\omega_0 \sin\left(\frac{\omega t}{2}\right)\right] e^{-i\omega_0 t/2} \quad \text{so}$$

$$\boxed{\begin{aligned} c_a(t) &= \left[\cos\left(\frac{\omega t}{2}\right) + i\left(\frac{\omega_0}{\omega}\right) \sin\left(\frac{\omega t}{2}\right)\right] e^{-i\omega_0 t/2} \\ \text{and} \quad c_b(t) &= \frac{2 <b|H_1|a>}{i\hbar\omega} \sin\frac{\omega t}{2} e^{i\omega_0 t/2}. \end{aligned}}$$

2.(j) Remember $|f|^2 = f^* f$, so to show $|c_a|^2 + |c_b|^2 = 1$,

$$\begin{aligned} |c_a|^2 &= c_a^* c_a \\ &= \left[\cos\left(\frac{\omega t}{2}\right) - i\left(\frac{\omega_0}{\omega}\right) \sin\left(\frac{\omega t}{2}\right)\right] e^{i\omega_0 t/2} \left[\cos\left(\frac{\omega t}{2}\right) + i\left(\frac{\omega_0}{\omega}\right) \sin\left(\frac{\omega t}{2}\right)\right] e^{-i\omega_0 t/2} \\ &= \cos^2\left(\frac{\omega t}{2}\right) + i\left(\frac{\omega_0}{\omega}\right) \sin\left(\frac{\omega t}{2}\right) \cos\left(\frac{\omega t}{2}\right) - i\left(\frac{\omega_0}{\omega}\right) \sin\left(\frac{\omega t}{2}\right) \cos\left(\frac{\omega t}{2}\right) + \left(\frac{\omega_0}{\omega}\right)^2 \sin^2\left(\frac{\omega t}{2}\right) \\ &= \cos^2\left(\frac{\omega t}{2}\right) + \left(\frac{\omega_0}{\omega}\right)^2 \sin^2\left(\frac{\omega t}{2}\right), \end{aligned}$$

$$\begin{aligned} |c_b|^2 &= c_b^* c_b \\ &= \left[\frac{2\left(< b|H_1|a>\right)^*}{-i\hbar\omega} \sin\frac{\omega t}{2} e^{-i\omega_0 t/2}\right] \left[\frac{2\left(< b|H_1|a>\right)}{i\hbar\omega} \sin\frac{\omega t}{2} e^{i\omega_0 t/2}\right] \\ &= \frac{4\left|< b|H_1|a>\right|^2}{\hbar^2\omega^2} \sin^2\left(\frac{\omega t}{2}\right). \end{aligned}$$

From part (b),

$$\alpha^2 = \frac{\left|< a\middle|H_1\middle|b>\right|^2}{\hbar^2} = \frac{\left|< b\middle|H_1\middle|a>\right|^2}{\hbar^2}$$
$$\Rightarrow \quad \left|c_b\right|^2 = \frac{4\alpha^2}{\omega^2}\sin^2\left(\frac{\omega t}{2}\right).$$

From part (d),

$$\begin{aligned} i\omega &= \sqrt{-\omega_0^2 - 4\alpha^2} \\ \Rightarrow \quad -\omega^2 &= -\omega_0^2 - 4\alpha^2 \\ \Rightarrow \quad \omega^2 &= \omega_0^2 + 4\alpha^2 \\ \Rightarrow \quad \alpha^2 &= \frac{\omega^2 - \omega_0^2}{4} \end{aligned}$$

$$\begin{aligned} \Rightarrow \quad \left|c_b\right|^2 &= \frac{4}{\omega^2}\frac{\omega^2 - \omega_0^2}{4}\sin^2\left(\frac{\omega t}{2}\right) \\ &= \left(1 - \frac{\omega_0^2}{\omega^2}\right)\sin^2\left(\frac{\omega t}{2}\right) \\ &= \sin^2\left(\frac{\omega t}{2}\right) - \left(\frac{\omega_0^2}{\omega^2}\right)\sin^2\left(\frac{\omega t}{2}\right). \end{aligned}$$

Adding this to the expression for $\left|c_a\right|^2$,

$$\boxed{\begin{aligned} \left|c_a\right|^2 + \left|c_b\right|^2 &= \cos^2\left(\frac{\omega t}{2}\right) + \left(\frac{\omega_0}{\omega}\right)^2\sin^2\left(\frac{\omega t}{2}\right) + \sin^2\left(\frac{\omega t}{2}\right) - \left(\frac{\omega_0^2}{\omega^2}\right)\sin^2\left(\frac{\omega t}{2}\right) \\ &= \cos^2\left(\frac{\omega t}{2}\right) + \sin^2\left(\frac{\omega t}{2}\right) = 1. \end{aligned}}$$

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3. Compare the results of time-dependent perturbation theory with the exact results for the two level system subject to the perturbation Hamiltonian

$$H_1(t') = \begin{pmatrix} 0 & H'_{ab} \\ H'_{ba} & 0 \end{pmatrix} \quad \text{for} \quad 0 \le t' \le t,$$

$$H_1(t') = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \quad \text{for} \quad t' < 0 \ \text{ or } \ t' > t.$$

(a) Write down the first-order approximation $c_b^{(1)}(t)$. You should find that

$$c_b^{(1)}(t) \ = \ (i\hbar)^{-1} \int_0^t H'_{ba} \exp(i\omega_0 t')\, dt'.$$

(b) Do the integral in part a to find the first-order approximation $c_b^{(1)}(t)$. You should find

$$c_b^{(1)}(t) \ = \ -\frac{H'_{ba}}{\hbar\omega_0} \ (\ \exp(i\omega_0 t) \ - \ 1\ )\,.$$

(c) Explain why the first-order approximation $c_b^{(1)}(t)$ is also equal to the second-order approximation $c_b^{(2)}(t)$.

(d) Now write down the approximation up to second-order $c_a^{(2)}(t)$. You should find

$$c_a^{(2)}(t) \ = \ 1 \ - \ \frac{1}{\hbar^2} \int_0^t H'_{ab} \exp(-i\omega_0 t') \left[\int_0^{t'} H'_{ba} \exp(i\omega_0 t'') dt'' \right] \ dt'.$$

(e) Do the integrals in part d to find the second-order approximation $c_a^{(2)}(t)$. You should find

$$c_a^{(2)}(t) \ = \ 1 \ - \ \frac{\mid H'_{ab} \mid^2}{i\hbar^2\omega_0} \left[t' \ + \ \frac{\exp\left(-i\omega_0 t'\right)}{i\omega_0} \right]_{t'=0}^{t'=t}.$$

(f) To compare the exact result for $c_b(t)$ with the first-order perturbative result $c_b^{(1)}(t)$, note that the exact frequency ω only differs from the unperturbed frequency ω_0 in second-order in H'_{ba}. Thus to get the first-order approximation from the exact result

$$c_b(t) = \frac{2 \ < b \mid H_1 \mid a >}{i\hbar\omega} \ \exp\left(\frac{i\omega t}{2}\right) \ \sin\left(\frac{\omega t}{2}\right)\,,$$

start by replacing the exact frequency by ω by ω_0. Then expand the sine function as a sum of exponential functions, and combine the exponentials. You should find

$$c_b(t) \;\simeq\; -\frac{H'_{ba}}{\hbar\omega_0}\;(\,\exp(i\omega_0 t)\;-\;1\,)\,.$$

(g) Unfortunately, it is much more difficult to compare the exact result for $c_a(t)$ with the second-order perturbative result $c_b^{(1)}(t)$! However, again note that the exact frequency ω differs from the unperturbed frequency ω_0 in second-order in H'_{ba}, *i.e.*,

$$\omega \;=\; \omega_0\; sqrt\left(\frac{4\;|\,H'_{ab}\,|^2}{\hbar^2{\omega_0}^2}\right) \;\simeq\; \omega_0\left(1\;+\;\frac{2\;|\,H'_{ab}\,|^2}{\hbar^2{\omega_0}^2}\right).$$

So, you should find

$$\omega \;=\; \omega_0 \;+\; \frac{2\;|\,H'_{ab}\,|^2}{\hbar^2\omega_0}$$

$$\left(\frac{\omega}{\omega_0}\right) \;=\; 1\;+\;\frac{2\;|\,H'_{ab}\,|^2}{\hbar^2{\omega_0}^2}.$$

(h) Next expand the sines and cosines in the exact solution

$$c_a(t) = \exp\,(\frac{-i\omega_0 t}{2})\;\left[\cos\,(\frac{\omega t}{2})\;+\;i\;\left(\frac{\omega_0}{\omega}\right)\;\sin\,(\frac{\omega t}{2})\right],$$

using the approximations

$$\cos\,(x+\epsilon)\;\simeq\;cos(x)\;-\;\epsilon\;\sin\,(x)$$

$$\sin\,(x+\epsilon)\;\simeq\;sin(x)\;+\;\epsilon\;\cos\,(x)$$

to obtain

$$\cos\,(\frac{\omega t}{2})\;=\;\cos\,(\frac{\omega_0 t}{2}\;+\;\frac{|\,H'_{ab}\,|^2 t}{\hbar^2\omega_0})\;=\;\cos\,(\frac{\omega_0 t}{2})\;-\;\frac{|\,H'_{ab}\,|^2\;\;t}{\hbar^2\omega_0}\;\sin\,(\frac{\omega_0 t}{2})$$

$$\sin\,(\frac{\omega t}{2})\;=\;\sin\,(\frac{\omega_0 t}{2}\;+\;\frac{|\,H'_{ab}\,|^2 t}{\hbar^2\omega_0})\;=\;\sin\,(\frac{\omega_0 t}{2})\;+\;\frac{|\,H'_{ab}\,|^2\;\;t}{\hbar^2\omega_0}\;\cos\,(\frac{\omega_0 t}{2})$$

Finally, put all of these approximations back into the exact solution, expand the sines and cosines as exponentials, multiply everything out, and keep the terms to second order in H'_{ab}. You should find

$$c_a(t) \simeq 1 - \frac{|H'_{ab}|^2}{\hbar^2\omega_0}\left[-it + \frac{1}{\omega_0}\left(1 - \exp(-i\omega_0 t)\right)\right].$$

3.(a) Using the equation

$$\frac{dc_b}{dt} = \frac{1}{i\hbar}H'_{ba}e^{i\omega_0 t}$$
$$\Rightarrow \quad dc_b = \frac{1}{i\hbar}H'_{ba}e^{i\omega_0 t}dt.$$

Assuming that c_b, which is an explicit function of time, varies slowly, we find

$$\boxed{c_b^{(1)} = \frac{1}{i\hbar}\int_0^t H'_{ba}e^{i\omega_0 t'}dt'.}$$

3.(b) If $H'_{ba}(t)$ is constant or varies slowly,

$$c_b^{(1)} = \frac{H'_{ba}}{i\hbar}\int_0^t e^{i\omega_0 t'}dt'$$
$$= \frac{H'_{ba}}{i\hbar}\frac{1}{i\omega_0}e^{i\omega_0 t'}\Big|_0^t$$

$$\boxed{\Rightarrow \quad c_b^{(1)} = -\frac{H'_{ba}}{\hbar\omega_0}\left(e^{i\omega_0 t} - 1\right).}$$

3.(c) We have $c_a(0) = 1$, and $c_b(0) = 0$ from the previous problem. To zeroth order, meaning no perturbation, the coefficients remain $c_a^{(0)}(t) = 1$ and $c_b^{(0)}(t) = 0$ for all t. The first order approximations are

$$\frac{dc_a^{(1)}(t)}{dt} = \frac{1}{i\hbar}H'_{ab}e^{-i\omega_0 t}\left(c_b^{(0)}\right) = \frac{1}{i\hbar}H'_{ab}e^{-i\omega_0 t}(0) = 0$$

$$\Rightarrow \quad c_a^{(1)}(t) = 1$$

because the derivative being zero tells us it does not change from its initial condition. For the other coefficient,

$$\frac{dc_b^{(1)}}{dt} = \frac{1}{i\hbar}H'_{ba}e^{i\omega_0 t}\left(c_a^{(0)}\right) = \frac{1}{i\hbar}H'_{ba}e^{i\omega_0 t}(1) = \frac{1}{i\hbar}H'_{ba}e^{i\omega_0 t}$$

$$\Rightarrow \quad c_b^{(1)} = -\frac{H'_{ba}}{\hbar\omega_0}\left(e^{i\omega_0 t} - 1\right)$$

from part (b). The second order approximation for c_a is

$$\frac{dc_a^{(2)}(t)}{dt} = \frac{1}{i\hbar} H'_{ab} e^{-i\omega_0 t} \left(c_b^{(1)} \right) = \frac{1}{i\hbar} H'_{ab} e^{-i\omega_0 t} \left(-\frac{H'_{ba}}{\hbar\omega_0} \left(e^{i\omega_0 t} - 1 \right) \right)$$

which we will use in part (d). For c_b,

$$\frac{dc_b^{(2)}}{dt} = \frac{1}{i\hbar} H'_{ba} e^{i\omega_0 t} \left(c_a^{(1)} \right) = \frac{1}{i\hbar} H'_{ba} e^{i\omega_0 t} (1) = \frac{1}{i\hbar} H'_{ba} e^{i\omega_0 t}.$$

This is the same as the first order derivative and part (b), so

$$c_b^{(2)}(t) = -\frac{H'_{ba}}{\hbar\omega_0} \left(e^{i\omega_0 t} - 1 \right).$$

As indicated, $c_b^{(1)}(t) = c_b^{(2)}(t)$. Examining the equations, this is a consequence of the fact $c_a^{(1)} = 1$, which is a consequence of the fact $c_a^{(0)} = 1$, which is a consequence of the fact $c_a(0) = 1$. In other words,

$$\boxed{c_b^{(1)}(t) = c_b^{(2)}(t) \quad \text{as a consequence of the initial conditions.}}$$

The initial conditions indicate the system is wholly in one of the two levels and there is a complete absence of the system in the other level. If there was a general linear combination

$$\Psi(0) = c_a \psi_a + c_b \psi_b$$

where both c_a and c_b were non-zero, we would expect different order approximations to vary.

3.(d) To find the second order approximation $c_a^{(2)}(t)$, we examine the derivative developed in part (c), specifically

$$\frac{dc_a^{(2)}(t)}{dt} = \frac{1}{i\hbar} H'_{ab} e^{-i\omega_0 t} \left(c_b^{(1)} \right)$$

which we can write

$$\frac{dc_a^{(2)}(t)}{dt} = \frac{1}{i\hbar} H'_{ab} e^{-i\omega_0 t} \left[\frac{1}{i\hbar} \int_0^t H'_{ba} e^{i\omega_0 t'} dt' \right].$$

Again assuming constant or slowly varying conditions,

$$c_a^{(2)}(t) = -\frac{1}{\hbar^2} \int_0^t H'_{ab} e^{-i\omega_0 t'} \left[\int_0^{t'} H'_{ba} e^{i\omega_0 t''} dt'' \right] dt'.$$

If zeroth, $c_a^{(0)}(t) = 1$, and first order, $c_a^{(1)}(t) = 0$, approximations are included,

$$\boxed{c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t H'_{ab} e^{-i\omega_0 t'} \left[\int_0^{t'} H'_{ba} e^{i\omega_0 t''} dt'' \right] dt'.}$$

3.(e) Once more, if the perturbation is constant or slowly varying, we can evaluate this integral as

$$
\begin{aligned}
c_a^{(2)}(t) &= 1 - \frac{1}{\hbar^2} \int_0^t H'_{ab} e^{-i\omega_0 t'} \left[H'_{ba} \int_0^{t'} e^{i\omega_0 t''} dt'' \right] dt' \\
&= 1 - \frac{\left|H'_{ab}\right|^2}{\hbar^2} \int_0^t e^{-i\omega_0 t'} \left[\int_0^{t'} e^{i\omega_0 t''} dt'' \right] dt' \\
&= 1 - \frac{\left|H'_{ab}\right|^2}{\hbar^2} \int_0^t e^{-i\omega_0 t'} \left[\frac{1}{i\omega_0} e^{i\omega_0 t''} \right]_0^{t'} dt' \\
&= 1 - \frac{\left|H'_{ab}\right|^2}{i\omega_0 \hbar^2} \int_0^t e^{-i\omega_0 t'} \left[e^{i\omega_0 t'} - 1 \right] dt' \\
&= 1 - \frac{\left|H'_{ab}\right|^2}{i\hbar^2 \omega_0} \int_0^t \left[1 - e^{-i\omega_0 t'} \right] dt' \\
&= 1 - \frac{\left|H'_{ab}\right|^2}{i\hbar^2 \omega_0} \left[t' - \frac{1}{-i\omega_0} e^{-i\omega_0 t'} \right]_0^t
\end{aligned}
$$

$$
\boxed{\Rightarrow \quad c_a^{(2)}(t) = 1 - \frac{\left|H'_{ab}\right|^2}{i\hbar^2 \omega_0} \left[t' + \frac{1}{i\omega_0} e^{-i\omega_0 t'} \right]_0^t ,}
$$

which is the form indicated in the garden path handout. We will want this in a form free of the variable of integration for part (h), so

$$
c_a^{(2)}(t) = 1 - \frac{\left|H'_{ab}\right|^2}{i\hbar^2 \omega_0} \left[t + \frac{1}{i\omega_0} e^{-i\omega_0 t} - \frac{1}{i\omega_0} \right]. \tag{1}
$$

3.(f) We would like to compare exact results with approximations. Looking first at $c_b(t)$, the exact result from problem 2, part (i) is

$$
c_b(t) = \frac{2 <b\big|H_1\big|a>}{i\hbar\omega} \sin\left(\frac{\omega t}{2}\right) e^{i\omega_0 t/2}.
$$

The exact frequency ω differs from the unperturbed frequency ω_0 in second order in H'_{ba}, and we have repeatedly assumed constant or slowly varying conditions to evaluate integrals. These factors are consistent with the assumption $\omega_0 \approx \omega$. Using this in the exact result, and updating notation to include $H'_{ba} = <b\big|H_1\big|a>$,

$$
\begin{aligned}
c_b(t) &\approx \frac{2H'_{ba}}{i\hbar\omega_0} \sin\left(\frac{\omega_0 t}{2}\right) e^{i\omega_0 t/2} \\
&= \frac{2H'_{ba}}{i\hbar\omega_0} \left(\frac{e^{i\omega_0 t/2} - e^{-i\omega_0 t/2}}{2i} \right) e^{i\omega_0 t/2}
\end{aligned}
$$

$$\Rightarrow \quad c_b(t) \approx -\frac{H'_{ba}}{\hbar\omega_0}\left(e^{i\omega_0 t}-1\right).$$

which is exactly the same form previously developed for $c_b^{(1)}(t) = c_b^{(2)}(t)$.

3.(g) Comparing results for $c_a(t)$ is a longer process. From problem 2, parts (b), (d), and (j), remember

$$\omega^2 = \omega_0^2 + 4\alpha^2 = \omega_0^2 + \frac{4\left|H'_{ba}\right|^2}{\hbar^2} = \omega_0^2\left[1+\frac{4\left|H'_{ba}\right|^2}{\hbar^2\omega^2}\right]$$

$$\Rightarrow \quad \omega = \omega_0\left[1+\frac{4\left|H'_{ba}\right|^2}{\hbar^2\omega^2}\right]^{1/2}.$$

Using the binomial theorem and excluding higher order terms as negligible,

$$\omega \approx \omega_0\left[1+\frac{1}{2}\frac{4\left|H'_{ba}\right|^2}{\hbar^2\omega^2}\right]$$

$$\Rightarrow \quad \frac{\omega}{\omega_0} \approx \left[1+\frac{2\left|H'_{ba}\right|^2}{\hbar^2\omega^2}\right].$$

3.(h) Using the approximations,

$$\cos(x+\epsilon) \approx \cos(x) - \epsilon\sin(x),$$
$$\sin(x+\epsilon) \approx \sin(x) + \epsilon\cos(x),$$

where

$$\omega \approx \omega_0 + \frac{2\left|H'_{ba}\right|^2}{\hbar^2\omega_0} \qquad \text{and} \qquad \epsilon = \frac{2\left|H'_{ba}\right|^2}{\hbar^2\omega_0} = \frac{2\alpha^2}{\omega_0}, \qquad \text{since}\alpha = \frac{\left|H'_{ba}\right|}{\hbar}.$$

Then

$$\begin{aligned}
\cos\left(\frac{\omega t}{2}\right) &\approx \cos\left[\frac{t}{2}\left(\omega_0 + \frac{2\left|H'_{ba}\right|^2}{\hbar^2\omega_0}\right)\right] \\
&= \cos\left(\frac{\omega_0 t}{2} + \frac{\alpha^2 t}{\omega_0}\right) \\
&\approx \cos\left(\frac{\omega_0 t}{2}\right) - \frac{\alpha^2 t}{\omega_0}\sin\left(\frac{\omega_0 t}{2}\right), \qquad \text{and} \\
\sin\left(\frac{\omega t}{2}\right) &\approx \sin\left[\frac{t}{2}\left(\omega_0 + \frac{2\left|H'_{ba}\right|^2}{\hbar^2\omega_0}\right)\right] \\
&= \sin\left(\frac{\omega_0 t}{2} + \frac{\alpha^2 t}{\omega_0}\right) \\
&= \sin\left(\frac{\omega_0 t}{2}\right) + \frac{\alpha^2 t}{\omega_0}\cos\left(\frac{\omega_0 t}{2}\right).
\end{aligned}$$

Using $\beta_0 = \omega_0 t/2$, these are

$$\cos\left(\frac{\omega t}{2}\right) \approx \cos\left(\beta_0\right) - \frac{\alpha^2 t}{\omega_0}\sin\left(\beta_0\right),$$

$$\sin\left(\frac{\omega t}{2}\right) \approx \sin\left(\beta_0\right) + \frac{\alpha^2 t}{\omega_0}\cos\left(\beta_0\right).$$

Since

$$\begin{aligned}
\frac{\omega}{\omega_0} &\approx 1 + \frac{2\alpha^2}{\omega_0^2} \\
\frac{\omega_0}{\omega} &= \left(1 + \frac{2\alpha^2}{\omega_0^2}\right)^{-1} \\
&\approx \left(1 - \frac{2\alpha^2}{\omega_0^2}\right) \qquad \text{if} \quad \alpha << 1.
\end{aligned}$$

Remember the exact result from problem 2, part i, which is given by

$$c_a(t) = \left[\cos\left(\frac{\omega t}{2}\right) + i\left(\frac{\omega_0}{\omega}\right)\sin\left(\frac{\omega t}{2}\right)\right]e^{-i\omega_0 t/2}.$$

Substituting the approximations in the exact result for $c_a(t)$, we obtain

$$\begin{aligned}
c_a(t) &\approx \left[\cos\beta_0 - \frac{\alpha^2 t}{\omega_0}\sin\beta_0 + i\left(\frac{\omega_0}{\omega}\right)\left(\sin\beta_0 + \frac{\alpha^2 t}{\omega_0}\cos\beta_0\right)\right]e^{-i\beta_0} \\
&\approx \left[\cos\beta_0 - \frac{\alpha^2 t}{\omega_0}\sin\beta_0 + i\left(1 - \frac{2\alpha^2}{\omega_0^2}\right)\left(\sin\beta_0 + \frac{\alpha^2 t}{\omega_0}\cos\beta_0\right)\right]e^{-i\beta_0} \\
&= \cos\beta_0 e^{-i\beta_0} - \frac{\alpha^2 t}{\omega_0}\sin\beta_0 e^{-i\beta_0} + i\sin\beta_0 e^{-i\beta_0} + i\frac{\alpha^2 t}{\omega_0}\cos\beta_0 e^{-i\beta_0} - i\frac{2\alpha^2}{\omega_0^2}\sin\beta_0 e^{-i\beta_0} - i\frac{\alpha^4 t}{\omega_0^3}\cos\beta_0 e^{-i\beta_0}.
\end{aligned}$$

We will discard the last term as negligible since it is fourth degree in a quantity << 1. Then we find

$$\cos\beta_0 e^{-i\beta_0} = \left(\frac{e^{i\beta_0} + e^{-i\beta_0}}{2}\right)e^{-i\beta_0} = \frac{1}{2}\left(1 + e^{-i2\beta_0}\right),$$

$$\sin\beta_0 e^{-i\beta_0} = \left(\frac{e^{i\beta_0} - e^{-i\beta_0}}{2i}\right)e^{-i\beta_0} = \frac{1}{2i}\left(1 - e^{-i2\beta_0}\right).$$

The approximation for $c_a(t)$ becomes

$$
\begin{aligned}
c_a(t) &\approx \frac{1}{2}\left[\left(1+e^{-i2\beta_0}\right) - \frac{\alpha^2 t}{i\omega_0}\left(1-e^{-i2\beta_0}\right) + \left(1-e^{-i2\beta_0}\right) + i\frac{\alpha^2 t}{\omega_0}\left(1+e^{-i2\beta_0}\right) - \frac{2\alpha^2}{\omega_0^2}\left(1-e^{-i2\beta_0}\right)\right] \\
&= \frac{1}{2}\left[1+\cancel{e^{-i2\beta_0}} - \frac{\alpha^2 t}{i\omega_0} + \frac{\alpha^2 t}{i\omega_0}e^{-i2\beta_0} + 1 - \cancel{e^{-i2\beta_0}} + i\frac{\alpha^2 t}{\omega_0} + i\frac{\alpha^2 t}{\omega_0}e^{-i2\beta_0} - \frac{2\alpha^2}{\omega_0^2} + \frac{2\alpha^2}{\omega_0^2}e^{-i2\beta_0}\right] \\
&= \frac{1}{2}\left[2 + i\frac{\alpha^2 t}{\omega_0} - \cancel{i\frac{\alpha^2 t}{\omega_0}e^{-i2\beta_0}} + i\frac{\alpha^2 t}{\omega_0} + \cancel{i\frac{\alpha^2 t}{\omega_0}e^{-i2\beta_0}} - \frac{2\alpha^2}{\omega_0^2} + \frac{2\alpha^2}{\omega_0^2}e^{-i2\beta_0}\right] \\
&= \frac{1}{2}\left[2 + 2i\frac{\alpha^2 t}{\omega_0} - \frac{2\alpha^2}{\omega_0^2} + \frac{2\alpha^2}{\omega_0^2}e^{-i2\beta_0}\right] \\
&= 1 + i\frac{\alpha^2 t}{\omega_0} - \frac{\alpha^2}{\omega_0^2} + \frac{\alpha^2}{\omega_0^2}e^{-i2\beta_0} \\
&= 1 + \frac{\alpha^2}{\omega_0}\left[it - \frac{1}{\omega_0} + \frac{1}{\omega_0}e^{-i2\beta_0}\right] \\
&= 1 + \frac{i\alpha^2}{\omega_0}\left[t - \frac{1}{i\omega_0} + \frac{1}{i\omega_0}e^{-i2\beta_0}\right].
\end{aligned}
$$

Multiplying numerator and denominator by i, and using $\alpha = \left|H'_{ba}\right|/\hbar$ and $\beta_0 = \omega_0 t/2$, we find

$$
\boxed{\Rightarrow \quad c_a(t) \approx 1 - \frac{\left|H'_{ba}\right|}{i\hbar^2\omega_0}\left[t + \frac{1}{i\omega_0}e^{-i\omega_0 t} - \frac{1}{i\omega_0}\right],}
$$

which is exactly the same as equation (1) from part e.

---

4. An electron in the $n = 3$, $l = 0$, $m = 0$ state of hydrogen decays by a sequence of electric dipole transitions to the ground state. The selection rules for electric dipole transitions are that $\Delta m = \pm 1$ or 0 and that $\Delta l = \pm 1$. In this problem you are only asked to consider the transitions where n changes, so the nine possible transitions are:

$$| \; 3,0,0 \; > \Rightarrow | \; 2,1,1 \; >$$
$$| \; 3,0,0 \; > \Rightarrow | \; 2,1,0 \; >$$
$$| \; 3,0,0 \; > \Rightarrow | \; 2,1,-1 >$$
$$| \; 3,0,0 \; > \Rightarrow | \; 2,0,0 \; >$$
$$| \; 3,0,0 \; > \Rightarrow | \; 1,0,0 \; >$$

$$| \; 2,1,1 \; > \Rightarrow | \; 1,0,0 \; >$$
$$| \; 2,1,0 \; > \Rightarrow | \; 1,0,0 \; >$$
$$| \; 2,1,-1 > \Rightarrow | \; 1,0,0 \; >$$
$$| \; 2,0,0 \; > \Rightarrow | \; 1,0,0 \; >$$

(a) Which of these nine transitions obey the $\Delta m = \pm 1$ or 0 dipole selection rule?

(b) Which of these nine transitions obey the $\Delta l = \pm 1$ dipole selection rule?

(c) The dipole allowed transitions must obey both rules. Which six of the nine transitions are dipole allowed?

(d) List all of the allowed dipole transition routes, which pass through the $n = 2$ states, from the $| \; 3,0,0 \; >$ state to the $| \; 1,0,0 \; >$ state, *i.e.,* list the three dipole allowed routes which have the form:

$$| \; 3,0,0 \; > \Rightarrow | \; 2,?,? \; > \Rightarrow | \; 1,0,0 \; > .$$

(e) Write down the integral for the dipole matrix element from the $| \; 3,0,0 \; >$ state to the $| \; 2,1,0 \; >$ state. Show that this matrix element only depends on the z component of the $\mathbf{r}$ operator, *i.e.,* show that

$$< \; 2,1,0 \; | \mathbf{r} | \; 3,0,0 \; > = < \; 2,1,0 \; | \, z \, | \; 3,0,0 \; > \; \mathbf{k}.$$

(f) Do the integral that you wrote down in part e. You should find $< \; 2,1,0 \; | \, z \, | \; 3,0,0 \; > =$

$$\left[\sqrt{\frac{3}{4\pi}} \sqrt{\frac{1}{24}} \, a^{-\frac{3}{2}} \right] \left[\sqrt{\frac{1}{4\pi}} \, \frac{2}{\sqrt{27}} \, a^{-\frac{3}{2}} \right] \int_0^\infty \left[r \, \cos(\theta) \, \exp\left(\frac{-r}{2a}\right) \left(1 - \frac{2r}{3a} + \frac{2r^2}{27a^2} \right) \right]$$

$$\times \left[r \ \cos(\theta) \ \exp\left(\frac{-r}{3a}\right)\right] \ r^2 \ dr \ \sin\theta \ d\theta \ \ d\phi$$

so

$$< \ 2,1,0 \ \mid z \mid \ 3,0,0 \ > = \ - \left[\frac{2^8 \ 3^4}{5^6 \ \sqrt{6}} \right] \ a.$$

(g) Write down the integrals for the dipole matrix elements from the $\mid \ 3,0,0 \ >$ state to the $\mid \ 2,1,\pm 1 \ >$ states. Show that these matrix elements only depend on the x and y components of the **r** operator, *i.e.*, show that

$$< \ 2,1,\pm 1 \ \mid \mathbf{r} \mid \ 3,0,0 \ > = < \ 2,1,\pm 1 \ \mid x \mid \ 3,0,0 \ > \ \mathbf{i} + \ < \ 2,1,\pm 1 \ \mid y \mid \ 3,0,0 \ > \ \mathbf{j}.$$

(h) Now show that these x and y matrix elements are almost identical, *i.e.*, show that

$$\pm \ < \ 2,1,\pm 1 \ \mid x \mid \ 3,0,0 \ > \ = \ i \ < \ 2,1,\pm 1 \ \mid y \mid \ 3,0,0 \ > \ .$$

Explain how you can use this to make your life simpler, *i.e.*, explain why you can just calculate one integral and still obtain all four matrix elements!!!

(i) Do the x integral you wrote down in part g. You should find $< \ 2,1,\pm 1 \ \mid x \mid \ 3,0,0 \ > =$

$$\left[\sqrt{\frac{3}{8\pi}} \sqrt{\frac{1}{24}} \, a^{-\frac{3}{2}} \right] \left[\sqrt{\frac{1}{4\pi}} \, \frac{2}{\sqrt{27}} \, a^{-\frac{3}{2}} \right] \int_0^\infty \left[r \ \sin(\theta) \ \exp(\pm i\phi) \ \exp\left(\frac{-r}{2a}\right) \left(1 \ - \ \frac{2r}{3a} \ + \ \frac{2r^2}{27a^2} \right)\right]$$

$$\times \left[r \ \cos(\theta) \ \exp\left(\frac{-r}{3a}\right)\right] \ r^2 \ dr \ \sin\theta \ d\theta \ d\phi$$

so

$$< \ 2,1,\pm 1 \ \mid x \mid \ 3,0,0 \ > = \ \pm \left[- \ \frac{2^7 \ 3^4}{5^6 \ \sqrt{3}} \right] \ a.$$

(j) According to Fermi's Golden Rule Number 2, the electric dipole transition rates are proportional to the squares of the matrix elements. Calculate the squares of these matrix elements and show that the two of the three decay routes have identical transition rates and that the third route has twice the transition rate,*i.e.,* show that

$$\frac{1}{2} \ \mid < \ 2,1,0 \ \mid \mathbf{r} \mid \ 3,0,0 \ > \mid^2 = \mid < \ 2,1,1 \ \mid \mathbf{r} \mid \ 3,0,0 \ > \mid^2 = \mid < \ 2,1,-1 \ \mid \mathbf{r} \mid \ 3,0,0 \ > \mid^2 .$$

So, one half go by one decay route, and one quarter each go by the other two decay routes.

(k) Now the spontaneous emission rates via these three routes are given by

$$A \;=\; \frac{\omega^3 \;\; | < \mathbf{r} > |^2}{3\;\pi\;\epsilon_0\;\hbar\;c^3},$$

so the the total decay rate is given by

$$R \;=\; 3\;A \;=\; 3\left(\frac{e^2}{3\;\pi\;\epsilon_0\;\hbar\;c^3}\right)\left(\frac{-5\;E_1}{36\;\hbar}\right)^3\left(\frac{2^{15}\;3^7}{5^{12}}\right)\;a^2 \;=\; 6.32\;\times\;10^6\;\text{seconds}^{-1},$$

and the lifetime of the $|\;\; 3,0,0\;\;>$ state is given by $\tau \;=\; (1/R) \;=\; 1.58\;\times\;10^{-7}$ seconds.

4.(a) For an electron transition between the $n = 3, l = 0, m = 0$ and ground states, given that it can but does not have to go to the ground state directly, there are nine possible transitions.

All nine possible transitions obey the $\Delta m = \pm 1$ or 0 selection rule.
The nine possible transitions are

$$|3,0,0> \;\rightarrow\; |2,1,1>$$
$$|3,0,0> \;\rightarrow\; |2,1,0>$$
$$|3,0,0> \;\rightarrow\; |2,1,-1>$$
$$|3,0,0> \;\rightarrow\; |2,0,0>$$
$$|3,0,0> \;\rightarrow\; |1,0,0>$$

$$|2,1,1> \;\rightarrow\; |1,0,0>$$
$$|2,1,0> \;\rightarrow\; |1,0,0>$$
$$|2,1,-1> \;\rightarrow\; |1,0,0>$$
$$|2,0,0> \;\rightarrow\; |1,0,0>$$

4.(b)

Six of these these transitions obey the $\Delta l = \pm 1$ selection rule. These six allowed transitions are

$$
\begin{aligned}
&|3,0,0\!> \;\rightarrow |2,1,1\!> \\
&|3,0,0\!> \;\rightarrow\; |2,1,0\!> \\
&|3,0,0\!> \;\rightarrow\; |2,1,-1\!> \\
\\
&|2,1,1\!> \;\rightarrow\; |1,0,0\!> \\
&|2,1,0\!> \;\rightarrow\; |1,0,0\!> \\
&|2,1,-1\!> \;\rightarrow\; |1,0,0\!>
\end{aligned}
$$

4.(c)

The six transitions listed in part b obey both dipole transition rules.

4.(d)

The three allowed transitions via an intermediate state are

$$
\begin{aligned}
&|3,0,0\!> \rightarrow |2,1,1\!> \rightarrow\; |1,0,0\!> \\
&|3,0,0\!> \rightarrow\; |2,1,0\!> \rightarrow\; |1,0,0\!> \\
&|3,0,0\!> \rightarrow\; |2,1,-1\!> \rightarrow\; |1,0,0\!>
\end{aligned}
$$

4.(e) The transition

$$
\begin{aligned}
<\!2,1,0\big|\,\vec{r}\,\big|3,0,0\!> \;&= \;<\!\psi_{210}\big|\,\vec{r}\,\big|\psi_{300}\!> \\
&= \;<\!R_{21}Y_{10}\big|\,\vec{r}\,\big|R_{30}Y_{00}\!> \\
&= \int R_{21}Y_{10}\,\vec{r}\,R_{30}Y_{00}\,dV \\
&= \int R_{21}R_{30}r^2\,dr \int Y_{10}\,\vec{r}\,Y_{00}\,d\Omega
\end{aligned}
$$

The angular part of this equation is

$$
\int \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta\,\vec{r}\,\left(\frac{1}{4\pi}\right)^{1/2} d\Omega = \frac{\sqrt{3}}{4\pi}\int \vec{r}\,\cos\theta\,d\Omega.
$$

Remember $\vec{z} = \vec{r}\cos\theta = z\hat{k}$ so generalizing back into Dirac notation,

$$<2,1,0|\,\vec{r}\,|3,0,0> \,=\, <2,1,0|\,z\,|3,0,0>\,\hat{k}.$$

4.(f) Evaluating the integral by inserting the appropriate radial and angular functions, we find that the matrix element we seek $<2,1,0|\,z\,|3,0,0>$ is equal to the integral

$$I \;=\; \int_{-\infty}^{\infty}\left(\frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}e^{-r/2a}\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta\right)^{*}\,(\,z\,)\,\frac{2}{\sqrt{27}}a^{-3/2}\left(1-\frac{2r}{3a}+\frac{2}{27}\frac{r^2}{a^2}\right)e^{-r/3a}\left(\frac{1}{4\pi}\right)^{1/2}\,dV.$$

Factoring out the constants and simplifying, we find:

$$\begin{aligned}
I \;&=\; \frac{1}{\sqrt{24}}\frac{2}{\sqrt{27}}\frac{1}{a^4}\left(\frac{3}{4\pi}\right)^{1/2}\left(\frac{1}{4\pi}\right)^{1/2}\int_{-\infty}^{\infty} r\,e^{-r/2a}\cos\theta\,(\,r\cos\theta\,)\,\left(1-\frac{2r}{3a}+\frac{2}{27}\frac{r^2}{a^2}\right)e^{-r/3a}\,dV \\
&= \frac{1}{12\pi\sqrt{6}a^4}\int_{-\infty}^{\infty} r^2\cos^2\theta\left(1-\frac{2r}{3a}+\frac{2}{27}\frac{r^2}{a^2}\right)e^{-5r/6a}\,dV
\end{aligned}$$

And by doing the angular integrals, we can reduce the problem to the radial integrals that we must do

$$\begin{aligned}
I \;&=\; \frac{1}{12\pi\sqrt{6}a^4}\int_0^{\infty} r^4e^{-5r/6a}\left(1-\frac{2r}{3a}+\frac{2}{27}\frac{r^2}{a^2}\right)dr\int_0^{\pi}\cos^2\theta\sin\theta\,d\theta\int_0^{2\pi}d\phi. \\
&= \frac{1}{12\pi\sqrt{6}a^4}\int_0^{\infty} r^4e^{-5r/6a}\left(1-\frac{2r}{3a}+\frac{2}{27}\frac{r^2}{a^2}\right)dr\int_0^{\pi}\cos^2\theta\sin\theta\,d\theta\,(2\pi) \\
&= \frac{1}{6\sqrt{6}a^4}\int_0^{\infty}\left(r^4e^{-5r/6a}-\frac{2}{3a}r^5e^{-5r/6a}+\frac{2}{27a^2}r^6e^{-5r/6a}\right)dr\,\left(\frac{\cos^3\theta}{3}\Big|_0^{\pi}\right) \\
&= \frac{1}{6\sqrt{6}a^4}\int_0^{\infty}\left(r^4e^{-5r/6a}-\frac{2}{3a}r^5e^{-5r/6a}+\frac{2}{27a^2}r^6e^{-5r/6a}\right)dr\,\left(\frac{-1-1}{3}\right) \\
&= -\frac{1}{9\sqrt{6}a^4}\left(\int_0^{\infty} r^4e^{-5r/6a}\,dr-\frac{2}{3a}\int_0^{\infty} r^5e^{-5r/6a}\,dr+\frac{2}{27a^2}\int_0^{\infty} r^6e^{-5r/6a}\,dr\right). \qquad (1)
\end{aligned}$$

We can evaluate all three radial integrals using form 3.381.4 on page 317 of Gradshteyn and Ryzhik, which is

$$\int_0^{\infty} x^{\nu-1}e^{-\mu x}\,dx = \frac{1}{\mu^{\nu}}\Gamma(\nu), \qquad \text{Re}\;\mu>0, \qquad \text{Re}\;\nu\;>0.$$

For the first integral, $\nu=5$ and $\mu=5/6a$, so

$$\int_0^{\infty} r^4e^{-5r/6a}\,dr = \frac{1}{(5/6a)^5}\Gamma(5) = \frac{6^5a^5}{5^5}4\cdot3\cdot2 = 24\frac{6^5a^5}{5^5}.$$

For the second integral, $\nu=6$ and $\mu=5/6a$, so

$$\frac{2}{3a}\int_0^{\infty} r^5e^{-5r/6a}\,dr = \frac{1}{(5/6a)^6}\Gamma(6) = \frac{2}{3a}\frac{6^6a^6}{5^6}5\cdot4\cdot3\cdot2 = 80\frac{6^6a^5}{5^6}.$$

For the third integral, $\nu = 7$ and $\mu = 5/6a$, so

$$\frac{2}{27a^2}\int_0^\infty r^6 e^{-5r/6a}\,dr = \frac{1}{(5/6a)^7}\Gamma(7) = \frac{2}{27a^2}\frac{6^7 a^7}{5^7} 6\cdot 5\cdot 4\cdot 3\cdot 2 = \frac{160}{3}\frac{6^7 a^5}{5^7}.$$

Substituting these into equation (1),

$$\begin{aligned}
<2,1,0\big|\, z\,\big|3,0,0> &= -\frac{1}{9\sqrt{6}a^4}a^5\left(24\frac{6^5}{5^5} - 80\frac{6^6}{5^6} + \frac{160}{3}\frac{6^7}{5^7}\right)\\
&= -\frac{a}{9\sqrt{6}}\frac{6^5}{5^6}\left(120 - 80\cdot 6 + \frac{160\cdot 6^2}{3\cdot 5}\right)\\
&= -\frac{6^5 a}{5^6 3^2\sqrt{6}}\,(120 - 480 + 384)\\
&= -\frac{6^5 a}{5^6 3^2\sqrt{6}}\,(24)\\
&= -\frac{2^5 3^5 a}{5^6 3^2\sqrt{6}}\,(2^3\cdot 3)
\end{aligned}$$

$$\Rightarrow \quad <2,1,0\big|\, z\,\big|3,0,0> = -\frac{2^8 3^4}{5^6\sqrt{6}}a$$

4.(g) The integrals for $<2,1,\pm 1\big|\,\vec{\mathbf{r}}\,\big|3,0,0>$ are easier. These integral depend only on the x and y components of the $\vec{\mathbf{r}}$ operator. Here

$$\begin{aligned}
<2,1,\pm1\big|\,\vec{\mathbf{r}}\,\big|3,0,0> &= \int R_{21}^* Y_{1,\pm1}^*\big(\vec{\mathbf{r}}\big) R_{30} Y_{00}\, dV\\
&= \int R_{21}R_{30}r^2\,dr \int Y_{1,\pm1}^*\big(\vec{\mathbf{r}}\big)Y_{00}\,d\Omega.
\end{aligned}$$

The angular integral is

$$\begin{aligned}
\int Y_{1,\pm1}^*\big(\vec{\mathbf{r}}\big)Y_{00}\,d\Omega &= \int \left(\mp\left(\frac{3}{8\pi}\right)^{1/2}\right)\sin\theta e^{\mp i\phi}\big(\vec{\mathbf{r}}\big)\left(\frac{1}{4\pi}\right)^{1/2} d\Omega\\
&= \mp\left(\frac{3}{8\pi}\right)^{1/2}\left(\frac{1}{4\pi}\right)^{1/2}\int \sin\theta e^{\mp i\phi}\big(\vec{\mathbf{r}}\big)\,d\Omega\\
&= \mp\frac{1}{4\pi}\sqrt{\frac{3}{2}}\int \big(\vec{\mathbf{r}}\big)\sin\theta\,(\cos\phi \mp i\sin\phi)\,d\Omega\\
&= \mp\frac{1}{4\pi}\sqrt{\frac{3}{2}}\int \big(\vec{\mathbf{r}}\sin\theta\cos\phi \mp i(\vec{\mathbf{r}}\sin\theta\sin\phi)\big)\,d\Omega.
\end{aligned}$$

Realizing $\vec{\mathbf{r}}\sin\theta\cos\phi = \vec{\mathbf{x}} = x\hat{\mathbf{i}}$ and $\vec{\mathbf{r}}\sin\theta\sin\phi = \vec{\mathbf{y}} = y\hat{\mathbf{j}}$, we can write this

$$\int Y_{1,\pm1}^*\big(\vec{\mathbf{r}}\big)Y_{00}\,d\Omega = \mp\frac{1}{4\pi}\sqrt{\frac{3}{2}}\int \left(x\hat{\mathbf{i}} \mp i(y\hat{\mathbf{j}})\right)\,d\Omega,$$

i.e., we can look at directional or angular dependence as a function of $\vec{\mathbf{x}}$ and $\vec{\mathbf{y}}$ only. Generalizing back into Dirac notation, which is representation free so the constants are irrelevant,

$$\begin{aligned} <2,1,\pm1\big|\,\vec{\mathbf{r}}\,\big|3,0,0> &= <2,1,\pm1\big|\,x\hat{\mathbf{i}} \mp i(y\hat{\mathbf{j}})\,\big|3,0,0> \\ &= <2,1,\pm1\big|\,x\,\big|3,0,0>\hat{\mathbf{i}} \;\mp\; <2,1,\pm1\big|\,iy\,\big|3,0,0>\hat{\mathbf{j}} \end{aligned}.$$

The sign "$\mp$" between the two elements reflects only a phase convention, and we will choose without loss of generality the "+" sign for our phase so

$$\boxed{<2,1,\pm1\big|\,\vec{\mathbf{r}}\,\big|3,0,0> = <2,1,\pm1\big|\,x\,\big|3,0,0>\hat{\mathbf{i}} \;+\; <2,1,\pm1\big|\,iy\,\big|3,0,0>\hat{\mathbf{j}}.}$$

4.(h) To show

$$<2,1,\pm1\big|\,x\,\big|3,0,0> = \; i<2,1,\pm1\big|\,y\,\big|3,0,0>$$

consider the commutator $[L_z,x] = i\hbar y$, and the eigenvalue equation $L_z|n,l,m> = m\hbar|n,l,m>$. In general

$$\begin{aligned} <n',l',m'\big|\,[L_z,x]\,\big|n,l,m> &= <n',l',m'\big|\,i\hbar y\,\big|n,l,m> \\ &= i\hbar<n',l',m'\big|\,y\,\big|n,l,m>. \end{aligned}$$

This must be the same as $<n',l',m'\big|\,[L_z,x]\,\big|n,l,m>$ when the commutator is evaluated explicitly, *i.e.*,

$$\begin{aligned} i\hbar<n',l',m'\big|\,y\,\big|n,l,m> &= <n',l',m'\big|\,[L_z,x]\,\big|n,l,m> \\ &= <n',l',m'\big|\,L_zx - xL_z\,\big|n,l,m> \end{aligned}$$

where L_z can operate to the left or right. So

$$\begin{aligned} i\hbar<n',l',m'\big|\,y\,\big|n,l,m> &= <n',l',m'\big|\,m'\hbar x - xm\hbar\,\big|n,l,m> \\ &= <n',l',m'\big|\,(m'-m)\hbar x\,\big|n,l,m> \\ &= (m'-m)\hbar<n',l',m'\big|\,x\,\big|n,l,m> \end{aligned}$$

$$\Rightarrow \quad (m'-m)<n',l',m'\big|\,x\,\big|n,l,m> = \; i<n',l',m'\big|\,y\,\big|n,l,m>.$$

For the specific states of interest

$$(1-0)<2,1,1\big|\,x\,\big|3,0,0> = \; i<2,1,1\big|\,y\,\big|3,0,0>$$

$$\Rightarrow \quad <2,1,1\big|\,x\,\big|3,0,0> = \; i<2,1,1\big|\,y\,\big|3,0,0>,$$

and

$$(-1-0)<2,1,-1\big|\,x\,\big|3,0,0> = \; i<2,1,-1\big|\,y\,\big|3,0,0>$$

$$\Rightarrow \quad -<2,1,-1\big|\,x\,\big|3,0,0> = \; i<2,1,-1\big|\,y\,\big|3,0,0>,$$

so

$$\boxed{\pm<2,1,\pm1\big|\,x\,\big|3,0,0> = \; i<2,1,\pm1\big|\,y\,\big|3,0,0>.}$$

There are four matrix elements here. If we evaluate the two integrals in x though, we have the two integrals in y from the above relation. Also, because of the symmetry in ϕ, we can do both integrals in x at the same time, so in effect, we have only one integral to evaluate to get all four matrix elements.

4.(i) To evaluate the integrals in x, remember $x = r\sin\theta\cos\phi$, and

$$\pm <2,1,\pm 1\big|\, x \,\big|3,0,0> = \pm <2,1,\pm 1\big|\, r\sin\theta\cos\phi \,\big|3,0,0> \quad \text{so}$$

$$\begin{aligned}
\pm <2,1,\pm 1\big|\, x \,\big|3,0,0> &= \int_{-\infty}^{\infty} R_{21}^* Y_{1,\pm 1}^* \, r\sin\theta\cos\phi \, R_{30} Y_{00} \, r^2 \Omega \\
&= \int_0^{\infty} R_{21} R_{30} r^3 \, dr \int Y_{1,\pm 1}^* \, \sin\theta\cos\phi \, Y_{00} \, d\Omega
\end{aligned}$$

$$= \int_0^{\infty} \frac{1}{\sqrt{24}} a^{-3/2} \frac{r}{a} e^{-r/2a} \frac{2}{\sqrt{27}} a^{-3/2} \left(1 - \frac{2r}{3a} + \frac{2}{27}\frac{r^2}{a^2}\right) e^{-r/3a} r^3 \, dr \int \mp\sqrt{\frac{3}{8\pi}} \sin\theta e^{\mp i\phi} (\sin\theta\cos\phi) \sqrt{\frac{1}{4\pi}} \, d\Omega$$

$$= \mp \frac{1}{\sqrt{24}} \frac{2}{\sqrt{27}} \frac{1}{a^4} \sqrt{\frac{3}{8\pi}} \sqrt{\frac{1}{4\pi}} \int_0^{\infty} r^4 e^{-5r/6a} \left(1 - \frac{2r}{3a} + \frac{2}{27}\frac{r^2}{a^2}\right) dr \int_0^{\pi} \sin^3\theta \, d\theta \int_0^{2\pi} \cos\phi e^{\mp i\phi} \, d\phi, \qquad (1)$$

where the third factor of $\sin\theta$ is from $d\Omega = \sin\theta \, d\theta \, d\phi$. The constants are

$$\mp \frac{1}{\sqrt{24}} \frac{2}{\sqrt{27}} \frac{1}{a^4} \sqrt{\frac{3}{8\pi}} \sqrt{\frac{1}{4\pi}} = \mp \frac{1}{\sqrt{2^3 \cdot 3}} \frac{2}{\sqrt{3^3}} \frac{1}{a^4} \frac{1}{4\pi} \frac{\sqrt{3}}{\sqrt{2}} = \mp \frac{2\sqrt{3}}{\sqrt{2^4 \cdot 3^4}} \frac{1}{4\pi a^4} = \mp \frac{1}{24\pi a^4 \sqrt{3}}.$$

The azimuthal integral is

$$\begin{aligned}
\int_0^{2\pi} \cos\phi e^{\mp i\phi} \, d\phi = \int_0^{2\pi} \cos\phi (\cos\phi \mp i\sin\phi) \, d\phi &= \int_0^{2\pi} \cos^2\phi \, d\phi \mp i \int_0^{2\pi} \cos\phi \sin\phi) \, d\phi \\
= \left[\frac{1}{2}\phi + \frac{1}{4}\sin(2\phi)\right]_0^{2\pi} \mp i \left[\frac{1}{2}\sin^2\phi\right]_0^{2\pi} &= \left[\frac{1}{2} 2\pi - 0 + 0 - 0\right] \mp i \, [0 - 0] = \pi.
\end{aligned}$$

The polar integral is

$$\int_0^{\pi} \sin^3\theta \, d\theta = -\frac{1}{3}\Big[(\cos\theta)(\sin^2\theta + 2)\Big]_0^{\pi} = -\frac{1}{3}\left[(-1)(0+2) - (1)(0+2)\right] = -\frac{1}{3}\left[-2 - 2\right] = \frac{4}{3}.$$

The radial integral becomes three integrals

$$\int_0^{\infty} r^4 e^{-5r/6a} \left(1 - \frac{2r}{3a} + \frac{2}{27}\frac{r^2}{a^2}\right) dr = \int_0^{\infty} r^4 e^{-5r/6a} \, dr - \frac{2}{3a} \int_0^{\infty} r^5 e^{-5r/6a} \, dr + \frac{2}{27a^2} \int_0^{\infty} r^6 e^{-5r/6a} \, dr$$

and we have already evaluated these integrals Using the results of part (f),

$$\int_0^{\infty} r^4 e^{-5r/6a} \, dr = 24 \frac{6^5 a^5}{5^5},$$

$$\frac{2}{3a} \int_0^{\infty} r^5 e^{-5r/6a} \, dr = 80 \frac{6^6 a^5}{5^6},$$

$$\frac{2}{27a^2} \int_0^{\infty} r^6 e^{-5r/6a} \, dr = \frac{160}{3} \frac{6^7 a^5}{5^7}.$$

Compiling these six results, equation (1) becomes

$$\begin{aligned}
\pm <2,1,\pm1\big|\, x\,\big|3,0,0> &= \mp\frac{1}{24\pi a^4\sqrt{3}}\pi\frac{4}{3}\left(24\frac{6^5a^5}{5^5}-80\frac{6^6a^5}{5^6}+\frac{160}{3}\frac{6^7a^5}{5^7}\right)\\
&= \mp\frac{1}{18a^4\sqrt{3}}\frac{6^5a^5}{5^6}\left(24\cdot5-80\cdot6+\frac{160}{3}\frac{6^2}{5}\right)\\
&= \mp\frac{a}{2\cdot3^2\sqrt{3}}\frac{6^5}{5^6}\,(120-480+384)\\
&= \mp\frac{a}{2\cdot3^2\sqrt{3}}\frac{2^5\cdot3^5}{5^6}\,(24)\\
&= \mp\frac{2^5\cdot3^5\cdot2^3\cdot3}{2\cdot3^2\cdot5^6\sqrt{3}}a
\end{aligned}$$

$$\Rightarrow \quad <2,1,\pm1\big|\, x\,\big|3,0,0> = \pm\left[-\frac{2^7\cdot3^4}{5^6\sqrt{3}}\right]a,$$

and

$$<2,1,\pm1\big|\, y\,\big|3,0,0> = \pm i\,\left[-\frac{2^7\cdot3^4}{5^6\sqrt{3}}\right]a.$$

4.(j) According to Fermi's Golden Rule Number 2, the electric dipole transition rates are proportional to the squares of the matrix elements. We have all three matrix elements so we can calculate the relative rates of decays for the three paths. From part f, we have

$$\big|<2,1,0\big|\,\vec{\mathbf{r}}\,\big|3,0,0>\big|^2 = \left[-\frac{2^8\cdot3^4}{5^6\sqrt{6}}a\right]^2 = \frac{2^{16}\cdot3^8}{5^{12}\cdot6}a^2 = \frac{2^{15}\cdot3^7}{5^{12}}a^2,$$

and from parts g and i, we have

$$<2,1,\pm1\big|\,\vec{\mathbf{r}}\,\big|3,0,0> = <2,1,\pm1\big|\, x\,\big|3,0,0> \pm i <2,1,\pm1\big|\, y\,\big|3,0,0>,$$

so the total transition rate is the sum of the x and y induced rates, and is twice as large as the individual x and y matrix elements squared:

$$\big|<2,1,\pm1\big|\,\vec{\mathbf{r}}\,\big|3,0,0>\big|^2 = 2\left[\mp\frac{2^7\cdot3^4}{5^6\sqrt{3}}a\right]^2 = \frac{2^{15}\cdot3^7}{5^{12}}a^2.$$

Consequently, we conclude that the three decay rates are equal:

$$\big|<2,1,0\big|\,\vec{\mathbf{r}}\,\big|3,0,0>\big|^2 = \big|<2,1,1\big|\,\vec{\mathbf{r}}\,\big|3,0,0>\big|^2 = \big|<2,1,-1\big|\,\vec{\mathbf{r}}\,\big|3,0,0>\big|^2.$$

4.(k) The spontaneous emission rates are given by

$$A = \frac{\omega^3 \left| q < \psi_b \right| \vec{\mathbf{r}} \left| \psi_a > \right|^2}{3\pi\epsilon_0 \hbar c^3} \qquad \text{where} \qquad \omega = \frac{E_b - E_a}{\hbar}.$$

These are given by

$$\begin{aligned}
A_{3,0,0\to 2,1,0} &= \frac{\left[13.6/2^2 - 13.6/3^2\right]^3 \frac{1}{\hbar^3} e^2}{3\pi\epsilon_0 \hbar c^3} \left| <3,0,0 \right| \vec{\mathbf{r}} \left| 2,1,0> \right|^2 \\
&= \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{4}{3} \frac{1}{\hbar^4 c^3} \left[\frac{13.6}{4} - \frac{13.6}{9}\right]^3 \frac{2^{15} \cdot 3^7}{5^{12}} a^2 \\
&= (1.440\,\mathrm{eV} \cdot \mathrm{nm}) \frac{4}{3} \frac{(2\pi)^4}{h^4 c^3} \left[3.40 - 1.51\right]^3 (\mathrm{eV})^3\, 0.294 a^2 \\
&= \frac{(1.440\,\mathrm{eV} \cdot \mathrm{nm})}{(hc)^3} \frac{64\pi^4}{3h} \left[1.89\right]^3\ \mathrm{eV}^3\, (0.294)(0.0529\,\mathrm{nm})^2 \\
&= \frac{(1.440\,\mathrm{eV} \cdot \mathrm{nm})}{(1.240 \times 10^3\,\mathrm{eV} \cdot \mathrm{nm})^3} \frac{2078.06}{h} \left[6.75\right]\ (0.294)(0.00280)\,\mathrm{eV}^3 \mathrm{nm}^2 \\
&= \frac{(1.440\,\mathrm{eV} \cdot \mathrm{nm})}{1.907 \times 10^9\,\mathrm{eV}^3 \cdot \mathrm{nm}^3} \frac{11.547}{h}\,\mathrm{eV}^3 \mathrm{nm}^2 \\
&= \frac{8.72^{-9}\,\mathrm{eV}}{4.136 \times 10^{-15} \mathrm{eV} \cdot \mathrm{s}} \\
&= 2.11 \times 10^6\,\mathrm{s}^{-1}
\end{aligned}$$

$$\Rightarrow \qquad \tau_{3,0,0\to 2,1,0} = \frac{1}{A} = 4.75 \times 10^{-7}\,\mathrm{s}.$$

The spontaneous emission rates for $< 2,1,1 \left| \vec{\mathbf{r}} \right| 3,0,0 >$ and $< 2,1,-1 \left| \vec{\mathbf{r}} \right| 3,0,0 >$ are calculated similarly, and since the matrix elements are identical in value, we find:

$$A_{3,0,0\to 2,1,1} = A_{3,0,0\to 2,1,-1} = A_{3,0,0\to 2,1,0} = 2.11 \times 10^6\,\mathrm{s}^{-1}.$$

So the rate via each path is the same:

$$\begin{aligned}
\tau_{3,0,0\to 2,1,1} &= \frac{1}{A} = 4.75 \times 10^{-7}\,\mathrm{s} \\
\tau_{3,0,0\to 2,1,-1} &= \frac{1}{A} = 4.75 \times 10^{-7}\,\mathrm{s} \\
\tau_{3,0,0\to 2,1,0} &= \frac{1}{A} = 4.75 \times 10^{-7}\,\mathrm{s},
\end{aligned}$$

and the total decay rate is set by

$$A_T = 3(2.11 \times 10^6\,\mathrm{s}^{-1}) = 6.33 \times 10^6\,\mathrm{s}^{-1},$$

which gives us the lifetime

$$\boxed{\tau_T = \frac{1}{A_T} = 1.58 \times 10^{-7}\,\mathrm{s}.}$$

---

5. This is the good old "drop a potential brick in the quantum mechanical square well" problem. Note that the perturbation H_1 is turned on at $t = 0$ and is turned off at $t = T$, so we can use the equation for the probability of making a transition from state i to state f due to a constant perturbation from $t = 0$ to $t = T$, *i.e.*, we can use

$$P(i \to f) \ = \ 4 \ | < f \mid H_1 \mid i > |^2 \ \frac{\sin^2 \left((E_f \ - \ E_i) \ t/2\hbar \right)}{(\ E_f \ - \ E_i \ )^2}.$$

(a) Write down the equation for the eigenenergies of the simple, unperturbed square well and use this equation to calculate $E_f \ - \ E_i \ = \ E_2 \ - \ E_1$. You should find

$$E_2 \ - \ E_1 \ = \ \frac{3 \ \pi^2 \ \hbar^2}{2 \ m \ a^2}.$$

(b) Write down the wavefunctions for the unperturbed oscillator in the $n = 1$ and $n = 2$ states and use them to write down the position space integral that corresponds to the matrix element $< 2 \mid H_1 \mid 1 >$. You should find

$$< 2 \mid H_1 \mid 1 > = \int_0^a \psi_2^*(x) \ \ V_0 \ \ \psi_1(x) \ dx,$$

so

$$< 2 \mid H_1 \mid 1 > = \int_0^{a/2} \sqrt{\frac{2}{a}} \ \sin\left(\frac{2\pi x}{a}\right) \ \ V_0 \ \ \sqrt{\frac{2}{a}} \ \sin\left(\frac{\pi x}{a}\right) \ dx.$$

(c) Do the integral in part b. You should find

$$< 2 \mid H_1 \mid 1 > = \frac{2 \ V_0}{a} \left[\frac{\sin\left(\pi x/a\right)}{2(\pi/a)} \ - \ \frac{\sin\left(3\pi x/a\right)}{2(3\pi/a)} \right]_{x=0}^{x=\frac{a}{2}} \ = \ \frac{4 \ V_0}{3 \ \pi}.$$

(d) Combine your computed matrix element squared with your sinc function to obtain the trantion probability $P(\ 1 \ \to \ 2 \ )$. You should obtain

$$P(\ 1 \ \to \ 2 \ ) \ = \ \left[\frac{16 \ m \ a^2 \ V_0}{9 \ \pi^3 \ \hbar^2} \ \sin\left(\frac{3 \ \pi^2 \ \hbar \ T}{4 \ m \ a^2} \right) \right]^2.$$

(e) Plot $P(\ 1 \ \to \ 2 \ )$ *versus* time and explain physically why the probability of finding the particle in the $n = 2$ state oscillates in time.

5.(a) For an infinite square well of width a which is unperturbed, we have

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

So, for a transition from the $n = 2$ first excited state to the $n = 1$ ground state, the energy difference is given by

$$\boxed{E_2 - E_1 = (2^2 - 1^2)\frac{\pi^2\hbar^2}{2ma^2} = \frac{3\pi^2\hbar^2}{2ma^2}.}$$

5.(b) The wave functions for the unperturbed, infinite square well when the left edge is defined as zero are given by

$$\psi_n = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

$$\Rightarrow \quad \psi_1 = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right), \qquad \psi_2 = \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right).$$

If at time $t = 0$ the well is perturbed, the potential becomes

$$V(x) = \begin{cases} V_0, & \text{if } 0 \le x \le a/2, \\ 0, & \text{if } a/2 \le x \le a, \\ \infty & \text{otherwise.} \end{cases}$$

For $V_0 << E_1$, we obtain

$$H = H_0 + H_1 \qquad \text{where} \qquad H_1 = V_0$$

$$\Rightarrow \quad <2|\, H_1\, |1> \; = \int_0^a \psi_2^*\, V_0\, \psi_1\, dx$$

$$= \int_0^{a/2} \psi_2^*\, V_0\, \psi_1\, dx + \int_{a/2}^a \psi_2^*\,(0)\,\psi_1\, dx.$$

The second integral is zero because the potential is zero in that region, so we find

$$\boxed{<2|\, H_1\, |1> \; = \int_0^{a/2} \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)\, V_0 \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)\, dx.}$$

5.(c) Let's evaluate this integral

$$\begin{aligned}
<2|\, H_1 \,|1> &= \frac{2V_0}{a} \int_0^{a/2} \sin\left(\frac{2\pi x}{a}\right) V_0 \sin\left(\frac{\pi x}{a}\right) dx \\
&= \frac{2V_0}{a} \left[\frac{\sin\left[(2\pi/a - \pi/a)\, x\right]}{2\,(2\pi/a - \pi/a)} - \frac{\sin\left[(2\pi/a + \pi/a)\, x\right]}{2\,(2\pi/a + \pi/a)} \right]_0^{a/2} \\
&= \frac{V_0}{a} \left[\frac{\sin\left[(\pi/a)\, x\right]}{(\pi/a)} - \frac{\sin\left[(3\pi/a)\, x\right]}{(3\pi/a)} \right]_0^{a/2} \\
&= \frac{V_0}{3\pi} \Big[3 \sin\left[(\pi/a)\, x\right] - \sin\left[(3\pi/a)\, x\right] \Big]_0^{a/2} \\
&= \frac{V_0}{3\pi} \left[3 \sin(\pi/2) - 0 - \sin(3\pi/2) + 0 \right] \\
&= \frac{V_0}{3\pi} \left[3\,(1) - (-1) \right]
\end{aligned}$$

$$\Rightarrow \quad <2|\, H_1 \,|1> = \frac{4V_0}{3\pi}.$$

5.(d) Using Fermi's First Golden Rule, we find

$$P(i \to f) = 4 \left| <f|\, H_1 \,|i> \right|^2 \frac{\sin^2\left((E_f - E_i)t/2\hbar\right)}{(E_f - E_i)^2},$$

$$\begin{aligned}
\Rightarrow \quad P(1 \to 2) &= 4 \left| \frac{4V_0}{3\pi} \right|^2 \frac{\sin^2\left(\frac{3\pi^2\hbar^2}{2ma^2} \frac{t}{2\hbar}\right)}{\left(\frac{3\pi^2\hbar^2}{2ma^2}\right)^2} \\
&= 2^2 \left(\frac{4V_0}{3\pi}\right)^2 \left(\frac{2ma^2}{3\pi^2\hbar^2}\right)^2 \sin^2\left(\frac{3\pi^2\hbar^2}{2ma^2} \frac{t}{2\hbar}\right)
\end{aligned}$$

$$\Rightarrow \quad P(i \to f) = \left[\frac{16ma^2V_0}{9\pi^3\hbar^2} \sin\left(\frac{3\pi^2\hbar t}{4ma^2}\right) \right]^2.$$

5.(e) The last result can be rewritten as

$$P(i \to f) = \left[\frac{16ma^2V_0}{9\pi^3\hbar^2} \right]^2 \sin^2\left(\frac{3\pi^2\hbar t}{4ma^2}\right).$$

It is clear that as a function of time this is a sine squared function. Its maxima are equal to

$$\left[\frac{16ma^2V_0}{9\pi^3\hbar^2} \right]^2.$$

Its zeroes are located at

$$Kt = j\pi \quad \Rightarrow \quad t = \frac{j\pi}{K} = \frac{4ma^2}{3\pi^2\hbar} j\pi = \frac{4ma^2}{3\pi\hbar} j, \quad j = 0, 1, 2, 3, \ldots.$$

A graph of the probability versus time looks like this

The probability of finding the particle in the $n = 2$ state oscillates in time, or $P = P(t)$. This is because there are no stationary states for a system having a time dependent Hamiltonian. A general state will be a linear combination of all possible states, and the coefficients of the possible states are themselves changing in time. The probability of the system being in a given state, say $n = 2$, is proportional to the square of appropriate coefficient, here c_2, which is a function of time, $c_2 = c_2(t)$, given a time dependent Hamiltonian.
