**J15Q.2 (Solution by Jim Wu)**

A hydrogen atom located at $\vec{r} = 0$ is initially in the $2s$ state when an ion of charge $Q$ passes by it. Assume the ion moves with constant velocity $\vec{v} = v\hat{y}$ on a straight line whose closest approach to the hydrogen atom is $\vec{b} = b\hat{z}$, with $b > a_B$, where $a_B$ is the Bohr radius. While the ion passes by, the electron in the atom experiences a time-dependent potential

$$V_1(\vec{r}, t) = \frac{Qe}{|\vec{b} + \vec{v}t - \vec{r}|}$$

We are interested in calculating the transition probability to one of the $2p$ states. In this problem, you may assume that the $2s$ and $2p$ states are degenerate.

(a) Find an expansion of $V_1(\vec{r}, t)$ that is valid at all times and that is appropriate for calculating the transition probability in the limit $b \gg a_B$. Identify the leading term in this expansion that will give a non-vanishing amplitude between the $2s$ and at least one of the $2p$ states in first-order time-dependent perturbation theory.

(b) Use first-order time-dependent perturbation theory, calculate to leading order in $a_B/b$ the probability that the atom winds up in a $2p$ state.

**Solution:**

(a) According to first-order time-dependent perturbation theory, the probability amplitude for transitioning from initial state $i$ to final state $f$ after time $t$ is given by

$$a(t) = \delta_{fi} - \frac{i}{\hbar} \int_{-\infty}^{t} e^{i(E_f - E_i)t'} \langle f | V_1(t') | i \rangle \, dt'$$

The potential felt by the electron of the hydrogen atom due to the passing ion can be expanded via a multipole expansion in spherical harmonics:

$$\begin{aligned} V_1(\vec{r}, t) &= \frac{Qe}{|\vec{b} + \vec{v}t - \vec{r}|} \\ &= Qe \sum_{\ell=0}^{\infty} \frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} (-1)^m \frac{r_<^\ell}{r_>^{\ell+1}} Y_{\ell m}(\theta, \phi) Y^*_{\ell m}(\theta', \phi') \end{aligned}$$

where the coordinates of the position vectors are $\vec{r} = (r, \theta, \phi)$ and $\vec{R} = \vec{b} + \vec{b}t = (r', \theta', \phi')$, and $r_< = \min(r, R)$ and $r_> = \max(r, R)$. This can be derived from the multipole expansion using Legendre polynomials of $\cos\theta$ and then substituting the relation between Legendre polynomials and spherical harmonics.

In the approximation that $b \gg a_B$, then $R \gg r$ and so the potential can be approximated for all space as

$$V_1 = Qe \sum_{\ell=0}^{\infty} \frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} \frac{r^\ell}{R^{\ell+1}} Y_{\ell m}(\theta, \phi) Y^*_{\ell m}(\theta', \phi')$$

We will make a small error for large values of $r$ when we do the integral $\langle f|V_1|i\rangle$.

This is an advantageous expansion as the potential is expressed in terms of the symmetries of the hydrogen atoms and we can exploit the orthogonality of spherical harmonics:

$$\int d\Omega Y_{\ell,m} Y_{\ell',m'} = \delta_{\ell\ell'}\delta_{mm'}$$

If our initial state is the $2s$ orbital with $Y_{0,0} = \sqrt{\frac{1}{4\pi}}$, then the only term in the expansion that yields a non-zero probability of $2s \to 2p$ transition contains a $Y_{\ell m}(\theta,\phi)$ that matches that of the $2p$ orbital of interest.

(b) Recall the hydrogen wave functions for the $n=2$ state:

$$\phi_{2s} = \frac{1}{2\sqrt{2\pi a_B^3}}\left(1-\frac{r}{2a_B}\right)e^{-r/(2a_B)} = 2\left(\frac{1}{2a_B}\right)^{3/2}\left(1-\frac{r}{2a_B}\right)e^{-r/(2a_B)}Y_{0,0}(\theta,\phi) = \mathcal{R}_{2,0}Y_{0,0}$$

$$\phi_{2p,0} = \frac{z}{4\sqrt{2\pi a_B^5}}e^{-r/(2a_B)} = \frac{1}{\sqrt{3}}\left(\frac{1}{2a_B}\right)^{3/2}\frac{r}{a_B}e^{-r/(2a_B)}Y_{1,0}(\theta,\phi) = \mathcal{R}_{2,1}Y_{1,0}$$

$$\phi_{2p,\pm1} = \frac{x\pm iy}{8\sqrt{\pi a_B^5}}e^{-r/(2a_B)} = \frac{1}{\sqrt{3}}\left(\frac{1}{2a_B}\right)^{3/2}\frac{r}{a_B}e^{-r/(2a_B)}Y_{1,\pm1}(\theta,\phi) = \mathcal{R}_{2,1}Y_{1,\pm1}$$

where $\mathcal{R}_{n\ell}(r)$ are the radial wave functions of the hydrogen atom.

First, let's compute $\langle f|V_1|i\rangle$ for all three transitions of interest:

$$\begin{aligned}
\langle\phi_{2p,0}|V_1|\phi_{2s}\rangle &\approx \int \mathcal{R}_{2,1}^*(r)Y_{1,0}^*(\theta,\phi)\left((-1)^0\frac{4\pi Qer}{3R^2}Y_{1,0}(\theta,\phi)Y_{1,0}^*(\theta',\phi')\right)R_{2,0}Y_{0,0}r^2\sin\theta\, drd\theta d\phi \\
&= \frac{4\pi Qe}{3R^2\sqrt{4\pi}}Y_{1,0}^*(\theta',\phi')\int_0^\infty drR_{2,1}R_{2,0}r^3\int d\Omega\; Y_{1,0}^*(\theta,\phi)Y_{1,0}(\theta,\phi) \\
&= \frac{\sqrt{4\pi}Qe}{3R^2}\sqrt{\frac{3}{4\pi}}\cos\theta'\int_0^\infty\frac{2}{\sqrt{3}}\left(\frac{1}{2a_B}\right)^3\left(\frac{r}{a_B}-\frac{r^2}{2a_B^2}\right)r^3e^{-r/a_B}\,dr \\
&= \frac{Qe}{12R^2a_B^3}\cos\theta'\left[a_B^4\int_0^\infty u^4e^{-u}\,du - \frac{a_B^4}{2}\int_0^\infty u^5e^{-u}\,du\right] \\
&= \frac{Qea_B}{12R^2}\cos\theta'\left(4! - \frac{1}{2}(5!)\right) \\
&= \frac{3Qea_B}{R^2}\cos\theta' \\
\langle\phi_{2p,\pm1}|V_1|\phi_{2s}\rangle &\approx \int \mathcal{R}_{2,1}^*(r)Y_{1,\pm1}^*(\theta,\phi)\left((-1)^{\pm1}\frac{4\pi Qer}{3R^2}Y_{1,\pm1}(\theta,\phi)Y_{1,\pm1}^*(\theta,\phi)\right)\mathcal{R}_{2,0}Y_{0,0}(\theta,\phi)r^2\sin\theta\, drd\theta d\phi \\
&= -\frac{\sqrt{4\pi}Qe}{3R^2}Y_{1,\pm1}^*(\theta',\phi')\int drR_{2,1}R_{2,0}r^3\int d\Omega Y_{1,\pm1}^*(\theta,\phi)Y_{1,\pm1}(\theta,\phi) \\
&= -\frac{\sqrt{4\pi}Qe}{3R^2}\left(\mp\sqrt{\frac{3}{8\pi}}e^{\mp i\phi'}\sin\theta'\right)\left(-\frac{9a_B}{\sqrt{3}}\right) \\
&= \mp\frac{3Qea_B}{\sqrt{2}R^2}e^{\mp i\phi}\sin\theta'
\end{aligned}$$

The vector $\vec{R} = b\hat{\mathbf{z}} + vt\hat{\mathbf{y}}$ has magnitude $R = \sqrt{b^2 + v^2t^2}$ and the spherical angles are $\theta = \cos^{-1}\left(\frac{b}{R}\right) = \sin^{-1}\left(\frac{vt}{R}\right)$ and $\phi = \frac{\pi}{2}$. So,

$$\langle \phi_{2p,0}|V_1|\phi_{2s}\rangle = -\frac{3Qea_Bb}{(v^2t^2+b^2)^{3/2}} \qquad \langle \phi_{2p,\pm 1}|V_1|\phi_{2s}\rangle = \pm i\frac{3Qea_Bvt}{\sqrt{2}(v^2t^2+b^2)^{3/2}}$$

Now, since the $2s$ and $2p$ states are degenerate, then the probabilities of transitioning from $2s$ to one of the $2p$ states are

$$\begin{aligned}
P_{2s\to 2p,0}(t) \approx |a_{2s\to 2p,0}(t)|^2 &= \left|-\frac{i}{\hbar}\int_{-\infty}^{t}\frac{3Qea_Bb}{(v^2t^2+b^2)^{3/2}}\,dt\right|^2 \\
&= \left|\frac{i}{\hbar}\left(\frac{3Qea_Bb}{b^2}\left(\frac{t}{\sqrt{v^2t^2+b^2}}+\frac{1}{v}\right)\right|^2 \\
&= \frac{9Q^2e^2a_B^2}{\hbar^2b^2}\left(\frac{t}{\sqrt{v^2t^2+b^2}}+\frac{1}{v}\right)^2 \\
P_{2s\to 2p,\pm 1}(t) \approx |a_{2s\to 2p,\pm 1}(t)^2 &= \left|\pm\frac{1}{\hbar}\int_{-\infty}^{t}\frac{3Qea_Bvt}{\sqrt{2}(v^2t^2+b^2)^{3/2}}dt\right|^2 \\
&= \left|\mp\frac{1}{\hbar}\left(\frac{3Qea_B}{\sqrt{2}v\sqrt{v^2t^2+b^2}}\right)\right|^2 \\
&= \frac{9Q^2e^2a_B^2}{2\hbar^2v^2\left(v^2t^2+b^2\right)}
\end{aligned}$$

and the total probability to transition to any of the $2p$ states is

$$P(t) \approx \frac{9Q^2e^2a_B^2}{\hbar^2b^2}\left[\left(\frac{t}{\sqrt{v^2t^2+b^2}}+\frac{1}{v}\right)^2 + \frac{b^2}{2v^2(v^2t^2+b^2)}\right]$$

and as $t \to \infty$, we have

$$\boxed{P_{2s\to 2p} \approx \frac{36Q^2e^2a_B^2}{\hbar^2v^2b^2}}$$

Note that as $t \to \infty$, the probability of the atom transitioning to the $\phi_{2p,\pm 1}$ states is zero in our approximation. The full solution requires the full $V_1$ spherical harmonics expansion considering both $r < R$ and $r > R$. In this case, we would have two integrals for $\langle f|V_1|i|rangle$, the former from 0 to $R$ and the latter from $R$ to infinity. Of course, this would make integration much more difficult, especially once we have to compute the probability amplitudes for transitioning.

Let's check the limits! The probability decreases for increasing $b$ and $v$, which makes sense since the electron in the hydrogen atom barely "feels" the effect of a faraway ion and does not have enough time to respond to a fast moving ion. Furthermore, larger $Q$ implies a stronger potential and thus a higher probability of transitioning.

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