Physics 402
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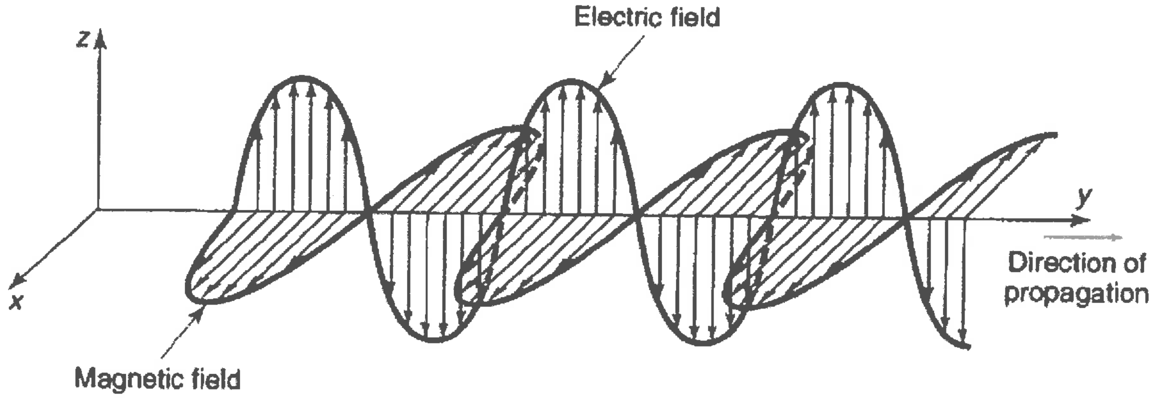
Discussion Worksheet

1. **Electric quadrupole matrix element selection rules**. Suppose we relax the constraint that the electric field is uniform over the size of an atom. By expanding the traveling wave (see Fig. below) electric field $\vec{E}(y,t) = E_0 \hat{z}\cos(ky - \omega t)$, find the potential experienced by the electron in the atom to next order of approximation ($ky << 1$). This is the electric quadrupole potential. Estimate how big the correction is relative to the original term for optical radiation. *Hint*: $\cos(A - B) = \cos(A)\cos(B) + \sin(A)\sin(B)$



$\vec{E}(y,t) = E_0 \hat{z} \cos(ky - \omega t)$ Travelling wave passing through the atom.

In the dipole approximation we assume that the electric field is uniform over the size of the atom. Essentially we assume $ky = 0$ so that $\vec{E}(t) = E_0 \hat{z} \cos(\omega t)$.

Use the suggested trigonometric expansion:

$$\vec{E}(y,t) = E_0 \hat{z}\left[\cos(ky)\cos(\omega t) + \sin(ky)\sin(\omega t)\right]$$

Keep terms to only first order in $ky << 1$.

$$\vec{E}(y,t) \simeq E_0 \hat{z}\left[1 \cos(\omega t) + ky \sin(\omega t)\right]$$

The interaction potential is

$$\mathcal{H}'(\vec{r},t) = -\int^{\vec{r}} \vec{F}\cdot d\vec{r} = -\int^{\vec{r}} q\vec{E}\cdot d\vec{r} = -q\int_0^z E_0\left[\cos(\omega t) + ky\sin(\omega t)\right]dz$$

$$= -qE_0\left[z\cos(\omega t) + kyz\sin(\omega t)\right]$$

Dipole approximation perturbing Hamiltonian

Quadrupole approximation perturbing Hamiltonian

2. What is the form of the quadrupole matrix element? For the hydrogen atom, what selection rules on changes in the quantum number m arise from this type of matrix element?

For the Hydrogen atom, the quadrupole matrix element will be of the form

$$|\langle n'l'm'| zy |nlm\rangle|^2$$

Recall that

$$x = r\sin\theta \cos\phi$$
$$y = r\sin\theta \sin\phi$$
$$z = r\cos\theta$$

As far as the ϕ-integral of the matrix element is concerned, we will get

from $y = r\sin\theta \sin\phi$

$$\langle n'l'm'|zy|nlm\rangle \propto \int_0^{2\pi} e^{-im'\phi} \sin\phi \, e^{im\phi} \, d\phi$$

$$= \int_0^{2\pi} \left[e^{-im'\phi} \frac{e^{i\phi} - e^{-i\phi}}{2i} e^{im\phi} \right] d\phi$$

$$= \frac{1}{2i} \int_0^{2\pi} \left[e^{i(m-m'+1)\phi} - e^{i(m-m'-1)\phi} \right] d\phi$$

$$= 0 \quad \text{unless} \quad m - m' \pm 1 = 0 \quad \text{or} \quad \Delta m = \pm 1$$

This is the same selection rule that we got in the dipole approximation.

However, for matrix elements like $\langle n'l'm'| xy |nlm\rangle$, which come from other polarization directions, one finds a selection rule of $\Delta m = \pm 2$.

Also note that $zy \sim r^2 \left(Y_2^1(\theta,\phi) - Y_2^{-1}(\theta,\phi) \right)$, and this leads to the selection rule $\Delta l = \pm 2$.