14.1: Time-Dependent Vector Potentials

The full N-electron non-relativistic Hamiltonian H discussed earlier in this text involves the kinetic energies of the electrons and of the nuclei and the mutual Coulombic interactions among these particles

$$H = \sum_{a=1,M} -\left(\frac{\hbar^2}{2m_a}\right)\nabla_a^2 + \sum_j \left[\left(-\frac{\hbar^2}{2m_e}\right)\nabla_j^2 - \sum_a Z_a \frac{e^2}{r_{j,a}}\right] + \sum_{j<k}\frac{e^2}{r_{j,k}} + \sum_{a<b} Z_a Z_b \frac{e^2}{R_{a,b}}.$$

When an electromagnetic field is present, this is not the correct Hamiltonian, but it can be modified straightforwardly to obtain the proper H.

The Time-Dependent Vector $\mathbf{A}(\mathbf{r},t)$ Potential

The only changes required to achieve the Hamiltonian that describes the same system in the presence of an electromagnetic field are to replace the momentum operators $\mathbf{P}_a$ and $\mathbf{p}_j$ for the nuclei and electrons, respectively, by (**P\(_a\) - Z_a e/c **A**(R_a,t)) and ($\mathbf{p}_j$ - e/c **A**(rj ,t)). Here Za e is the charge on the ath nucleus, -e is the charge of the electron, and c is the speed of light.

The vector potential **A** depends on time t and on the spatial location **r** of the particle in the following manner:

$$\mathbf{A}(\mathbf{r},t) = 2\mathbf{A}_0 cos(\omega t - \mathbf{k}\cdot\mathbf{r}).$$

The circular frequency of the radiation ω (radians per second) and the wave vector **k** (the magnitude of **k** is |**k**| = $\frac{2\pi}{\lambda}$, where λ is the wavelength of the light) control the temporal and spatial oscillations of the photons. The vector $\mathbf{A}_o$ characterizes the strength (through the magnitude of $\mathbf{A}_o$) of the field as well as the direction of the **A** potential; the direction of propagation of the photons is given by the unit vector **k**/|**k**|. The factor of 2 in the definition of **A** allows one to think of $\mathbf{A}_0$ as measuring the strength of both $e^{i(\omega t-\mathbf{k}\cdot\mathbf{r})}$ and $e^{i(\omega t-\mathbf{k}\cdot\mathbf{r})}$ components of the $cos(\omega t - \mathbf{k}\cdot\mathbf{r})$ function.

The Electric $\mathbf{E}(\mathbf{r},t)$ and Magnetic $\mathbf{H}(\mathbf{r},t)$ Fields

The electric $\mathbf{E}(\mathbf{r},t)$ and magnetic $\mathbf{H}(\mathbf{r}$,t) fields of the photons are expressed in terms of the vector potential **A** as

$$\mathbf{E}(\mathbf{r},t) = -\frac{1}{3}\frac{\partial \mathbf{A}}{\partial t} = \frac{\omega}{c}\mathbf{A}_0 \sin(\omega t - \mathbf{k}\cdot\mathbf{r})$$

$$\mathbf{H}(\mathbf{r},t) = \nabla\ \mathbf{x}\ \mathbf{A}\ =\ \mathbf{k}\ \mathbf{x}\ \mathbf{A}_o 2\sin(\omega t - \mathbf{k}\cdot\mathbf{r}).$$

The **E** field lies parallel to the $\mathbf{A}_o$ vector, and the **H** field is perpendicular to $\mathbf{A}_o$; both are perpendicular to the direction of propagation of the light **k**/|**k**|. **E** and **H** have the same phase because they both vary with time and spatial location as $\sin(\omega t - \mathbf{k}\cdot\mathbf{r})$. The relative orientations of these vectors are shown below.

Figure 14.1.1: Insert caption here!

The Resulting Hamiltonian

Replacing the nuclear and electronic momenta by the modifications shown above in the kinetic energy terms of the full electronic and nuclear-motion hamiltonian results in the following **additional** factors appearing in H:

$$H_{int} = \sum_j \left[\frac{ie\hbar}{m_e c}\mathbf{A}(r_j,t)\cdot\nabla_j + \left(\frac{e^2}{2m_e c^2}\right)|\mathbf{A}(r_j,t)|^2\right] +$$

$$\sum_a \left[\left(iZ_a\frac{e\hbar}{m_a c}\right)\mathbf{A}(R_a,t)\cdot\nabla_a + \left(\frac{Z_a^2 e^2}{2m_a c^2}\right)|\mathbf{A}(R_a,t)|^2\right].$$

These so-called interaction perturbations H_{int} are what induces transitions among the various electronic/vibrational/rotational states of a molecule. The one-electron additive nature of H_{int} plays an important role in determining the kind of transitions that H_{int} can induce. For example, it causes the most intense electronic transitions to involve excitation of a single electron from one orbital to another (e.g., the Slater-Condon rules).
