

7.3: Quantum Mechanical Electric Dipole Hamiltonian

Now we are in a position to substitute the quantum mechanical momentum for the classical momentum:

$$\bar{p} = -i\hbar\bar{\nabla} \quad (7.3.1)$$

Here the vector potential remains classical and only modulates the interaction strength:

$$V(t) = \frac{i\hbar}{2m} q(\bar{\nabla} \cdot \bar{A} + \bar{A} \cdot \bar{\nabla}) \quad (7.3.2)$$

We can show that $\bar{\nabla} \cdot \bar{A} = \bar{A} \cdot \bar{\nabla}$. For instance, if we are operating on a wavefunction on the right, we can use the chain rule to write $\bar{\nabla} \cdot (\bar{A}|\psi\rangle) = (\bar{\nabla} \cdot \bar{A})|\psi\rangle + \bar{A} \cdot (\bar{\nabla}|\psi\rangle)$. The first term is zero since we are working in the Coulomb gauge ($\bar{\nabla} \cdot \bar{A} = 0$). Now we have

$$V(t) = \frac{i\hbar q}{m} \bar{A} \cdot \bar{\nabla} \quad (7.3.3)$$

$$= -\frac{q}{m} \bar{A} \cdot \hat{p} \quad (7.3.4)$$

We can generalize Equation 7.3.4 for the case of multiple charged particles, as would be appropriate for interactions involving a molecular Hamiltonian:

$$V(t) = -\sum_j \frac{q_j}{m_j} \bar{A}(\bar{r}_j, t) \cdot \hat{p}_j \quad (7.3.5)$$

$$= -\sum_j \frac{q_j}{m_j} \left[A_0 \hat{\varepsilon} \cdot \hat{p}_j e^{i(\bar{k} \cdot \bar{r}_j - \omega t)} + A_0^* \hat{\varepsilon} \cdot \hat{p}_j^\dagger e^{-i(\bar{k} \cdot \bar{r}_j - \omega t)} \right] \quad (7.3.6)$$

Under most of the circumstances we will encounter, we can neglect the wave vector dependence of the interaction potential. This applies if the wavelength of the field is much larger than the dimensions of the molecules we are interrogating, i.e., ($\lambda \rightarrow \infty$) and $|k| \rightarrow 0$). To see this, let's define r_o as the center of mass of a molecule and expand about that position:

$$e^{i\bar{k} \cdot \bar{r}_i} = e^{i\bar{k} \cdot \bar{r}_0} e^{i\bar{k} \cdot (\bar{r}_i - \bar{r}_0)} \quad (7.3.7)$$

$$= e^{i\bar{k} \cdot \bar{r}_0} e^{i\bar{k} \cdot \delta \bar{r}_i} \quad (7.3.8)$$

For interactions with UV, visible, and infrared radiation, wavelengths are measured in hundreds to thousands of nanometers. This is orders of magnitude larger than the dimensions that describe charge distributions in molecules ($\delta \bar{r}_i = \bar{r}_i - \bar{r}_0$). Under those circumstances $|k|\delta r \ll 1$, and setting $\bar{r}_0 = 0$ means that $e^{i\bar{k} \cdot \bar{r}} \rightarrow 1$. This is known as the **electric dipole approximation**. Implicit in this is also the statement that all molecules within a macroscopic volume experience an interaction with a spatially uniform, homogeneous electromagnetic field.

Certainly there are circumstances where the electric dipole approximation is poor. In the case where the wavelength of light is on the same scale as molecular dimensions, the light will now have to interact with spatially varying charge distributions, which will lead to scattering of the light and interferences between the scattering between different spatial regions. We will not concern ourselves with this limit further. We also retain the spatial dependence for certain other types of light-matter interactions. For instance, we can expand Equation 7.3.8 as

$$e^{i\bar{k} \cdot \bar{r}_i} \approx e^{i\bar{k} \cdot \bar{r}_0} \left[1 + i\bar{k} \cdot (\bar{r}_i - \bar{r}_0) + \dots \right] \quad (7.3.9)$$

We retain the second term for quadrupole transitions: charge distribution interacting with gradient of electric field and magnetic dipole (Section 6.7).

Now, using $A_0 = iE_0/2\omega$, we write Equation 7.3.4 as

$$V(t) = \frac{-iqE_0}{2m\omega} [\hat{\varepsilon} \cdot \hat{p} e^{-i\omega t} - \hat{\varepsilon} \cdot \hat{p} e^{i\omega t}] \quad (7.3.10)$$

$$= \frac{-qE_0}{m\omega} (\hat{\varepsilon} \cdot \hat{p}) \sin \omega t \quad (7.3.11)$$

$$= \frac{-q}{m\omega} (\bar{E}(t) \cdot \hat{p}) \quad (7.3.12)$$

or for a collection of charged particles (molecules):

$$V(t) = - \left(\sum_j \frac{q_j}{m_j} (\hat{\varepsilon} \cdot \hat{p}_j) \right) \frac{E_0}{\omega} \sin \omega t \quad (7.3.13)$$

This is the interaction Hamiltonian in the electric dipole approximation.

In Equation 7.3.9, the second term must be considered in certain cases, where variation in the vector potential over the distance scales of the molecule must be considered. This will be the case when one describes interactions with short wavelength radiation, such as x-rays. Then the scattering of radiation by electronic states of molecules and the interference between transmitted and scattered field are important. The second term is also retained for electric quadrupole transitions and magnetic dipole transitions, as described in the appendix in Section 6.7. Electric quadrupole transitions require a gradient of electric field across the molecule, and is generally an effect that is $\sim 10^{-3}$ of the electric dipole interaction.

Transition Dipole Matrix Elements

We are seeking to use this Hamiltonian to evaluate the transition rates induced by $V(t)$ from our first-order perturbation theory expression. For a perturbation

$$V(t) = V_0 \sin \omega t \quad (7.3.14)$$

the rate of transitions induced by field is

$$w_{k\ell} = \frac{\pi}{2\hbar} |V_{k\ell}|^2 [\delta(E_k - E_\ell - \hbar\omega) + \delta(E_k - E_\ell + \hbar\omega)] \quad (7.3.15)$$

which depends on the matrix elements for the Hamiltonian in Equation 7.3.13. Note in first-order perturbation matrix element calculations one uses unperturbed wavefunctions. Thus, we evaluate the matrix elements of the electric dipole Hamiltonian using the eigenfunctions of H_0 :

$$V_{k\ell} = \langle k | V_0 | \ell \rangle = \frac{-qE_0}{m\omega} \langle k | \hat{\varepsilon} \cdot \hat{p} | \ell \rangle \quad (7.3.16)$$

We can evaluate $\langle k | \hat{p} | \ell \rangle$ using an expression that holds for any one-particle Hamiltonian:

$$[\hat{r}, \hat{H}_0] = \frac{i\hbar\hat{p}}{m} \quad (7.3.17)$$

This expression gives

$$\langle k | \hat{p} | \ell \rangle = \frac{m}{i\hbar} \langle k | \hat{r} \hat{H}_0 - \hat{H}_0 \hat{r} | \ell \rangle \quad (7.3.18)$$

$$= \frac{m}{i\hbar} (\langle k | \hat{r} | \ell \rangle E_\ell - E_k \langle k | \hat{r} | \ell \rangle) \quad (7.3.19)$$

$$= im\omega_{k\ell} \langle k | \hat{r} | \ell \rangle \quad (7.3.20)$$

So we have

$$V_{k\ell} = -iqE_0 \frac{\omega_{k\ell}}{\omega} \langle k | \hat{\varepsilon} \cdot \hat{r} | \ell \rangle \quad (7.3.21)$$

or for many charged particles

$$V_{k\ell} = -iE_0 \frac{\omega_{k\ell}}{\omega} \left\langle k \left| \hat{\varepsilon} \cdot \sum_j q_j \hat{r}_j \right| \ell \right\rangle \quad (7.3.22)$$

The matrix element can be written in terms of the dipole operators, which describes the spatial distribution of charges,

$$\hat{\mu} = \sum_j q_j \hat{r}_j \quad (7.3.23)$$

We can see that it is the quantum analog of the classical dipole moment, which describes the distribution of charge density ρ in the molecule:

$$\bar{\mu} = \int d\vec{r} \vec{r} \rho(\vec{r}) \quad (7.3.24)$$

The strength of interaction between light and matter is given by the matrix element in the dipole operator,

$$\mu_{fi} \equiv \langle f | \bar{\mu} \cdot \hat{\epsilon} | i \rangle \quad (7.3.25)$$

which is known as the transition dipole moment. In order that we have absorption, the part $\langle f | \mu | i \rangle$, which is a measure of change of charge distribution between $|f\rangle$ and $|i\rangle$, should be non-zero. In other words, the incident radiation has to induce a change in the charge distribution of matter to get an effective absorption rate. This matrix element is the basis of selection rules based on the symmetry of the matter charge eigenstates. The second part, namely the electric field polarization vector says that the electric field of the incident radiation field must project onto the matrix elements of the dipole moment between the final and initial states of the charge distribution.

Then the matrix elements in the electric dipole Hamiltonian are

$$V_{k\ell} = -iE_0 \frac{\omega_{k\ell}}{\omega} \mu_{kl} \quad (7.3.26)$$

This expression allows us to write in a simplified form the well-known interaction potential for a dipole in a field:

$$V(t) = -\bar{\mu} \cdot \bar{E}(t) \quad (7.3.27)$$

Note that we have reversed the order of terms because they commute. This leads to an expression for the rate of transitions between quantum states induced by the light field:

$$w_{k\ell} = \frac{\pi}{2\hbar} |E_0|^2 \frac{\omega_{k\ell}^2}{\omega^2} |\bar{\mu}_{kl}|^2 [\delta(E_k - E_\ell - \hbar\omega) + \delta(E_k - E_\ell + \hbar\omega)] \quad (7.3.28)$$

$$= \frac{\pi}{2\hbar^2} |E_0|^2 |\bar{\mu}_{kl}|^2 [\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega)] \quad (7.3.29)$$

In essence, Equation 7.3.29 is an expression for the absorption and emission spectrum since the rate of transitions can be related to the power absorbed from or added to the light field. More generally, we would express the spectrum in terms of a sum over all possible initial and final states, the eigenstates of H_0 :

$$w_{fi} = \sum_{i,f} \frac{\pi}{\hbar^2} |E_0|^2 |\mu_{fi}|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega)] \quad (7.3.30)$$

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