14.2: Time-Dependent Perturbation Theory

The mathematical machinery needed to compute the rates of transitions among molecular states induced by such a time-dependent perturbation is contained in time dependent perturbation theory (TDPT). The development of this theory proceeds as follows. One first assumes that one has in-hand **all** of the eigenfunctions $\{\Phi_k\}$ and eigenvalues $\{E_k^0\}$ that characterize the Hamiltonian H^0 of the molecule in the absence of the external perturbation:

$$H^0\Phi_k = E_k^0\Phi_k.$$

One then writes the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = (H^0 + H_{int})\Psi$$

in which the full Hamiltonian is explicitly divided into a part that governs the system in the absence of the radiation field and H_{int} which describes the interaction with the field.

Perturbative Solution

By treating H^0 as of zeroth order (in the field strength $|\mathbf{A}_0|$), expanding Ψ order-by order in the field-strength parameter:

$$\Psi = \Psi^0 + \Psi^1 + \Psi^2 + \Psi^3 + \dots,$$

realizing that Hint contains terms that are both first- and second- order in $|\mathbf{A}_0|$

$$H_{int}^1 = \sum_j\left[\left(\frac{ie\hbar}{m_e c}\right)\mathbf{A}(r_j,t)\cdot\nabla_j\right] + \sum_a\sum_a\left[\left(\frac{iZ_a e\hbar}{m_a c}\right)\mathbf{A}(R_a,t)\cdot\nabla_a\right],$$

$$H_{int}^2 = \sum_j\left[\left(\frac{e^2}{2m_e c^2}\right)|\mathbf{A}(r_j,t)|^2\right] + \sum_a\left[\left(\frac{Z_a^2 e^2}{2m_a c^2}\right)|\mathbf{A}(R_a,t)|^2\right],$$

and then collecting together all terms of like power of $|\mathbf{A}_0|$, one obtains the set of time dependent perturbation theory equations. The lowest order such equations read:

$$i\hbar\frac{\partial\Psi^0}{\partial t} = H^0\Psi^0$$

$$i\hbar\frac{\partial\Psi^1}{\partial t} = (H^0\Psi^1 + H_{int}^1\Psi^0)$$

$$i\hbar\frac{\partial\Psi^2}{\partial t} = (H^0\Psi^2 + H_{int}^2\Psi^0 + H_{int}^1\Psi^1).$$

The zeroth order equations can easily be solved because H^0 is independent of time. Assuming that at $t = -\infty$, $\Psi = \psi_i$ (we use the index i to denote the initial state), this solution is:

$$\Psi^0 = \Phi_i e^{\frac{-iE_i^0 t}{\hbar}}.$$

The first-order correction to Ψ^0, Ψ^1 can be found by (i) expanding Ψ^1 in the complete set of zeroth-order states $\{\Phi_f\}$:

$$\Psi^1 = \sum_f \Phi_f <\Phi_f|\Psi^1> = \sum_f \Phi_f C_f^1,$$

(ii) using the fact that

$$H^0\Phi_f = E_f^0\Phi_f$$

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and (iii) substituting all of this into the equation that Y1 obeys. The resultant equation for the coefficients that appear in the first-order equation can be written as

$$i\hbar\frac{\partial C_f^1}{\partial t} = \sum_k [E_k^0 C_k^1 \delta_{f,k}] + <\Phi_f|H_{int}^1|\Phi_i> e^{\frac{-iE_i^0 t}{\hbar}},$$

or

$$i\hbar\frac{\partial C_f^1}{\partial t} = E_f^0 C_f^1 + <\Phi_f|H_{int}^1|\Phi_i> e^{\frac{-iE_i^0 t}{\hbar}}.$$

Defining

$$C_f^1(t) = D_f^1(t) e^{\frac{-iE_f^0 t}{\hbar}}.$$

his equation can be cast in terms of an easy-to-solve equation for the D_f^1 coefficients:

$$i\hbar\frac{\partial D_f^1}{\partial t} = <\Phi_f|H_{int}^1|\Phi_i> e^{\frac{i[E_f^0 - E_i^0]t}{\hbar}}.$$

Assuming that the electromagnetic field $\mathbf{A}(\mathbf{r}, t)$ is turned on at t=0, and remains on until t = T, this equation for D_f^1 can be integrated to yield:

$$D_f^1(t) = \frac{1}{(i\hbar)}\int_0^T <\Phi_f|H_{int}^1|\Phi_i> e^{\frac{i[E_f^0 - E_i^0]t'}{\hbar}} dt'.$$