Atomic transitions 1

Let $\Psi(\mathbf{r},t)$ be the following linear combination of two wave functions where $c_a(t)$ and $c_b(t)$ are dimensionless time-dependent coefficients such that $|c_a(t)|^2 + |c_b(t)|^2 = 1$.

$$\Psi(\mathbf{r},t) = c_a(t)\psi_a(\mathbf{r})\exp\left(-\tfrac{i}{\hbar}E_a t\right) + c_b(t)\psi_b(\mathbf{r})\exp\left(-\tfrac{i}{\hbar}E_b t\right)$$

Let the Hamiltonian be

$$H(\mathbf{r},t) = H_0(\mathbf{r}) + H_1(\mathbf{r},t)$$

where

$$H_0\psi_a = E_a\psi_a, \quad H_0\psi_b = E_b\psi_b$$

We want to find solutions for $c_a(t)$ and $c_b(t)$. Start with the Schrödinger equation.

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

Evaluate the left side of the Schrödinger equation.

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\Psi = {} & \overbrace{E_a c_a(t)\psi_a(\mathbf{r})\exp\left(-\tfrac{i}{\hbar}E_a t\right) + E_b c_b(t)\psi_b(\mathbf{r})\exp\left(-\tfrac{i}{\hbar}E_b t\right)}^{\text{cancels with other side of Schrödinger equation}} \\ & + i\hbar\frac{dc_a(t)}{dt}\psi_a(\mathbf{r})\exp\left(-\tfrac{i}{\hbar}E_a t\right) + i\hbar\frac{dc_b(t)}{dt}\psi_b(\mathbf{r})\exp\left(-\tfrac{i}{\hbar}E_b t\right) \end{aligned}$$

Evaluate the right side of the Schrödinger equation.

$$H\Psi = \overbrace{E_a c_a(t)\psi_a(\mathbf{r})\exp\left(-\tfrac{i}{\hbar}E_a t\right) + E_b c_b(t)\psi_b(\mathbf{r})\exp\left(-\tfrac{i}{\hbar}E_b t\right)}^{\text{cancels with other side of Schrödinger equation}} + H_1\Psi$$

After cancellations

$$i\hbar\frac{dc_a(t)}{dt}\psi_a(\mathbf{r})\exp\left(-\tfrac{i}{\hbar}E_a t\right) + i\hbar\frac{dc_b(t)}{dt}\psi_b(\mathbf{r})\exp\left(-\tfrac{i}{\hbar}E_b t\right) = H_1\Psi \tag{1}$$

Evaluate the inner product of ψ_a and equation (1) to obtain

$$\begin{aligned} i\hbar\frac{dc_a(t)}{dt}\exp\left(-\tfrac{i}{\hbar}E_a t\right) &= \langle\psi_a|H_1|\Psi\rangle \\ &= c_a(t)\langle\psi_a|H_1|\psi_a\rangle\exp\left(-\tfrac{i}{\hbar}E_a t\right) + c_b(t)\langle\psi_a|H_1|\psi_b\rangle\exp\left(-\tfrac{i}{\hbar}E_b t\right) \end{aligned} \tag{2}$$

Evaluate the inner product of ψ_b and equation (1) to obtain

$$\begin{aligned} i\hbar\frac{dc_b(t)}{dt}\exp\left(-\tfrac{i}{\hbar}E_b t\right) &= \langle\psi_b|H_1|\Psi\rangle \\ &= c_a(t)\langle\psi_b|H_1|\psi_a\rangle\exp\left(-\tfrac{i}{\hbar}E_a t\right) + c_b(t)\langle\psi_b|H_1|\psi_b\rangle\exp\left(-\tfrac{i}{\hbar}E_b t\right) \end{aligned} \tag{3}$$

Let it be the case that the following amplitudes vanish.

$$\langle\psi_a|H_1|\psi_a\rangle = 0, \quad \langle\psi_b|H_1|\psi_b\rangle = 0$$

Then equations (2) and (3) simplify as

$$i\hbar\frac{dc_a(t)}{dt}\exp\left(-\tfrac{i}{\hbar}E_a t\right) = c_b(t)\langle\psi_a|H_1|\psi_b\rangle\exp\left(-\tfrac{i}{\hbar}E_b t\right) \tag{4}$$

$$i\hbar\frac{dc_b(t)}{dt}\exp\left(-\tfrac{i}{\hbar}E_b t\right) = c_a(t)\langle\psi_b|H_1|\psi_a\rangle\exp\left(-\tfrac{i}{\hbar}E_a t\right) \tag{5}$$

Let $E_b > E_a$ and let

$$\omega_0 = \frac{E_b - E_a}{\hbar}$$

Rewrite equations (4) and (5) as

$$\begin{aligned}
\frac{d}{dt}c_a(t) &= -\frac{i}{\hbar}c_b(t)\langle\psi_a|H_1|\psi_b\rangle\exp(-i\omega_0 t)\\
\frac{d}{dt}c_b(t) &= -\frac{i}{\hbar}c_a(t)\langle\psi_b|H_1|\psi_a\rangle\exp(i\omega_0 t)
\end{aligned}$$

Let the initial conditions be $c_a(0) = 1$ and $c_b(0) = 0$. It was shown in "Perturbation example" that the first-order perturbation solutions are

$$\begin{aligned}
c_a(t) &= 1\\
c_b(t) &= -\frac{i}{\hbar}\int_0^t \langle\psi_b|H_1(\mathbf{r},t')|\psi_a\rangle\exp(i\omega_0 t')\,dt'
\end{aligned}$$

The integral is not as bad as it looks because $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ are independent of time t. For $H_1(\mathbf{r},t)$ representing an electric plane wave, the integrand reduces to a simple exponential of t' which is easily solved.