Atomic transitions 1

Let $\Psi(\mathbf{r},t)$ be the following linear combination of two atomic states.

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

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.

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\Psi = {} & \overbrace{E_a\psi_a(\mathbf{r})c_a(t)\exp\left(-\tfrac{i}{\hbar}E_a t\right) + E_b\psi_b(\mathbf{r})c_b(t)\exp\left(-\tfrac{i}{\hbar}E_b t\right)}^{\text{cancels with right side}} \\ & + i\hbar\psi_a(\mathbf{r})\dot{c}_a(t)\exp\left(-\tfrac{i}{\hbar}E_a t\right) + i\hbar\psi_b(\mathbf{r})\dot{c}_b(t)\exp\left(-\tfrac{i}{\hbar}E_b t\right) \end{aligned}$$

Evaluate the right side of the Schrödinger equation.

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

After cancellations

$$i\hbar\psi_a(\mathbf{r})\dot{c}_a(t)\exp\left(-\tfrac{i}{\hbar}E_a t\right) + i\hbar\psi_b(\mathbf{r})\dot{c}_b(t)\exp\left(-\tfrac{i}{\hbar}E_b t\right) = H_1\Psi \tag{1}$$

Take the inner product of (1) with ψ_a to obtain

$$i\hbar\dot{c}_a(t)\exp\left(-\tfrac{i}{\hbar}E_a t\right) = \langle\psi_a|H_1|\psi_a\rangle c_a(t)\exp\left(-\tfrac{i}{\hbar}E_a t\right) + \langle\psi_a|H_1|\psi_b\rangle c_b(t)\exp\left(-\tfrac{i}{\hbar}E_b t\right) \tag{2}$$

Take the inner product of (1) with ψ_b to obtain

$$i\hbar\dot{c}_b(t)\exp\left(-\tfrac{i}{\hbar}E_b t\right) = \langle\psi_b|H_1|\psi_a\rangle c_a(t)\exp\left(-\tfrac{i}{\hbar}E_a t\right) + \langle\psi_b|H_1|\psi_b\rangle c_b(t)\exp\left(-\tfrac{i}{\hbar}E_b t\right) \tag{3}$$

Let it be the case that diagonal elements vanish, that is,

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

Then (2) and (3) simplify as

$$\begin{aligned} i\hbar\dot{c}_a(t)\exp\left(-\tfrac{i}{\hbar}E_a t\right) &= \langle\psi_a|H_1|\psi_b\rangle c_b(t)\exp\left(-\tfrac{i}{\hbar}E_b t\right) \\ i\hbar\dot{c}_b(t)\exp\left(-\tfrac{i}{\hbar}E_b t\right) &= \langle\psi_b|H_1|\psi_a\rangle c_a(t)\exp\left(-\tfrac{i}{\hbar}E_a t\right) \end{aligned} \tag{4}$$

Let $E_b > E_a$ and let

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

Rewrite (4) as

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

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

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