

Atomic transitions 1

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

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

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.

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

Evaluate the right side of the Schrödinger equation.

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

After cancellations

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

Take the inner product ψ_a and equation (1) to obtain

$$\begin{aligned} i\hbar\dot{c}_a(t) \exp\left(-\frac{i}{\hbar}E_a t\right) \\ = \langle\psi_a|H_1|\Psi\rangle = \langle\psi_a|H_1|\psi_a\rangle c_a(t) \exp\left(-\frac{i}{\hbar}E_a t\right) + \langle\psi_a|H_1|\psi_b\rangle c_b(t) \exp\left(-\frac{i}{\hbar}E_b t\right) \end{aligned} \quad (2)$$

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

$$\begin{aligned} i\hbar\dot{c}_b(t) \exp\left(-\frac{i}{\hbar}E_b t\right) \\ = \langle\psi_b|H_1|\Psi\rangle = \langle\psi_b|H_1|\psi_a\rangle c_a(t) \exp\left(-\frac{i}{\hbar}E_a t\right) + \langle\psi_b|H_1|\psi_b\rangle c_b(t) \exp\left(-\frac{i}{\hbar}E_b t\right) \end{aligned} \quad (3)$$

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

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

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

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