4.9: The Quantum Jump

Quantum Jumps for an Electron in a One-dimensional Box

The phrases "quantum jump" and "quantum leap" are used in everyday discourse. This disguises the fact that scientists have always been somewhat troubled by the nature of the process by which a quantum system passes from one allowed energy state to another. McMillin [J. Chem. Ed. 55, 7 (1978)] has described an appealing model for "quantum jumps" that is referred to as the fluctuating dipole mechanism. This mechanism will be illustrated by considering spectroscopic transitions for an electron in a one-dimensional box of length a_o. Since only a brief outline of the mechanism can be provided here, please consult this reference for a thorough presentation of the theoretical background.

In order for an electron in a one-dimensional box to undergo a transition from one allowed energy state to another under the influence of electromagnetic radiation two criteria must be met according to the mechanism described by McMillin. First, the photons of the electromagnetic field must satisfy the Bohr frequency condition and have an energy which equals the difference in energy between the two states under consideration. Second, there must be a dipolar coupling between the electromagnetic field and the oscillating electron density in the box. This later criterion is, of course, the selection rule for the transition.

According to this model, when an electron in a box is subjected to a perturbation such as electromagnetic radiation, the electron responds by going into a state which is a linear superposition of the unperturbed states.

$$\Psi(x,\ t) = \sum_i \psi_i \exp\left(-\frac{iEt}{\hbar}\right)$$

If the square modulus, $\Psi(x,t)^*\Psi(x,t)$, of the time-dependent wavefunction associated with this linear superposition exhibits an asymmetric fluctuating charge density (an oscillating dipole moment) in the box, a coupling with the dipolar character of the electromagnetic field exists and a transition can occur. If the linear combination of states leads to a symmetric fluctuating charge density there is no coupling between the field and the electron density in the box and a transition is not possible.

The model is illustrated below first for the n = 1 to n = 2 allowed transition for the electron in a one- dimensional box. Note that for the 1 ---> 2 transition, shown immediately below, the electron density does oscillates from one side of the box to the other satisfying the mechanism's criterion for coupling with the external electromagnetic field.

The n = 1 to n = 2 Transition for the Particle in a Box is Allowed

In the space immediately below the wavefunction for the linear superposition of states is calculated and $\Psi^*\Psi$ is plotted to demonstrate that the 1 ---> 2 transition is allowed.

Initial and final energy states for the transition under study

$$n_i = 1 \quad n_f = 2 \quad E_i = \frac{n_i^2 \pi^2}{2} \quad E_f = \frac{n_f^2 \pi^2}{2}$$

Plot the wavefunction:

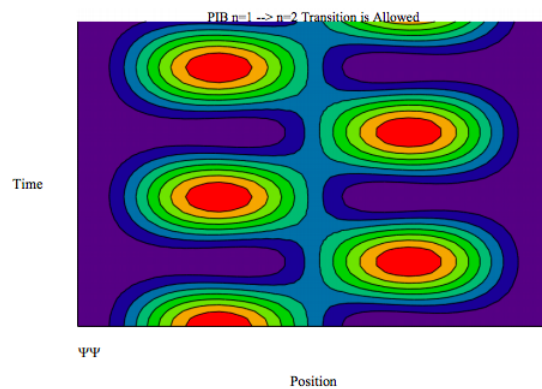$$j = 0..40 \quad x_j = \frac{j}{40} \quad k = 0..40 \quad t_k = \frac{k}{40}$$

Linear combination of ground state and excited states:

$$\Psi(x,\ t) = \sin(n_i \pi x) exp(-iE_i t) + \sin(n_f \pi x) exp(-iE_f t)$$

Calculate and plot $\Psi^*\Psi$:

$$\Psi\Psi_{(j,\ k)} = \overline{\Psi(x_j,\ t_k)}\,\Psi(x_j,\ t_k)$$

In this contour plot the horizontal axis is the spatial axis and time is graphed on the vertical axis.

PIB n=1 --> n=2 Transition is Allowed

Time

ΨΨ

Position

The n = 1 to n = 3 Transition for the Particle in a Box is Forbidden

However, for the 1 ---> 3 transition the electron density fluctuates symmetrically about the center of the box, and, therefore does not provide a mechanism for coupling with the external electromagnetic field.

Initial and final energy states for the transition under study

$$n_i = 1 \quad n_f = 3 \quad E_i = \frac{n_i^2 \pi^2}{2} \quad E_f = \frac{n_f^2 \pi^2}{2}$$
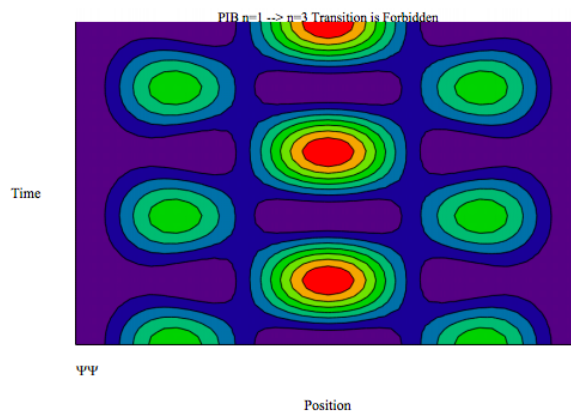
Plot the wavefunction:

$$j = 0 \,.\,.\, 40 \quad x_j = \frac{j}{40} \quad k = 0 \,.\,.\, 40 \quad t_k = 4\frac{k}{40}$$

Linear combination of ground state and excited states:

$$\Psi(x,\,t) = \sin(n_i \pi x) exp(-iE_i t) + \sin(n_f \pi x) exp(-iE_f t)$$

Calculate and plot Ψ*Ψ:

$$\Psi\Psi_{(j,\,k)} = \overline{\Psi(x_j,\,t_k)}\,\Psi(x_j,\,t_k)$$

PIB n=1 --> n=3 Transition is Forbidden

Time

ΨΨ

Position