

The Einstein A and B Coefficients

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Abstract

In this paper, the Einstein A and B coefficients and their historical derivation are reviewed. In addition, time-dependent perturbation theory is used as a tool in understanding how electromagnetic radiation interacts with atoms, causing transitions of its electrons among different energy levels. Both spontaneous emission and stimulated emission of radiation are also described.

1 Historical Context

‘A Splendid light has dawned on me about the absorption and emission of radiation.’ In a letter written by Albert Einstein to his friend Michel Besso in 1916, Einstein recounts his new insights into a new derivation of Planck’s radiation law.

He considered a gas of ‘molecules’ in thermodynamic equilibrium with electromagnetic radiation. Let energy levels of the molecules be denoted by E_m and also let the number of molecules in each energy level be N_m . By considering two such levels E_2 and E_1 with $E_2 > E_1$ and the possibility of transitioning between these levels, Einstein postulated that the number of transitions, in time dt , for the higher energy level E_2 to the lower state E_1 will consist of two components.

- The first component will arise from the spontaneous jump from E_2 to E_1 . The number of transitions will be given by the term $A_{21}N_2dt$. The coefficient A_{21} is related to the intrinsic probability of the jump and does not depend on the radiation density.

- The second component is a result of stimulated emission of radiation. The number of transitions will be given by $B_{21}N_2\rho dt$, which is proportional to the radiation density. The presence of this radiation will also induce jumps in the other direction (E_1 to E_2), and the number will be given by $B_{12}N_1\rho dt$, which is again proportional to the radiation density.

The A_{ij} ’s and B_{ij} ’s are called the Einstein A and B coefficients.

In equilibrium, the number of transitions from level 1 to 2 must be the same number of transitions from level 2 to 1.

$$N_2(A_{21} + B_{21}\rho) = N_1B_{12}\rho \quad (1)$$

Solving for ρ we get:

$$\rho = \frac{\left[\frac{A_{21}}{B_{21}}\right]}{\left[\frac{B_{12}}{B_{21}}\right] \left[\frac{N_2}{N_1}\right] - 1} \quad (2)$$

Boltzmann told us that the the number of particles in the E_m th energy level will be proportional to the density of states times the Boltzmann factor:

$$N_m = g_m e^{-\frac{E_m}{kT}} \quad (3)$$

Using this result for N_1 and N_2 in the previous result, we get:

$$\rho = \frac{\left[\frac{A_{21}}{B_{21}} \right]}{\left[\frac{B_{12}g_2}{B_{12}g_1} \right] e^{\frac{(E_1-E_2)}{kT}} - 1} \quad (4)$$

Also from Wien's displacement we conclude that $E_2 - E_1 = h\nu$. In the limit as $T \rightarrow \infty$, we expect ρ to reduce to the Rayleigh-Jean's law. If this is the case, then:

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3} \quad (5)$$

This leads to the relationship¹:

$$g_2 B_{12} = g_1 B_{21} \quad (6)$$

2 Time-Dependent Perturbation Theory

In order to understand how atoms interact with an electromagnetic field, we must use time-dependent perturbation theory as our tool of choice. Traditionally, the time dependence of the wavefunction is generally associated with this factor of $e^{-\frac{iEt}{\hbar}}$. This means that for $|\Psi|^2$ (and for other probabilities and expectation values), the time dependence will cancel. For transitions in atomic energies, a time dependence can be placed on the potential of the system. If the time dependent part of the Hamiltonian is small, it can be treated as a perturbation to the system.

Let us consider a system with two unperturbed states, ψ_a and ψ_b , which form an orthonormal basis. Any state can be expressed as a linear combination of these states:

$$\Psi(0) = c_a\psi_a + c_b\psi_b \quad (7)$$

¹Singh, V. Current Science, Vol. 89, No. 12, 25 December 2005

The normal quantum mechanical treatment gives us ² :

$$\Psi(t) = c_a\psi_a e^{-\frac{iE_a t}{\hbar}} + c_b\psi_b e^{-\frac{iE_b t}{\hbar}} \quad (8)$$

Now add the time-dependent perturbation, $H_{pert}(t)$. The only difference in the wavefunction is that the coefficients must be functions of time.

$$\Psi(t) = c_a(t)\psi_a e^{-\frac{iE_a t}{\hbar}} + c_b(t)\psi_b e^{-\frac{iE_b t}{\hbar}} \quad (9)$$

These new coefficients will be important for us to obtain since they will tell us how each state is populated as a function of time. If the system is initially in one state, and at some point later we measure it to be in the other state, a transition has occurred.

Solving for c_a and c_b can be done by mandating that the wavefunction satisfy the time-dependent Schrodinger equation:

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (10)$$

Where, $H = H_0 + H_{pert}(t)$. The result we end up with for our coefficients is:

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \quad (11)$$

$$\dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a \quad (12)$$

Where $\omega_0 = \frac{E_b - E_a}{\hbar}$, and $H'_{ij} = \langle i | H_{pert} | j \rangle$. Typically, $H'_{aa} = H'_{bb} = 0$.

3 Sinusoidal Perturbations

We've now seen how the coefficients of a two state system evolve in time in the presence of a time-dependent perturbation. For reasons that

²For more detailed calculations throughout section 2 and 3, see David J. Griffiths, *Introduction to Quantum Mechanics*, 2nd ed. (Pearson Prentice Hall, Upper Saddle River, New Jersey, 2005).

will become clear, let's now look at a periodic time-dependent perturbation of the form:

$$H_{pert}(\mathbf{r}, t) = V(\mathbf{r}) \cos(\omega t) \quad (13)$$

And,

$$H'_{ab} = V_{ab} \cos(\omega t) \quad (14)$$

Where:

$$V_{ab} = \langle \psi_a | V | \psi_b \rangle \quad (15)$$

We would now like to find the probability of transitioning from state $|\psi_a\rangle \rightarrow |\psi_b\rangle$. If initially the system is in state $|\psi_a\rangle$, we will set $c_a(0) = 1$, and integrate [6] to obtain $c_b(t)$. Then we look at $|c_b(t)|^2$ - the transition probability.

$$\begin{aligned} c_b(t) &\simeq -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'} dt' \\ c_b(t) &\simeq -\frac{iV_{ba}}{2\hbar} \int_0^t \left[e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'} \right] dt' \\ &= -\frac{V_{ba}}{2\hbar} \left[\frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega} \right] \quad (16) \end{aligned}$$

If we look only at driving frequencies around ω_0 , then the second term in [10] will dominate³. Perturbations at other frequencies will cause a negligible probability of transitioning.

$$c_b(t) \simeq -i \frac{V_{ab}}{\hbar} \frac{\sin \left[\frac{(\omega_0 - \omega)t}{2} \right]}{\omega_0 - \omega} e^{i \frac{(\omega_0 - \omega)t}{2}} \quad (17)$$

And finally,

$$P_{a \rightarrow b}(t) = |c_b(t)|^2 \simeq \frac{|V_{ab}|^2 \sin^2 \left[\frac{(\omega_0 - \omega)t}{2} \right]}{\hbar^2 (\omega_0 - \omega)^2} \quad (18)$$

³Just in case you're having a hard time seeing where this is going, when we apply this same method to electromagnetic radiation, $\omega \sim 10^{15} s^{-1}$, so this turns out to be a valid simplification.

4 Emission and Absorption of Radiation

Electromagnetic radiation is composed of mutually perpendicular oscillating electric and magnetic fields. When considering the interaction of an atom and a nearby electromagnetic wave, we can state that the neutral atom will respond primarily to the oscillating electric field. In addition to this, we can approximate the spatial variation of the field to be zero. This is a result of the atom being much smaller than the wavelength of the oscillating field. We can then express the electric field as:

$$|\vec{E}| = E_0 \cos(\omega t) \quad (19)$$

Choosing the direction of polarization to be in the \hat{k} direction, the perturbation Hamiltonian then becomes:

$$H_{pert} = -qE_0 z \cos(\omega t) \quad (20)$$

Where q is actually the electron charge. Why not the nuclear charge? The nucleus is much more massive than the electron. We make the approximation that the nucleus is stationary. The off-diagonal terms in the perturbation Hamiltonian matrix (responsible for the transition to come) will be:

$$H'_{ab} = -q \langle \psi_b | z | \psi_a \rangle E_0 \cos(\omega t) \quad (21)$$

It should also be pointed out that typically, the wavefunction ψ is an even or odd function of z , and hence the quantity $z|\phi|^2$ (odd - irrespective of ψ being even or odd) integrates to zero. This will justify the statement that the diagonal elements of the perturbation Hamiltonian, H_{pert} , will go to zero.

In addition, $p \equiv q \langle \psi_b | z | \psi_a \rangle$, is the electric dipole moment, and radiation of the sort given by [21] is called electric dipole radiation. In comparing our off diagonal matrix elements

with the general case for an oscillating perturbation in section 3, we see that:

$$V_{ba} = -pE_0 \quad (22)$$

If we now think about our atom in a lower state ψ_a with polarized monochromatic light incident on it, there will be some probability of transitioning to a state ψ_b . In light of [22], this probability will be:

$$P_{a \rightarrow b}(t) = \left(\frac{|p|E_0}{\hbar} \right)^2 \frac{\sin^2 \left[\frac{(\omega_0 - \omega)t}{2} \right]}{(\omega_0 - \omega)^2} \quad (23)$$

For this situation, the atom will be excited to a higher energy state, and will absorb $E_b - E_a = \hbar\omega_0$ worth of energy from the electromagnetic field. This process is aptly named absorption.

Using the exact same logic, we can run this whole process in reverse. An atom starts out in state ψ_b and electromagnetic radiation is incident upon it. In this case there are two things that could happen. If we were considering a system with greater than two states, there is a probability that it could again absorb additional energy from the field, transitioning the atom to a state say, ψ_c . But, there is also a probability of a transition from state ψ_b back down to state ψ_a . It is the latter case we will consider here. In order to find this probability, we must compute $P_{b \rightarrow a}(t) = |c_a(t)|^2$. Going through the calculation reveals that it's the same probability as the transition from ψ_a to ψ_b .

$$P_{b \rightarrow a}(t) = \left(\frac{|p|E_0}{\hbar} \right)^2 \frac{\sin^2 \left[\frac{(\omega_0 - \omega)t}{2} \right]}{(\omega_0 - \omega)^2} \quad (24)$$

In this situation the electromagnetic radiation is said to stimulate the emission of a photon, that is, the field will gain $\hbar\omega_0$ worth of energy. Basically, one photon comes in and two come out. This result has proven to be very important. This is the fundamental mechanism behind the laser (light amplification by

stimulated emission of radiation). This amplification could come from some sort of chain reaction of a container of atoms all in their excited state, releasing large amounts of photon at the same frequency. Also if you think about it, absorption is in direct competition with stimulated emission. That same photon which could cause a transition from state ψ_b to state ψ_a and produces two photons, could simply be absorbed by an atom in state ψ_a , in which case no amplification would be produced. In order to produce an effective laser, one must use a method known as population inversion such that most of the atoms in your sample are in state ψ_b .

The last mechanism to discuss is that of spontaneous emission. This is the spontaneous transition of an atom in state ψ_b to ψ_a which occurs independently of any applied external field. If the atom were completely independent of all outside perturbations however, spontaneous emission would not happen. Of course, one could never achieve a perfectly electromagnetic field-free space, and so this is why spontaneous emission is inevitable given these initial conditions.

Let us consider our same container of atoms, N_a being in the lower state ψ_a , and N_b being in the upper state ψ_b . The rate of spontaneous emission will be given by A_{ba} (same as A_{21} from previous section), making the number of atoms transitioning from state ψ_b will be $N_b A_{ba}$. If we take all processes into account,

$$\frac{dN_b}{dt} = -N_b A_{ba} - N_b B_{ba}(\omega_0) + N_a B_{ab}(\omega_0) \quad (25)$$

where $\rho(\omega_0)$ is the energy density in the field, evaluated at ω_0 . If in thermal equilibrium,

$$\frac{dN_b}{dt} = 0$$

And solving for $\rho(\omega_0)$:

$$\rho(\omega_0) = \frac{A_{ba}}{\left(\frac{N_a}{N_b} \right) B_{ab} - B_{ba}} \quad (26)$$

Substituting in for N_a and N_b in terms of their Boltzmann factor,

$$\rho(\omega_0) = \frac{A_{ba}}{e^{\frac{\hbar\omega_0}{kT}} B_{ab} - B_{ba}} \quad (27)$$

By comparing this to Planck's blackbody formula,

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\frac{\hbar\omega}{kT}} - 1} \quad (28)$$

We must conclude that $B_{ab} = B_{ba}$, and

$$A_{ba} = \frac{\omega_0^3 \hbar}{\pi^2 c^3} B_{ba}. \quad (29)$$

This gives us an expression for the spontaneous emission rate A_{ba} in terms of the stimulated emission rate B_{ba} . This rate of transition, expressed in terms of the dipole moment is⁴,

$$B_{ba} = \frac{\pi}{3\epsilon_0 \hbar^2} |p|^2 \quad (30)$$

We can finally re-express the spontaneous emission rate by combining [29] and [30] to achieve:

$$A_{ba} = \frac{\omega_0^3 |p|^2}{3\pi\epsilon_0 \hbar c^3} \quad (31)$$

References

1. Griffiths, David J. *Introduction to Quantum Mechanics*, 2nd ed. Pearson Prentice Hall, Upper Saddle River, New Jersey: 2005.
2. Hilborn, Robert C. Am. J. Phys. 50, 982986 (1982)
3. Singh, V. Current Science, Vol. 89, No. 12, 25 December 2005

⁴This result is given for a system under the influence of incoherent, unpolarized light incident from all directions. (See pages 352-254 David J. Griffiths, *Introduction to Quantum Mechanics*, 2nd ed. Pearson Prentice Hall, Upper Saddle River, New Jersey, 2005).