Electron-photon Interaction and Thermal Disequilibrium Irreversibility

(Article begins on next page)

03 May 2024

Original Paper

Electron-photon Interaction and Thermal Disequilibrium Irreversibility

Umberto Lucia

Dipartimento Energia "Galileo Ferraris", Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
E-Mail: umberto.lucia@polito.it

Abstract: Atoms continuously interact with the photons of the electromagnetic fields in their environment. This electromagnetic interaction is the consequence of the thermal non-equilibrium. It introduces an element of randomness to atomic and molecular motion, which brings to the decreasing of path probability required for microscopic reversibility of evolution. In any atomic electron-photon interaction an energy footprint is given to the atom, and the emitted photon looses energy. The emission of radiation isn't time reversible and this causes the irreversibility in macroscopic systems.

Keywords: Macroscopic Irreversibility; Microscopic Irreversibility; Quantum Mechanics; Quantum Thermodynamics; Schrödinger Equation

Macroscopic world is irreversible. This is our every day experience. A proof is clear: nobody can go backwards in time.

On the contrary, all the fundamental laws of physics are symmetric with respect to the inversion of the time arrow [1]. The first scientist to develop a convincing explanation of this paradox has been Ludwig Boltzmann, known for two basic contributions to physics: the physical and mathematical interpretation of the concept of entropy as a measure of what today we popularly name disorder of atoms, and the equation known as the Boltzmann equation [1]. This equation describes the statistical properties of a gas made up of molecules: it represents the first approach to govern the time evolution of a probability [1-3].

Boltzmann's approach to entropy behaviour involves his definition of statistical entropy that doesn't consider any molecular correlations [4-6], then introduced by Paul and Tatjana Pavlovna Ehrenfest as molecular chaos [4-7]. The time evolution of a closed system, in initial highly ordered state, generate a loss of the initial macroscopic as microscopic free energy in the form of molecular

correlations [5]. The mathematical-physical formulation is the increase of the Boltzmann entropy. But, microscopic laws are described by deterministic and reversible differential equations based on the Newton's classical dynamics or the quantum mechanical equations of motion with the consequence of resulting time reversible for conservative systems describable by a real Hamiltonian [4,5,8,9]. Gibbs included molecular correlations between particles in his approach to statistical thermodynamics, obtaining that the Gibbs entropy conserves the path probability stored in molecular correlations [10].

A fundamental problem in the present statistical mechanics is how indeterministic macroscopic irreversibility can result from deterministic and reversible microscopic motions [1-5, 11-18]. In this paper we want to show how the origin of irreversibility can be explained in the continuous electromagnetic interaction between atoms and environment due to the thermal disequilibrium.

To do so, we consider a Hydrogen-like atom in interaction with electromagnetic wave. The electromagnetic wave is no more than a flow of photons. They incomes into the atoms and outcomes from them. At atomic level, the photons can be absorbed by the atomic or molecule electrons, and an electronic energy transition occurs between energy levels of two atomic stationary states. Then, the photons can be also emitted by the excited electrons when they jump down into the energy level of the original stationary state. Apparently, there are no changes in the energy of the atom, but only in the electronic transition. But, on the contrary, there exists a change in the kinetic energy of the center of mass of the atom, but its amount is negligible in relation to the energy change in electronic transition and its time of occurrence (10^{-13} s) is greater than the time of electronic transition (10^{-15} s). But, its contribution to the energy balance becomes relevant when we consider a great number of interaction as it happens in macroscopic systems [16].

Indeed, any atomic stationary state is completely identify by its energy level, expressed by the principal quantum [22-29] number n. Any electronic transition, between two energy levels identified by f for final state and i for initial state, occurs following the quantum selection rule $\Delta n = n_f - n_i = \pm\, 1$. We develop our analysis by considering a Hydrogen-like atom, of atomic number Z, in interaction with an external electromagnetic wave. For such atom, following the approach used in spectroscopy [26-29], the external orbital electron can be identified by the following quantities:

1. The apparent atomic radius [22-29]:

$$r_n = \frac{4\pi\varepsilon_0\hbar^2}{m_e Z e^2}\, n^2 \tag{1}$$

   where ε_0 is the electric permittivity, $\hbar$ is the Dirac constant, m_e is the mass of the electron, e is the elementary charge, $n = 1, 2, 3, ...$, is the principal quantum number, always integer;

2. The energy of the atomic level [22-29]:

$$E_n = \frac{m_e Z^2 e^4}{32\pi^2\varepsilon_0^2\hbar^2}\, \frac{1}{n^2} \tag{2}$$

3. the Sommerfeld-Wilson rule [22-29]:

$$\oint p_e\, dr_n = p_e\, r_n = n\hbar \tag{3}$$

where $p_e = m_e v_e$ is the electronic momentum, with v_e its mean velocity inside the orbital, $p_e\, r_n$ is the angular momentum of the electron, being r_n defined by the relation (1). Without lacking of generality, we chose the geometric reference system in the center of mass of the nucleus, such that the atom is at

rest with null momentum $\mathbf{p}_{atm}$ at initial state, before the electromagnetic interaction. Its Schrödinger's equation, which is [22-29]:

$$\left[-\frac{\hbar^2}{2m_N}\nabla^2_{\mathbf{r}_N} - \frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_e} + V(\mathbf{r}_e - \mathbf{r}_N) \right]\psi(\mathbf{r}_N, \mathbf{r}_e) = E_{tot}\psi(\mathbf{r}_N, \mathbf{r}_e)$$

(4)

where m_N is the mass of the nucleus, m_e is the mass of the electron, $\mathbf{r}_N$ is the nucleus coordinate, $\mathbf{r}_e$ is the electron coordinate, $V(\mathbf{r}_e - \mathbf{r}_N)$ is the electrostatic potential, E_{tot} is the total energy and $\psi(\mathbf{r}_N, \mathbf{r}_e)$ is the wave function. Now, following the usual quantum mechanical approach [22-29] we introduce the quantities useful for the analysis of the two bodies problem:

1. The relative coordinates $\mathbf{r} = \mathbf{r}_N - \mathbf{r}_e$,
2. The coordinates of the center of mass $\mathbf{R} = (m_N\mathbf{r}_N + m_e\mathbf{r}_e)/(m_N + m_e)$,
3. The total mass $M = m_N + m_e$,
4. The reduced mass $\mu = (m_N^{-1} + m_e^{-1})^{-1}$,
5. The momentum of the center of mass $\mathbf{P} = M\dot{\mathbf{R}} = -i\hbar\nabla_{\mathbf{R}}$,
6. The momentum of the reduced mass particle $\mathbf{p} = \mu\dot{\mathbf{r}} = -i\hbar\nabla_{\mathbf{r}}$,
7. The wave function $\psi(\mathbf{r}, \mathbf{R}) = \varphi(\mathbf{r})\vartheta(\mathbf{R})$,
8. the energy $E_{CM} = \mathbf{P}^2/2M$ of the free particle center of mass,
9. the energy E_μ of the bound particle of reduced mass, such that $E_{tot} = E_{CM} + E_\mu$,
10. The electrostatic potential $V(\mathbf{r}) = -Ze^2/r$,

so, the equation (4) becomes [22-29]:

$$\left[\left(-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r}) \right) - \frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} \right]\psi(\mathbf{r}, \mathbf{R}) = E_{tot}\psi(\mathbf{r}, \mathbf{R})$$

(5)

Now, we introduce, in order to separate the equation (5) in the following two equations:

$$-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\vartheta(\mathbf{R}) = E_{CM}\vartheta(\mathbf{R})$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r}) \right)\varphi(\mathbf{r}) = E_\mu\varphi(\mathbf{r})$$

(6)

Now, we introduce the interaction with an external electromagnetic wave. The electromagnetic radiation is no more than a flux of photons, characterized by [22,29]:

1. An energy E_γ evaluated as:

$$E_\gamma = h\nu$$

(7)

where h is the Planck's constant (6.62607 × 10⁻³⁴ J s), and ν is the frequency of the electromagnetic wave;

2. A momentum p_γ evaluated as:

$$p_\gamma = \frac{h\nu}{c}$$

(8)

Now, considering an atom of principal quantum number n, and we define our control volume as the sphere of radius equal to $n + 1$ with center in the center of mass of the atom. So, the interaction between the electromagnetic radiation and the Hydrogen-like atom can be studied as the interaction

between the flux of photons with an open system (the atom of principal quantum number n), through the border of the control volume defined by the sphere of radius:

$$r = \frac{4\pi\varepsilon_0\hbar^2}{m_e Z e^2}(n+1)^2$$

(9)

with center in the center of the atomic nucleus. The atomic electron absorbs the incoming photon when its frequency ν is the resonant frequency, required by the transition between the initial E_i and final E_f energy levels [22-29], corresponding to the quantized energy:

$$\nu = \frac{E_f - E_i}{h}$$

(10)

where h is the Planck's constant. Emission of the this photon results in the reverse process. Considering the absorption process, at initial state we chose the geometric reference system in the center of mass of the nucleus, so the atom is at rest with null momentum $\mathbf{p}_{atm}$. The momentum of the incoming photon is $h\nu\,\mathbf{u}_c/c$, where $\mathbf{u}_c$ is the versor of propagation of the electromagnetic wave, and c is the velocity of light in vacuum. When an electron absorbs the incoming photon, the atomic momentum becomes [22-29]:

$$\mathbf{p}_{atm} = -\frac{h\nu}{c}\mathbf{u}_c$$

(11)

As a consequence of the absorption of the incoming photon, the electron undergoes an energy levels transition, from the stationary state of energy E_i to the stationary state E_f, and the final energy of the atom can be evaluated by using the energy balance analysis and it results:

$$E_f = E_i + h\nu - \frac{p_{atm}^2}{2M} = E_i + h\nu - \frac{(h\nu)^2}{2Mc^2}$$

(12)

where $p_{atm}^2/2M$ is the kinetic energy gained by the atom, and M is the mass of the atom. Consequently, we can obtain [22]:

$$h\nu = \frac{(E_f - E_i)}{1 - \dfrac{h\nu}{2Mc^2}}$$

(13)

In the same way, but for the emission of a photon, we can obtain [22]:

$$h\nu = \frac{(E_i - E_f)}{1 + \dfrac{h\nu}{2Mc^2}}$$

(14)

As a consequence of the absorption of the photon, the laws of conservation of momentum and energy due to the absorption of the photon, hold to:

$$\mathbf{P}' = M\,\dot{\mathbf{R}}'$$
$$\mathbf{p}' = \mu\,\dot{\mathbf{r}}'$$
$$\dot{\mathbf{r}}' = \dot{\mathbf{r}}'_e - \dot{\mathbf{r}}_N = \frac{\mathbf{p}'_e}{m_e} - \frac{\mathbf{p}_N}{m_N} = \frac{m_N\mathbf{p}'_e - m_e\mathbf{p}_N}{\mu M}$$
$$\dot{\mathbf{R}}' = \frac{m_e\dot{\mathbf{r}}'_e + m_N\dot{\mathbf{r}}_N}{M} = \frac{\mathbf{p}'_e + \mathbf{p}_N}{M}$$

(15)

where $\mathbf{p}_N$ is the momentum of the nucleus and $\mathbf{p}_e$ is the momentum of the electron, $\mu = \left(m_e^{-1} + m_N^{-1}\right)^{-1}$ and $M = m_e + m_N$. Consequently, the Schrödinger's equation becomes [22-29]:

$$-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 \vartheta(\mathbf{R'}) = E_{CM}\vartheta(\mathbf{R'})$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r'}}^2 + V(\mathbf{r'})\right)\varphi(\mathbf{r'}) = E_\mu \varphi(\mathbf{r'})$$

(16)

When the photon is emitted, following the same approach, we can obtain:

$$-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 \vartheta(\mathbf{R'}) = E_{CM}\vartheta(\mathbf{R'})$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right)\varphi(\mathbf{r}) = E_\mu \varphi(\mathbf{r})$$

(17)

with the wave function given as $\psi(\mathbf{r},\mathbf{R'}) = \varphi(\mathbf{r})\vartheta(\mathbf{R'})$. The wave function for the electron in a whole adsorption-emission process doesn't change, while the center of mass (approximately the atomic nucleus) wave function changes as follows:

$$\vartheta(\mathbf{R}) = \frac{1}{(2\pi)^{3/2}}\exp(i\mathbf{k}\cdot\mathbf{R}) \quad \text{before the interaction with} \quad \mathbf{k} = \sqrt{\frac{2M}{\hbar}E_{CM}}\ \mathbf{u}_{CM}$$

(18)

$$\vartheta(\mathbf{R}) = \frac{1}{(2\pi)^{3/2}}\exp(i\mathbf{k'}\cdot\mathbf{R}) \quad \text{after the interaction with} \quad \mathbf{k} = \sqrt{\frac{2M}{\hbar}\left(E_{CM} + \frac{m_e}{M}h\nu\right)}(\mathbf{u}_{CM} + \mathbf{u}_c)$$

Now, we can evaluate the energy footprint of the process as:

$$E_{ftp} = \Delta(h\nu) = \Delta E_{CM} = \langle\psi(\mathbf{r},\mathbf{R})|H|\psi(\mathbf{r},\mathbf{R'})\rangle = \frac{m_e}{M}h\nu$$

(19)

where H is the Hamiltonian of the interaction. As a consequence of this energy footprint in the electron-photon interaction due to the continuous thermal disequilibrium in the Universe, which is no more than an energy lost in any process, it occur a symmetry breaking in the energy level electronic transition. Our results agree with the results obtained by Doyle: the electromagnetic interaction adds an element of randomness to atomic and molecular motions, erasing classical path probability [4,5], and photon emission and absorption destroy nonlocal molecular correlations, justifying Boltzmann's assumption of molecular chaos [4,5].

Acknowledgement

References

1. C. Cercignani. *Ludwig Boltztnann. The Man Who Trusted Atoms* (Oxford University Press, Oxford, UK, 1998).

2. M.J. Klein. The development of Boltzmann's statistical ideas, in The Boltzmann equation: theory and applications. In E.G.D. Cohen, and W. Thirring Eds. *The Boltzmann Equation. Theory and Application* (Springer-Verlag, Vienna, 1973).

3. C. Cercignani. *The Boltzmann equation and its applications* (Springer-Verlag, New York, 1988).

4. R.O. Doyle. *Great Problems in Philosophy & Physics - Solved?* (Information Philosopher, Cambridge, 2016).

5. R.O. Doyle. The Origin of Irreversibility. *Information Philosopher*: http://www.informationphilosopher.org.

6. L. Boltzmann. Further studies on the thermal equilibrium of gas molecules. In S.G. Brush. *The Kinetic Theory of Gases* (Imperial College Press, London, 2003), 262-349.

7. P. Ehrenfest & T. Ehrenfest. *Conceptual Foundations of the Statistical Approach in Mechanics* (Cambridge University Press, Ithaca, NY, 1959).

8. D. Bohm. *Quantum Theory* (Prentice-Hall, New York, 1951).

9. R.C. Tolman. *Statistical Mechanics* (Claredon Press, Oxford, 1938).

10. J.W. Gibbs. *Elementary Principles of Statistical Mechanics* (Dover Publications, New York, 1960).

11. U. Lucia. Quanta and entropy generation. *Physica A* **419**, 115-121 (2015).

12. U. Lucia. Some considerations on molecular machines and Loschmidt paradox. *Chem. Phys. Lett.* **623**, 98-100 (2015).

13. U. Lucia. Second law considerations on the third law: From Boltzmann and Loschmidt paradox to non equilibrium temperature. *Physica A* **444**, 121-128 (2016).

14. U. Lucia. A Link between Nano- and Classical Thermodynamics: Dissipation Analysis (The Entropy Generation Approach in Nano-Thermodynamics). *Entropy* **17**, 1309-1328 (2015).

15. U. Lucia. Entropy production and generation: clarity from nanosystems considerations. Chem. Phys. Lett. **629**, 87-90 (2015).

16. U. Lucia. Macroscopic irreversibility and microscopic paradox: A Constructal law analysis of atoms as open systems. *Sci. Rep.* **6**, 35792 (2016).

17. N. G. van Kampen, Fundamental problems in statistical mechanics of irreversible processes. In E.G.D. Cohen. *Fundamental Problems in Statistical Mechanics* (North-Holland Pub. Co., Amsterdam, 1961), 173-202.

18. R.O. Doyle. The continuous spectrum of the hydrogen quasi-molecule. *J. Quant. Spectrosc. Radiat. Transfer* **8**, 1555-1569 (1968).

19. A. Annila. Natural thermodynamics. *Physica A* **444**, 843-852 (2016).

20. A. Annila, S. Salthe. Threads of time. *ISRN Thermodynamics* **850957**, 1–7 (2012).

21. A. Annila. The 2nd law of thermodynamics delineates dispersal of energy. *Int. Rev. Phys.* **4**, 29-34 (2010).

22. M. Alonso, E. Finn, *Quantum and Statistical Physics* (Addison-Wesley, Reading, 1968).

23. J.C. Slater, *Theory of Matter* (McGraw-Hill, New York, 1968).

24. M. Planck, *The Theory of Heat Radiation*. (Dover Publications, New York, 1991).

25. E. Schrödinger, *What's life* (Cambridge University Press, Cambridge, 1944).

26. G. Herzberg, *Atomic Spectra and Atomic Structure*. (Dover Press, New York, 1944).

27. W. Finkelnburg, *Structure of Matter* (Academic Press, New York, 1964).

28. L.D. Landau, E.M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Oxford, 1965).

29. R. Feynman, R.B. Leighton, M. Sans, M. *The Feynman Lectures on Physics*. Vol. III (Addison Wesley, Boston, 1964).