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# The Arrow of Time in Quantum Theory

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**Abstract**

In Classical Mechanics, time is reversible, i.e. implies no particular choice: only the observer knows in which direction it flows. The present Comment re-examines whether this remains true in Quantum Mechanics. In the context of Atomic Physics, it is concluded that the existence of an arrow of time depends on the manner in which the radiation field is introduced, which must be non-perturbative.

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## 1. Introduction

This paper explores how the arrow of time, distinguishing between past and future, appears in Quantum Mechanics. It is not present in all formulations of the theory. In particular, it is absent in the context of Schrödinger-type equations, which are reversible in time. We examine the minimum requirement for this arrow to appear in the context of Atomic Physics. It is shown to be related to the non-perturbative introduction of the radiation field, because of the specific form of Planck's Black-body Radiation law. It is also possible to introduce a direction of time by postulate in Scattering Theory which creates initial and final states by definition, but this provides no intrinsic reason for the existence of an arrow of time.

The nature of time in Elementary Quantum Mechanics remains somewhat mysterious because, in contrast with the other observables, it is in no way different from time in Classical Mechanics. It appears as a variable in the Schrödinger and Dirac equations but is not associated with a Hermitian operator and remains unquantized. It is also reversible, in the sense that stable eigenstates occur. This initial formulation of Quantum Mechanics, is referred to below as "elementary" in the sense that it does not include the radiation field, which remains external to the Schrödinger equation.

Nonetheless, Quantum Mechanics is applied to situations in which the distinction between past and future is essential, for example: in the decay of excited atomic states. It is therefore important to explore how and when the arrow of time appears as an inherent property of the theory and what minimum requirement this implies in its fundamental principles.

In the present paper, we briefly revisit how the theory is set up in order to identify what forces the distinction between past and future in Atomic Physics.

## 2. Background

As well-known, time is the one unquantized variable in Quantum Mechanics. It flows continuously 'like a river' in the sense implied by Newton, and is treated like a classical variable in Quantum Mechanics [1,2], which is unique. It appears through derivatives (i.e. infinitesimal intervals) in both the Schrödinger and the Dirac equations. One might be tempted to turn to the Theory of Relativity for further insight, because the Dirac Equation is obtained by imposing the Lorentz transformations on elementary Quantum Mechanics [3]. However, as Dirac himself observed, his equation is not truly relativistic, since it remains a single-particle equation. Furthermore, Relativity is none too helpful in this respect, because space and time are regarded as

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different dimensions of a single entity, space-time. Since space has no preferred direction, this provides no way of associating an arrow only with time.

More generally, there are few situations in Science which impose an arrow to distinguish between past and future. One has the Second law of Thermodynamics (extending also to Information theory), through the persistent growth of Entropy [4]. Another example is Hubble's law in Astronomy [5], leading to the continuing expansion of the Universe after the 'Big Bang' [6]. Finally, one thinks of Darwin's law of biological evolution, in his theory of species [7], a subject completely outside the scope of the present Comment.

Elementary Quantum Mechanics appeals to a number of fundamental principles: the quantisation of Energy (to introduce Planck Constant $\hbar$), the representation of physical 'observables' by Hermitian operators acting on wavefunctions whose modulus squared yields a probability of occurrence, the act of measurement, resulting in combinations of eigenvalues of these operators, the physical interpretation of the commutation properties of operators and the postulate of the Uncertainty Principle, all of which are given as fundamental axioms. The steps involved are fully described in refs [8,9]. The reader will note that the form of Planck's Black Body radiation law (also regarded as fundamental to Quantum Mechanics because it introduces the constant $\hbar$) is not actually required at this point, to set up the elementary form of the theory. This is because, strictly, the Schrödinger and Dirac equations only apply in absence of the radiation field.

These axioms alone, are still insufficient to set up elementary Quantum Mechanics. It is also necessary to find appropriate mathematical forms for each of the Hermitian operators representing a given physical variable, without which Quantum Mechanics would have no inherent structure. To assist in this process, Bohr and Sommerfeld proposed the so-called Correspondence Principle, based on the idea that, in the 'classical limit' (i.e. for $\hbar \to 0$) results obtained by Quantum Mechanics should merge seamlessly into those obtained by Classical Mechanics for the 'corresponding' system.. Specifically, they proposed their rule in reverse (i.e. going from classical to quantum physics by integration around a closed classical orbit, according to the formula:

$$\oint_C p\, dq = \left(n + \frac{1}{2}\right) \hbar\omega$$

where $p$ and $q$ are conjugate variables in the Hamiltonian, $n$ is referred to as the principal quantum number and $\hbar\omega$ is the quantum of energy. This approach works perfectly well for ideal systems such as a simple harmonic oscillator or a 'free' atom with a Newtonian central field, in which case the orbits in phase space close exactly. It no longer works for more complex systems, such as a 'real' Rydberg atom, whose field is not Newtonian, since the atom then radiates and has no stable orbits. To create an ideal atom, one begins by turning off both magnetism and the radiation field. Both are inconvenient, because they prevent orbits from closing. Hydrogen then becomes the microscopic analogue of Newton's two-body planetary system, with a central and purely inverse square law of force. Exact solutions for this case enable the Correspondence Principle, i.e. the quantum system exhibits specific closed orbits in the classical limit.

Problems appear, however, as soon as greater complexity is introduced. First, [10] the three-body problem of classical physics cannot be solved in closed form, because the orbits in this case never close. They are chaotic. This precludes exact solutions for classical few-particle systems with three or more constituents. Such systems are 'non-integrable' and must be handled perturbatively. A second important example of a classically chaotic system is the pendulum with a magnet (the quantum analogue of which is a Rydberg atom in an external magnetic field). In the classical limit, if the pendulum is supposed to 'write' on a piece of paper, however long one waits, the path followed by the pen would never repeat. Here again, the Correspondence Principle fails to take us from the classical to the quantum system. Somehow, time is involved in this failure: in a potentially chaotic situation, it might take an infinite time to decide whether an orbit is about to close or not. If we attempt to apply the Principle in reverse for such cases (i.e. going from quantum to classical physics) it is no longer clear what the classical limit would be, i.e. whether the whole of classical physics can be recovered, or only the part involving orbits which do close. Again, 'quantum chaos' does not exist also for another reason: the Uncertainty Principle does not allow one to verify orbital closure because of the granularity of space-time..

In the classical limit, a two-body planetary system exhibits stable closed orbits at any energy up to the escape threshold. Quantisation results in stable orbits of infinite duration only at specific energies given by the eigenstates. However, this infinite duration has the same origin as in Newtonian mechanics, implying no arrow of time. The dynamics are fully reversible. When invoking 'stable orbits' for an atom in the classical limit, it is important not to forget that, in reality, there are no stable classical orbits at all in this problem unless one turns off the effects of the electromagnetic field. Thus, the Correspondence Principle is fatally flawed (as first observed by Einstein) and can only serve for computational convenience in situations involving very high quantum states of Rydberg electrons.

Finally, we come to the 'Time-dependent' version of the Schrödinger equation: This is not really a different equation, but rather a mathematical extension of the original Schrödinger equation, obtained by writing the energy explicitly as its operator, namely a derivative with respect to time. In terms of basic principles, it contains no more than the original equation, and so contributes nothing more concerning the arrow of time. As will be seen in sections 2 and 3 below, it nonetheless provides the basis for perturbation theory leading to some further useful insights.

## 3. The Wigner Time Delay in Scattering Theory

Since Schrödinger-type equations have no preferred direction of time, it is not inconsistent to impose the existence of an arrow of time as an independent postulate. This is precisely what Wigner does [11] in Scattering Theory, by requiring that the scattering process should lead from an 'initial' to a 'final' state. In other words, this approach postulates an arrow of time which, however, is not an intrinsic property of the system unless this assumption is made. The advantage of doing this is to bring situations in which particles are separated from each other in initial or in final states (or both) within a formalism based on Schrödinger-type equations, i.e. to provide a general and direct extension of the theory to the continuum states above the threshold in Atomic Physics by the introduction of the scattering matrices, which have many interesting and useful analytic properties in atomic theory [12] backed up by many observations.

Although full nature of time still escapes analysis in this construction, an interesting new feature appears, known as the "Wigner time delay" [13], intrinsic to the scattering process. It appears as a result of the phase shifts induced during scattering process itself. It owes its appearance to the fact that processes allowing detection of the scattering wave-packet require its phase to be stationary. Otherwise, the superposition of many different phases during scattering by a dispersive potential would blank out any signal by phase cancellation for both incoming and outgoing waves. If the radial wave-packet is represented as

$$e^{ikr-Et+\varphi(k)} \equiv \Phi(k)$$

The stationarity condition, with the Wigner time delay $\tau_W$ defined by $\tau_W = \partial\varphi/\partial k$ yields

$$\frac{\partial\Phi}{\partial k} = r - kt + \frac{\partial\varphi}{\partial k} = r - k(t - \tau W) = 0$$

In experiments on atomic photoionisation [14], the scattering phase is augmented by the photoemission phase shift, given by the argument of the atomic dipole matrix element, resulting in a collective phase for the complete scattering process. To compute the atomic contribution, one appeals to perturbation theory within the framework of the time-dependent Schrödinger equation (section 1 above) with a partitioned Hamiltonian in the form

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$$i\hbar \frac{\partial \Psi}{\partial t} = \{ \mathrm{H_{atom}} + \mathrm{H_{pt}} \} \Psi$$

where $\mathrm{H_{atom}}$ stands for the field-free atomic contribution and $\mathrm{H_{pt}}$ for the perturbative scattering term. There are many approaches within atomic theory to compute these terms which, together with comparisons to observations in recent experiments, are fully discussed in the topical review [15] by Khefels.

What has attracted great interest is the fact that extremely short time delays (in the attosecond range) can be involved. For example, for Ne Schultze et al [14] report a Wigner time delay of 21 ± 5 as (2.1 $10^{-17}$ s). For comparison, the atomic unit of time (the time taken for a photon to cross the diameter of an H atom) is $10^{-17}$ s.

In practice, we note that what is measured in such experiments is not really a time, but rather a photoelectron spectral phase and its energy derivative, converted into the Wigner time delay through the conceptual framework of scattering theory.

Again, the ordering of time is imposed at the outset through the assumptions of the Wigner formalism, and so the arrow of time is introduced by postulate rather than as a consequence of the theory.

## 4. Introducing the Radiation Field

The next step in the present context is the introduction of the radiation field. Conventionally, this is done using the dipole approximation within a theoretical formalism due to Heitler [16]. Basically, the interaction with the oscillating electric component of electromagnetic radiation is treated as a perturbation of the free atom using the time-dependent Schrödinger equation given above and this results in a formula expressing the probability per unit time of both excitation from a state *i* to a state *j* of the atom by absorption of a photon and also the inverse process, from *j* to *i*, stimulating the emission of a photon, both of which occur simultaneously in the presence of the radiation field.

It was shown by Sommerfeld [17] that this description via the dipole approximation is incomplete, because it takes no account of the radiation pressure, or momentum of the photon, whose absorption or emission leads to recoil of the atom. He showed that the minimum requirement to describe the dynamics is to include also the quadrupole terms in the perturbative expansion. However, even in this higher level of approximation, the theory remains within the framework of perturbative extensions to the Schrödinger equation which, as argued above, provide no new insight concerning the arrow of time.

the next step was introduced by Einstein [18] who considered the problem from a completely new angle, and by Milne [19] who elaborated Einstein's argument in the context of stellar atmospheres. For the first time, Einstein introduced the radiation field in a non-perturbative way, by simplifying the atom to just two active states (1 and 2) and placing it in a bath of radiation in absence of collisions with other atoms. He argued that the only simple way for this isolated two-level atom to come into equilibrium with the radiation field is to apply what is called the 'Principle of Detailed Balance', namely that pairs of states should all be individually in equilibrium with each other in the presence of the radiation field, which is only possible if

$$g_1 \mathrm{B}_{12} = g_2 \mathrm{B}_{21}$$

where $g_1$ and $g_2$ are the statistical weights of levels 1 and 2, and the coefficients $B_{12}$ and $B_{21}$ are the probabilities per unit time for absorption of radiation from level 1 to level 2 and the probability of stimulated emission from level 2 to level 1 obtained from the Heitler theory in the dipole approximation. However, as argued by Einstein, this rule is not sufficient to recover a most fundamental property of radiation associated with the Quantum theory, namely Planck's Black Body Radiation law. In order to recover this law Einstein was obliged to introduce into the theory a new

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coefficient, which he called $A_{21}$, the probability per unit time of spontaneous decay from level 2 to level 1 in absence of any radiation field. He showed that, if

$$A_{21} \equiv \frac{2hv^3}{c^2} B_{21}$$

then Planck's Black Body Radiation Law is recovered. The two rules connecting the A and B coefficients are referred to as the Einstein-Milne relations.

The full significance of his A coefficient was unknown at the time even to Einstein. Only later was it discovered that the spontaneous emission coefficient is a consequence of quantum fluctuations in the radiation field, in other words, that quantum field theory is responsible for its existence [20]

By considering the equilibrium conditions and applying Detailed Balance to two- and three-level system, one finds that a population inversion requires at least three levels, and therefore that laser action by stimulated emission of radiation can only be achieved at the expense of energy. Laser light depends on the B coefficient and creates electromagnetic order, whereas spontaneous emission depending on the A coefficient results in the emission of incoherent light. Consequently, the statement that order is achieved at the expense of energy conforms to the second law of Thermodynamics, which is not surprising since the Einstein coefficients were imported into Quantum Mechanics via Planck's Black Body Radiation law, which itself results from Thermodynamics..

The second law of Thermodynamics, as pointed out in the Introduction, is one of the few laws of Physics which imposes an arrow on the direction of time. In the present instance, this appears as follows : if an isolated atom has been raised to an excited state, then it will decay back to its ground state by fluorescence in a time called the natural lifetime of that state, given by 1/A. This decay defines the arrow of time, since there exists no inverse process.

In practice, there is of course no such thing as a fully 'isolated' atom in nature. Were it to exist, the gedanken experiment would consist in exciting an atom initially, then turning off all external perturbations (collisions as well as the external radiation field) and seeking the moment when all fluorescence stops. This moment comes at a later time, so the arrow of time would be confirmed experimentally. However, it would not be sufficient to observe fluorescence from a single excited state, because individual excited states can also be populated by cascades from levels of higher energy which could in principle result in errors of interpretation This problem is well-known feature of Beam-Foil Spectroscopy [21] and complicates the measurement of lifetimes.

## 5. Conclusions

The present comment demonstrates that the minimum requirement for the existence of an arrow of time in Quantum Mechanics is the non-perturbative introduction of the radiation field via Planck's Black Body Radiation law and Einstein's A coefficient. This conclusion is reached within the context of Atomic Physics, which provides the simplest conceptual framework to set up Quantum Mechanics. There of course exist other phenomena such as radioactivity in the context of Nuclear forces which also imply an arrow of time, but whose analysis is more complicated because of the nature of the fields of force.

It is interesting to observe that time cannot be reduced to the properties of the variable $t$ in elementary quantum theory, since this theory captures only its cyclic or repetitive nature, as for the two-body planetary or Newtonian problem in absence of external perturbations. Thus, one can use the 'atomic pendulum' for states of very narrow natural linewidth to measure time intervals. However, the evolving or linear nature of time which determines its arrow is dependent on the A coefficient, so the quest for the best possible 'atomic clock' runs somewhat contrary to a full understanding of the physical properties of time.

Since long ago, philosophers have described the dual nature of time, which is both cyclic or repetitive and evolving or linear. Sometimes even, these two aspects were considered as alternative descriptions. The formalism of Quantum Mechanics supplemented by the introduction of both A and

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B coefficients, provides a description of this duality based sound scientific principles, showing that actually they are not alternative but complementary.

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