A qualitative discussion of the principles of quantum electrodynamics

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Preamble

> It is obvious, however, that whichever side we take concerning the nature of light, many, indeed almost all the circumstances concerning it, are incomprehensible, and beyond the reach of human understanding — *Encyclopaedia Britannica* article on "Light," 1792.

If the authors of the above extract were alive today, what would they think of mankind's current understanding of the microcosmos? Certainly, modern theories have resolved almost all the apparent contradictions concerning the nature of electromagnetic radiation, and in doing so have shed light on the rich tapestry that underlies the observable universe. But would not the authors have felt more comfortable simply designating the whole field as "unknowable", rather than plunging themselves into a world that contradicted all of the then existing laws governing the universe? Light as corpuscles rather than waves; particles travelling both forward and backward in time, or being created from empty space; reaching the limits of the knowable with the Uncertainty Principle—all of these staggering concepts were necessary to solve the riddle of the nature of light and matter, and it is into this strange and fascinating world that we must venture in order to discuss what has been described as "our best example of a good theory"[1]
: QED.

Introduction

The theory of quantum electrodynamics has been described as being hidden behind a dense smoke-screen of formalism[2], and it is the difficulty of the higher mathematics involved in the calculations associated with the theory that has determined the qualitative, rather than explicitly quantitative nature of this account. The author apologises in advance for the lack of long equations and tortuous proofs. I will, however, attempt to identify the fundamental concepts that underlie the framework of QED, and to recognise areas in which the application of the theory has been particularly successful.

After a brief discussion of the background and the historical development of QED, the structure of this essay will roughly follow the increasing complexity of the systems studied by the theory: an examination of the quantization of the electromagnetic field will lead to the phenomenon of coupling between electrons and photons (incorporating such concepts as stimulated and spontaneous emission). This in turn will lead to the more complex considerations involved in the interaction between molecules, including by way of example a brief treatment of the theoretical bases of the dispersion force and chiral discrimination. I will also refer to the corrected magnetic moment of the electron and attempt to discuss some of the questions of principle arising from the theory of quantum electrodynamics, such as that of renormalisation. I will conclude this report with an outline of some of the recent applications of the theory in the realms of physical and theoretical chemistry.

It should be pointed out at this point that the length of each section in this report is by no means related to the relative importance of each topic within the framework of light's interaction with matter. Rather, it is a result of a personal selection of a few of the fundamental concepts and examples of the applications present in the vast domain of quantum electrodynamics. For a more detailed and structured account the reader is referred to the books and articles listed in the Bibliography at the end of this essay.

It should also be noted that due to their inability to explain all of the observed phenomena described by quantum electrodynamics, semi-classical and neo-classical theories of electrodynamics[3] will not be discussed in this essay. However, it should be pointed out that these techniques, whilst not physically accurate, can often provide results that are in agreement with those obtained from quantum perturbation theory, although they involve far simpler calculations[4].

QED - a history of successes.

It has long been observed that the four fundamental forces of nature are gravity, electromagnetism, and the strong and weak nuclear forces. Quantum electrodynamics, a part of quantum field theory, provides us with a complete theoretical description of the second of these. R.P. Feynman has called QED "the jewel of physics—our proudest possession",[5] and it would not be an overstatement to say that this theory underlies every single aspect of chemistry. Not only does it unify elementary quantum mechanics and bring together quantum theory and relativity, but it also provides a prototype for theories that attempt to explain nuclear phenomena : quantum chromodynamics.

Some of the successes of QED include the calculation of the Lamb shift energy in the hydrogen emission spectrum, corrections to the magnetic moment of the electron, the rate of spontaneous emission of light from an excited atom (i.e. the Einstein A coefficient), scattering of light by free electrons, and, using the principle of renormalisation, a value for the electron rest-mass, m_o. All the above are examples of phenomena that could not be predicted by the classical theory.

QED is the most thoroughly checked theory of the subatomic world to date and the excellent correspondence of its theoretically predicted results and the experimentally measured ones gives testimony to its astounding accuracy. As an example of this, the discrepancy between the predicted and measured results for the magnetic moment of the electron is equivalent to a difference roughly the thickness of a human hair when measuring the distance from the east to west coasts of the USA[6].

After the advent of quantum mechanics in 1926, which provided a theory for the behaviour of electrons, there was the need to change the electromagnetic theory of Maxwell to bring it into line with the new developments of quantum mechanics. Dirac's first paper on the quantum theory of the electromagnetic field[7] appeared in 1927, and hence the theory of the interaction of light with matter, quantum electrodynamics, was born. From the outset, it provided many important results, but it was not until around 1948, when the principle of renormalisation was introduced, that finite and meaningful answers to questions concerning self-interactions of particles were able to be calculated. Since then, QED has been an exceedingly powerful tool for predicting events and providing results in phenomenal agreement with those observed.

Quantization of electromagnetic radiation - photons and probability amplitudes.

Light has long been considered to be made up of quanta of energy, called photons, and abundant evidence is available to support this hypothesis, an example being the photoelectric effect. However, there is one more feature that is essential to the understanding of the behaviour of light, and underscores the whole of the theory of quantum electrodynamics: the concept of probability amplitudes. A probability amplitude is a vector quantity, in the form of a complex number, associated with the movement of a photon from one point in space-time to another, and we can calculate the actual probability of any event occurring by taking the square of the modulus of this vector. We must consider that light will travel via all available routes and, additionally, we have the following rules for the combination of probability amplitudes:

1) If an event can occur in alternative ways, we must calculate the probability amplitudes for each of these different paths, then add them to obtain a final vector (whose square will give the total probability of the event taking place).

2) If an event occurs as a succession of steps, or depends on other events occurring concomitantly, then we must multiply the probability amplitudes for each of the steps in order to obtain a final value for the probability amplitude.[8]

This process of the combination of probability amplitudes can be illustrated by the following example, a variation of the Young two-slit experiment :

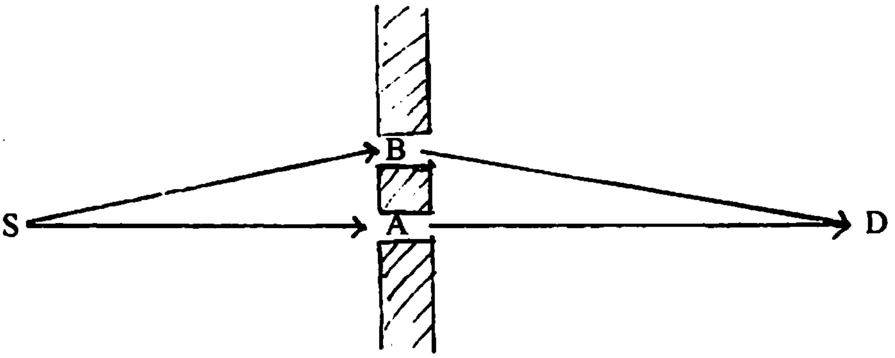

Fig. 1. *A low-intensity, monochromatic source, S, illuminates a screen with two closely-spaced slits A and B. A detector, D, registers the quantity of light reaching the other side.*

If the experimental set up is as shown in Fig. 1., we find a diffraction pattern produced on the other side of the screen, i.e. the amount of light registered at D varies between zero and a maximum value, depending on the separation between the two slits A and B. This can be understood by the fact that a photon from the source S has an amplitude to go via A *and* an amplitude to go via B. We must therefore add the two probability amplitudes : if these oppose each other we will get zero probability of the photon arriving at the detector, and if these reinforce each other we will get a maximum value, once we have squared the final probability amplitude.

If, however, we introduce detectors at A and B, capable of tracing the passage of a photon through either slit, we find that all interference effects disappear, and that the intensity of the light reaching D is constantly one half of the maximum value found previously. This can be understood by realising that we are now dealing with a system that has two distinguishable final states : a photon goes from S via A to D, *or* a photon goes via B to D. We must therefore calculate the probabilities for these two processes, then add the final *probabilities*, not amplitudes. Put another way, since "each photon interferes only with itself. Interference between different photons never occurs."[9], and as we are completely certain of the path taken by the photon, there is no other available path which it can take in order to produce interference phenomena.

The all-pervading importance of the concept of the probability amplitude cannot be overemphasised. Feynman has stated that the assertion of indeterminism was not the most fundamental innovation of quantum theory, and that "far more fundamental was the discovery that in nature the laws of combining probabilities were *not* those of the classical probability theory of Laplace"[10]. Dirac has taken a similar stand : ". . . I believe that the concept of the probability amplitude is perhaps the most fundamental concept of quantum theory. . ."[11].

The peculiar yet fundamental concept of the probability amplitude is responsible for *all* of the observable phenomena of light, from the refraction and reflection of light by water to the colours on soap bubbles and peacocks' tails, and it has an even greater rôle to play in the subatomic world, the realm of QED.

Interaction of light and matter - the coupling of electrons and photons.

In this section, in order to give an intuitive physical picture of the interactions that occur between photons and electrons we must make use of the idea of Feynman diagrams. A Feynman diagram is a two dimensional graph, with time as the y-co-ordinate and space as the x-co-ordinate. We can then "plot" the behaviour of particles within this system of co-ordinates. Conventionally, photons are represented by wavy lines, while massive particles are represented by straight lines. One of the results of quantum electrodynamics is that an electron has a certain amplitude to emit or absorb an electron, which is a constant. This coupling constant between charged particles and electromagnetic radiation is equivalent to the electric charge[12]. An example of such a coupling is shown in Fig. 2.

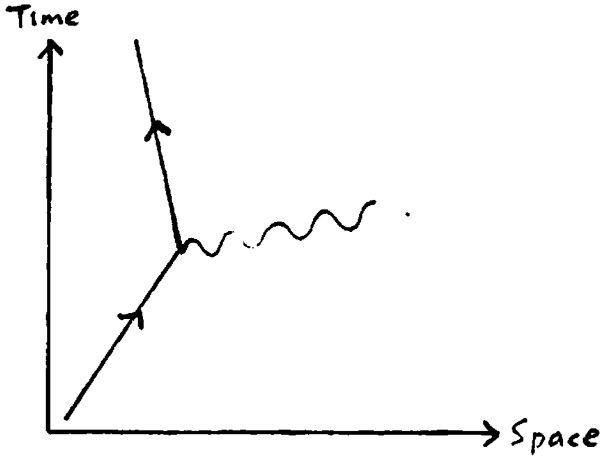

Fig. 2. *Feynman diagram for the coupling of an electron and a photon.*

The magnitude of the coupling between an electron and the electromagnetic field is related to a dimensionless constant known as the fine -structure (or Sommerfield) constant, α, that is defined by the following relationship:

$\alpha = 2\pi e^2/ch$ (this value is approximately equal to 1/137).

This constant was used by H.A. Bethe and others to compute a value for the Lamb Shift[13], thereby predicting an phenomenon that is unexplained by any other theory than QED.

A consequence of Dirac's relativistic treatment of the electron is the prediction of negative-energy particles. These particles are equal in mass to the electron but opposite in sign and are in fact positrons, the electron antiparticles. Feynman has interpreted these antiparticles as having acausal behaviour, and propagating backwards in time. When an electron and a positron combine, they annihilate each other, producing electromagnetic radiation (i.e. a photon) such as in Fig. 3. However, we must also consider the opposite case, which amounts to the same process, where a photon "materialises" to produce a positron and an electron pair[14] (Fig. 4). As the nature of the event observed depends only on the direction one takes in time, such interactions are simply referred to as couplings or collisions, and the causality or acausality of the events is therefore disregarded.

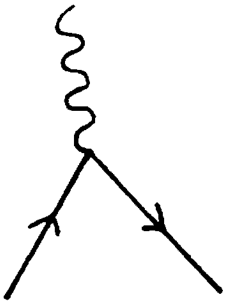

Fig. 3. *An electron and a positron annihilate each other to produce a photon.*

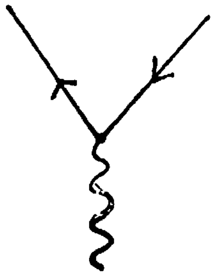

Fig. 4. *A photon "disintegrates", producing a positron and an electron pair.*

The application of the theory of quantum electrodynamics can now be summarised into three basic components. Firstly, the probability amplitude of a photon moving from point to point in space-time; secondly, the probability amplitude of an electron moving from point to point in space-time, and finally, the probability amplitude that there is a coupling between the two.

When we have taken into account the polarisation of the electrons (i.e. the Pauli exclusion Principle, discussed later), and when we analyse the above three elements using the laws of combination of probability amplitudes stated in the previous section, we can theoretically predict almost all the phenomena that are perceived by human senses.[15]

The exchange of photons - emission and absorption phenomena

By considering the problem of spontaneous emission, historically one of the earliest triumphs of quantum electrodynamics, we can shed light on some of the fundamental aspects of the theory. When Einstein examined the phenomenon of spontaneous emission, he gave the symbol A_{nm} to the probability that a spontaneous transition from an electronic state n to another state m (where $m < n$) will occur, with the accompanying emission of a photon. Later, Kramers and Heisenberg obtained a method to calculate the A_{nm} coefficient using quantum electrodynamic considerations. They found that :

$$A_{nm} = 8\pi e^2 |\mathbf{r}_{nm}|^2 \omega^3_{nm} / 3hc^3$$

Where $\mathbf{r}_{nm}$ is the matrix element connecting two atomic stationary states. In this way, the fundamental applicability of the theory to a process where a particle (photon) is produced was demonstrated.

I would now like to illustrate some of the concepts that are a consequence of QED by considering an example where we have an excited atom in free space. For this atom, the field acting on it can be divided conceptually into two parts. The first is the field from the atom, acting back on itself : this is termed the radiation reaction. The other is the zero-point or vacuum field : "empty" space has been shown by quantum electrodynamics to be composed of constant fluctuations. Classically, the de-excitation of the atom is attributed to the force of the radiation reaction damping the oscillating dipole, and the vacuum field does not contribute. The usual picture from QED is that spontaneous emission takes place as a result of the vacuum field fluctuations. This apparent contradiction is resolved via QED when we consider field operator orderings other than the normal-orderings used in the Heisenberg-picture approach[16]. In other words, the dilemma simply becomes a problem of interpretation with the two fields attributed with causing spontaneous emission being "two-sides of the same quantum-mechanical coin"[17].

The related process of stimulated emission (governed by the Einstein B coefficient, particularly relevant now that the phenomenon is commonplace due to the advent of the laser and its numerous applications, has also been treated quantum electrodynamically, with similar successful results. The theory has also predicted the observable phenomenon of the scattering of light by free electrons (Compton scattering). Following the processes outlined in the previous section can lead to an understanding of all processes of emission and absorption of photons, which, when treated using QED become simply an "exchange" of particles.

A QED Description of the Interactions Between Molecules[18].

Before discussing some of the more fundamental aspects of the theory of quantum electrodynamics in the next section, I would like to include a brief treatment of two aspects of the interactions that occur between molecules: the dispersion interaction and chiral discrimination. As stated in the introduction, this is a strictly qualitative account of the field of quantum electrodynamics. Therefore, I will make no attempt to derive the results, but instead will simply present them in order to serve as examples of the type of predictions that QED can be used to make, even when considering complex systems such as those involved in molecular interaction.

The Lennard-Jones Potential for two atoms of an inert gas, where r is the interatomic separation, predicts a long-range attractive force dependant on r^{-6} . This cohesive force, applicable not just to atoms but to neutral molecules beyond the overlapping distance, was attributed by London to the fluctuating transient dipoles induced by molecules in-phase with themselves. In quantum mechanical studies of this dispersion energy, London and Eisenschitz treated it as a second order effect of the electrostatic coupling. However, we will see that considerable improvements on these initial studies were possible within the framework of quantum electrodynamics.

In London's quantum theory of dispersion interaction the mechanism is through virtual[19] transitions in the molecules and it has been found that this is valid at short distances. To obtain a complete picture of dispersion forces, however, we must take into account the finite speed of propagation of light, which produces retardation effects. When these are accounted for, QED predicts a striking divergence from the classical view : the replacement .of the r^{-6} London dispersion term by an r^{-7} term at large intermolecular separation. This phenomenon, occurring when molecules are separated by a distance r much larger than the wavelengths of the molecular transitions (called the wave-zone) was predicted by Casimir and Polder[20] and later confirmed experimentally. For smaller separations (the near-zone), we find that the London potential applies, as was predicted initially.

The analysis of dispersion interactions using QED can be taken further when we consider the possibility of chiral discrimination. There is experimental evidence of discrimination in the interactions between enantiomeric forms of the same molecule and a quantum electrodynamical treatment of the dispersion interactions between chiral molecules predicts that chemically identical molecules of the same "handedness" repel, while those of opposite handedness attract. This interaction has been shown to be dependant on r^{-9} in the wave-zone, and r^{-6} in the near-zone[21].

Questions of Principle concerning QED

I would now like to leave the discussion of the application of quantum electrodynamics to molecular systems and instead concentrate on some of the more fundamental concepts involved in the theory, and any problems that are associated with it.

Dirac's original relativistic treatment of the electron predicted a value for its response to an external magnetic field, i.e. the magnetic moment of the electron. Later, measurements showed a very slight difference from this value, and it was realised that this correction term was due to the possibility that an electron could emit a photon and then re-absorb it (see Figs. 5 and 6), and other coupling processes that have an amplitude of occurring (Fig. 7). The accounting for the anomalous magnetic moment of the electron, and a subsequent prediction of its value is one of the great successes of QED, and the agreement with the experimentally measured result is phenomenal.

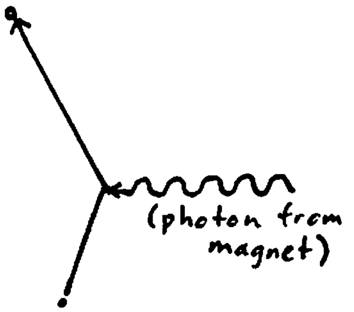

Fig. 5. *The Feynman diagram used for the first approximation to the magnetic moment of the electron, as calculated by Dirac.*

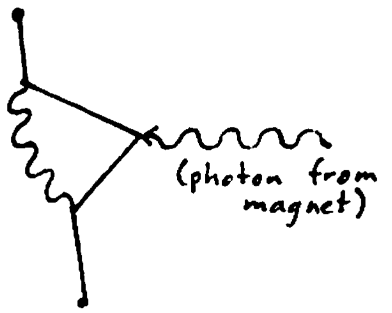

Fig. 6. *The Feynman diagram for the first correction term to the magnetic moment of the electron, the value of which was calculated by Schwinger in 1948.*

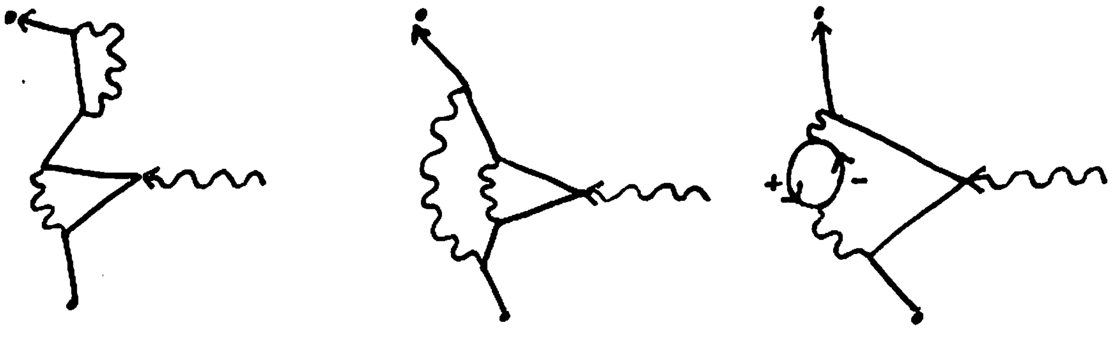

Fig. 7. *Feynman diagrams representing correction factors involving four extra couplings, including the creation of an electron-positron pair (far right).*

However, answers for the correction terms are dependent on a value for the "bare charge" of the electron, and it is here where difficulties arise.

The "bare charge" of the electron is the hypothetical charge of a point electron in the absence of any electromagnetic field. The problem arises in that real electrons can never be found in this state due to the effect of self-interaction (Fig. 8), for which the correction terms appear to be infinite. These difficulties were bypassed, but not solved, by the principle of renormalisation.

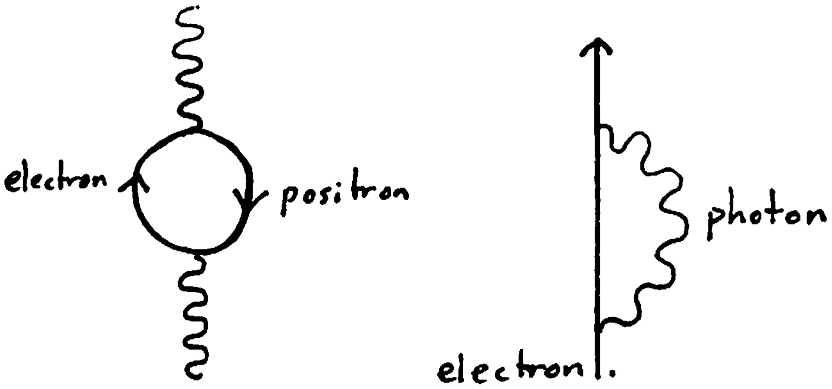

Fig. 8. *The self-interaction of electrons and photons.*

Feynman has called of renormalisation "a dippy process"[22] and stated:

> "Resorting to such hocus-pocus has prevented us from proving that QED is mathematically self-consistent"[23]

This view has also been expressed by others :

> "Although it is a completely satisfactory theory within a definite field of physical phenomena, modern quantum electrodynamics has the important drawback that in order to remove the divergences which arise in the theory additional concepts must be introduced which are neither contained in the fundamental formulation of the theory, nor reflected in its basic equations."24

It has been suggested that the lack of closure of the theory is due to the assumption that electrodynamics is totally isolated from the effects of the other three fundamental forces of nature (i.e. the strong, weak and gravitational interactions), and many theorists are today struggling to find a grand theory that would unify QED with the other forces. Whatever the fundamental reason, it does not detract from the resounding successes of QED in matching prediction to observation.

Another profound question arising in the context of QED is that of the actual electronic charge. To quote F. Rohrlich:

> "Given the minimum empirical data, i.e. any three data that determine the scales of length, time and mass such as m_e, h, and c, all other physical quantities should be derivable from theory. With units in which these are chosen as 1, why is the fundamental charge $e = (137)^{-1/2}$?"[25]

The question as to where this "magic" number comes from, though in no way hindering the application of QED, is still a great mystery.

Concluding Remarks

What I have attempted to present in this report is an overview of the vast and hugely powerful field of quantum electrodynamics. The fundamental equations governing the theory are believed to encompass all of atomic physics, chemistry, properties of bulk matter, and classical electromagnetics, and from it knowledge pertaining to all of these areas can be obtained. In fact, not only is it the most powerful theory ever in the realm of atomic physics, but it also serves as a prototype for a theory of nuclear interactions, quantum chromodynamics.

As QED is the theory behind all theories of molecular interaction, what sort of results can we hope for in the field of chemistry? A brief survey of recent literature has found QED applied to all manner of applications : the absorption of light by alkanes[26], flourescence lifetimes of polystyrene particles[27], lasers[28], semiconductor light-emitters[29], crystalline solids[30], not to mention the vast realm of spectroscopy[31], where it has found many of its greatest successes.

By considering the very nature of light and matter, quantum electrodynamics, the rigorous framework that underlies all of chemistry, cannot help but to add to the knowledge of humankind, and in doing so provide fundamental answers to unresolved mysteries of the microscopic world.

Footnotes

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[1] R.P. Feynman, *QED : The Strange Theory of Light and Matter*, Princeton University Press - Princeton NJ, (1985), p.152

[2] W.E. Thirring, *Principles of Quantum Electrodynamics*, Academic Press - London (1958), p.5.

[3] Semi-classical radiation theories treat the electromagnetic field classically while treating matter quantum mechanically.

[4] An good example is the calculation of the van der Waals forces between macroscopic objects, using stochastic electrodynamic theory. See T.H. Boyer, "A Brief Survey of Stochastic Electrodynamics", article in *Foundations of Radiation Theory and Quantum Electrodynamics*, Ed: A.O. Barut, Plenum Press - London (1980).pp. 49-64.

[5] R.P. Feynman, *QED : The Strange Theory of Light and Matter*, Princeton University Press - Princeton NJ, (1985), p.8.

[6] R.P. Feynman, *QED : The Strange Theory of Light and Matter*, Princeton University Press - Princeton NJ, (1985), p.7.

[7] P.A.M. Dirac, *Proc. R. Soc. London Ser. A* **114**, 243 (1927)

[8] R.P. Feynman, *QED : The Strange Theory of Light and Matter*, Princeton University Press - Princeton NJ, (1985), p.78.

[9] P.A.M. Dirac, *Principles of Quantum Mechanics*, 4th ed., Oxford University Press, London (1958), p. 9.

[10] R.P. Feynman, *Proceedings of the Second Berkeley Symposium on Mathematical Statistics and Probability*, University of California Press, Berkeley (1951), p. 533.

[11] P.A.M. Dirac, *Fields Quanta* **3**, 154 (1972).

[12] D.N. Lapedes, *McGraw-Hill Dictionary of Physics and Mathematics*, McGraw-Hill - London (1978).

[13] The Lamb Shift is the difference between the observed separation between the main components of the H_α line in the hydrogen spectrum, and its predicted value in the absence of quantum electrodynamic effects. This shift corresponds to the $2S_{1/2} \rightarrow 2P_{1/2}$ transition.

[14] As an interesting aside, Hawking's theory that black-holes are not really black (i.e. totally absorbing) rests on the idea that creation of positron-electron pairs near the event horizon can lead to one of the pair being "sucked in" while the other carries on in normal space. Thus do black holes "radiate" energy. (See S.W Hawking, *A Brief History of Time*, Bantam - London (1988))

[15] S.P. Parker, McGraw-Hill Encyclopaedia of Physics, McGraw-Hill - London (1983), p.895.

[16] For a complete discussion, see P.W. Milonni, *Phys. Lett. C* **25**, 1 (1976).

[17] I.R. Senitzky, *Phys. Rev. Lett.* **31**, 955 (1973).

[18] Much of the information in this section has been acquired from D.P. Craig & T. Thirunamachandran, *Molecular Quantum Electrodynamics*, Academic Press - London (1984), Chap. 7, pp.142-182.

[19] Processes of emission and absorption are referred to as being virtual due to the fact that they are not subject to conservation of energy. This is only applicable to intermediate states, however, as final states have to be so constrained.

[20] H.B.G. Casimir & D. Polder, *Phys. Rev.* **73**, 360 (1948)

[21] For calculations of this type, see Craig and Thirunamachandran, p.166 onwards.

[22] R.P. Feynman, *QED : The Strange Theory of Light and Matter*, Princeton University Press - Princeton NJ, (1985), p.128

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[23] R.P. Feynman, *QED : The Strange Theory of Light and Matter*, Princeton University Press - Princeton NJ, (1985), p.128

[24] A.I. Akhiezer & V.B. Berestetskii, *Quantum Electrodynamics*, Interscience - London (1965)

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[28] W. Becker, *Laser Part. Beams* **1991**, 9(2), 603-18.

[29] M. Yamanishi, *Japanese Journal of Applied Physics part 1*, **31-9A**, pp.2764-85, (1992).

[30] Numerous examples are available in the journal *Radiation Effects and Defects in Solids*.

[31] For a recent example in the field, see G.Gangopadhyay, *Phys. Rev. A*, **1991**, 93(11), p. 6424-

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