1 Quantization of Light and Matter

1.1 Why bother building ‘quantum mechanics‘ as a framework?

> All material particles have wave properties, which can be exhibited under suitable conditions. We have here a very striking and general example of the breakdown of classical mechanics—not merely an inaccuracy in its laws of motion, but *an inadequacy of its concepts to supply us with a description of atomic events.*
>
> – **P. A. M. Dirac** *The Principles of Quantum Mechanics* (4th ed., 1958)

In this section, we would like to walk through some experiments that illustrate Dirac’s claim and interestingly, several of them would involve shining light on stuff.

The Double Slit Experiment

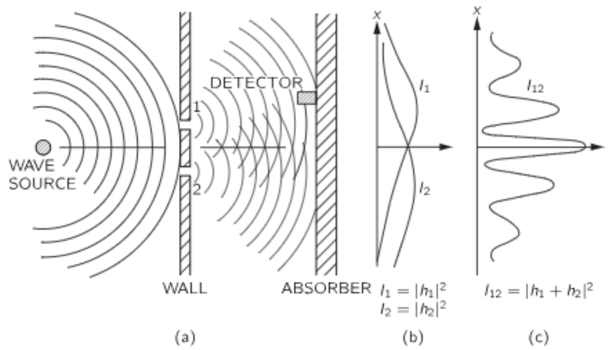

Fig. 1–2. Interference experiment with water waves.

Figure 1: Interference Experiment. Image Source: *The Feynman Lectures on Physics, Volume 3, Chapter 1, Fig. 1-2.*

As you may recall, the double slit experiment involves shining a coherent source of light on a screen with two closely spaced slits, with a screen placed at a suitable distance behind the slits (Young, 1804). The observation of interest is how the screen shows multiple peaks and troughs instead of two bands, indicating that light shows a ‘wave’ nature.[1]

The Most Beautiful Experiment in Physics[2]

The observations from the double-slit experiment with light cohere with the picture of electromagnetism, and can be perfectly explained by the addition of amplitudes of incident waves. Fascinatingly, the same thing happens with matter!

In 1974[3], Pier Giorgio Merli, Gian Franco Missiroli and Giulio Pozzi submitted an article where they describe a parallel experiment with electrons instead of light (Merli et al., 1976).

[1] This is an experiment that can be easily recreated at home with a laser pointer and a thin object, like a strand of hair or a small spring. The YouTube channel ’Looking Glass Universe’ presents a wonderful video that you may follow along to see the phenomenon yourself.

[2] In 2002 readers of *Physics World* voted Young’s double-slit experiment with single electrons as "the most beautiful experiment in physics" of all time. (Rosa, 2012). A documentary of the experiment was made in 2010. The most beautiful experiment (2010)

[3] A careful reader would notice that 1974 is nearly 50 years after the foundation of Quantum Mechanics was laid. Motivation for the wave-like properties of matter were provided with an experiment by C. Davisson and L. H. Germer that showed electrons being diffracted by crystals. The Merli-Missiroli-Pozzi experiment was chosen for its close parallel with Young’s Double-Slit experiment with light.

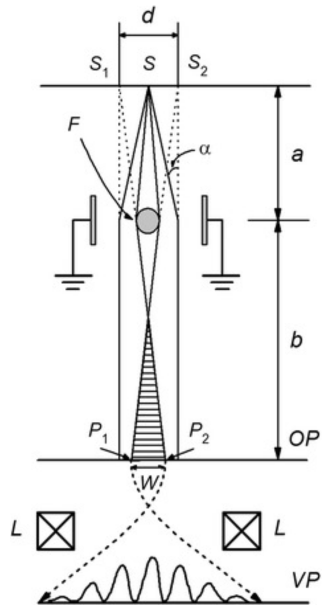

Figure 2: Schematic diagram of Merli, Missiroli and Pozzi's electron-biprism experimental apparatus. The electron beam would either deflect towards each other or away based on the sign of the potential used. Image Source: (Rosa, 2012) Fig. 2

Their set-up consisted of a thin wire placed between two grounded plates. The wire was set to a voltage V, causing electrons pointed at the set-up to deflect. These deflected electrons strike an observation plate, the signal from which is amplified and sent to a display.

The authors state that "a non-localized interference pattern will be produced". Even more striking is the observation that the interference pattern is formed even when the number of electrons incident is only one or a few.

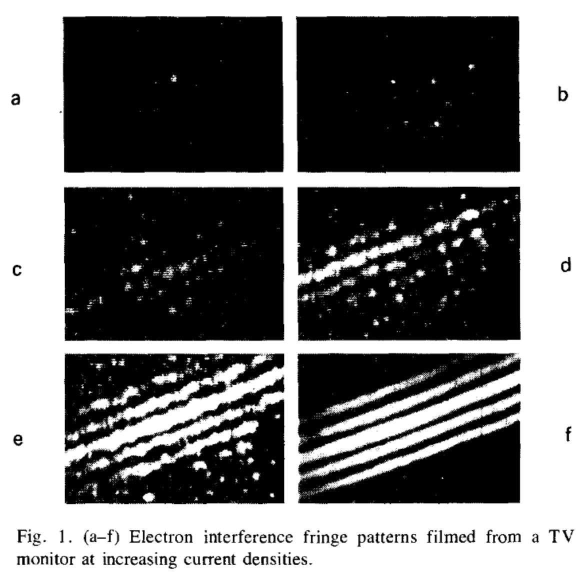

Figure 3: Image Source: (Merli et al., 1976) Fig. 1
The effect of the interference pattern can be equivalently observed if the current density is decreased so that on average only one or few electrons arrive at the final screen, but the storage time is increased to the order of minutes, giving the effect of the pattern being filled in as the experiment progresses.

If we were to think of electrons like particles, this observation would be quite unsettling. How are 'particles' interfering to produce the observed pattern? Moreover, how is a pattern observed even if only one electron passes through the apparatus at a given time?

The Photoelectric Effect

In 1887, Heinrich Hertz observed a curious phenomenon (Hertz, 1887). His apparatus consisted of a coil with a spark gap, and the spark would indicate detecting electromagnetic waves. To see the spark better, he enclosed the apparatus in a dark case and noticed that the length of spark observed decreased. He repeated the experiment with a multitude of materials, and noted that how transparent the enclosure is to UV light seemed to play an effect.[4]

A series of experiments following these observations eventually led the discovery of what is called the "Photoelectric Effect" which is the emission of electrons from a material caused by electromagnetic radiation. Once again, as you may recall from high-school physics, the emission of electrons was governed by the frequency of light shone on the metal, and increasing the intensity of light of lower frequency than necessary did not result in the emission of electrons. Albert Einstein, in his 1905 article, translated to "On a Heuristic Point of View about the Creation and Conversion of Light" wrote:

> the energy of a light wave emitted from a point source is *not* spread continuously over ever larger volumes, but consists of a finite number of energy quanta that are spatially localized at points of space, move without dividing and are absorbed or generated only as a whole.

This description sounds eerily similar to Einstein referring to light being like particles. We end the section quoting Feynman (*The Feynman Lectures on Physics, Volume 3, Chapter 1*)

> "Quantum mechanics" is the description of the behavior of matter and light in all its details and, in particular, of the happenings on an atomic scale. Things on a very small scale behave like nothing that you have any direct experience about. They do not behave like waves, they do not behave like particles, they do not behave like clouds, or billiard balls, or weights on springs, or like anything that you have ever seen.

Atomic Spectra

Over a series of experiments performed in the 1800s, it was observed that atoms emitted light whose spectrum

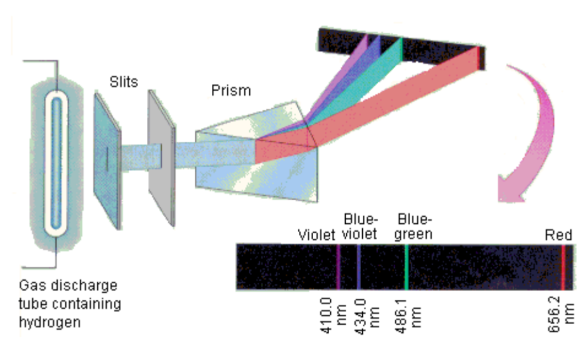

Figure 4: Image Source: https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch6/bohr.html

was discrete, moreover, the spectrum was unique to each element. The atomic spectrum of hydrogen turns out to be particularly important to the story of the development of Quantum Mechanics.

[4]Perhaps ironically, it was Hertz' experiments from around the same time that provided experimental support to electromagnetic waves as predicted by Maxwell.

In 1885, Balmer noted that the wavelengths of the visible spectral lines of hydrogen could be represented by a simple mathematical formula, and in 1888, Rydberg generalized Balmer's formula to predict the complete atomic hydrogen spectrum.

In 1913, Niels Bohr presented his theory of the atom, where he postulated stable electron orbits, that electromagnetic radiation is absorbed or emitted in quantized amounts, and a condition on the nature of stationary orbits allowed. These discretized circular orbits seemed to provide a solution, but had the issue of radiation and eventual collapse of the atom.

While the Bohr Model maps well to the empirically found Rydberg formula, better motivation for the conditions on the allowed stationary orbits and why an atom, once excited would spontaneously emit a photon and de-excite is not entirely evident.

Spontaneous Emission, and its Inhibition

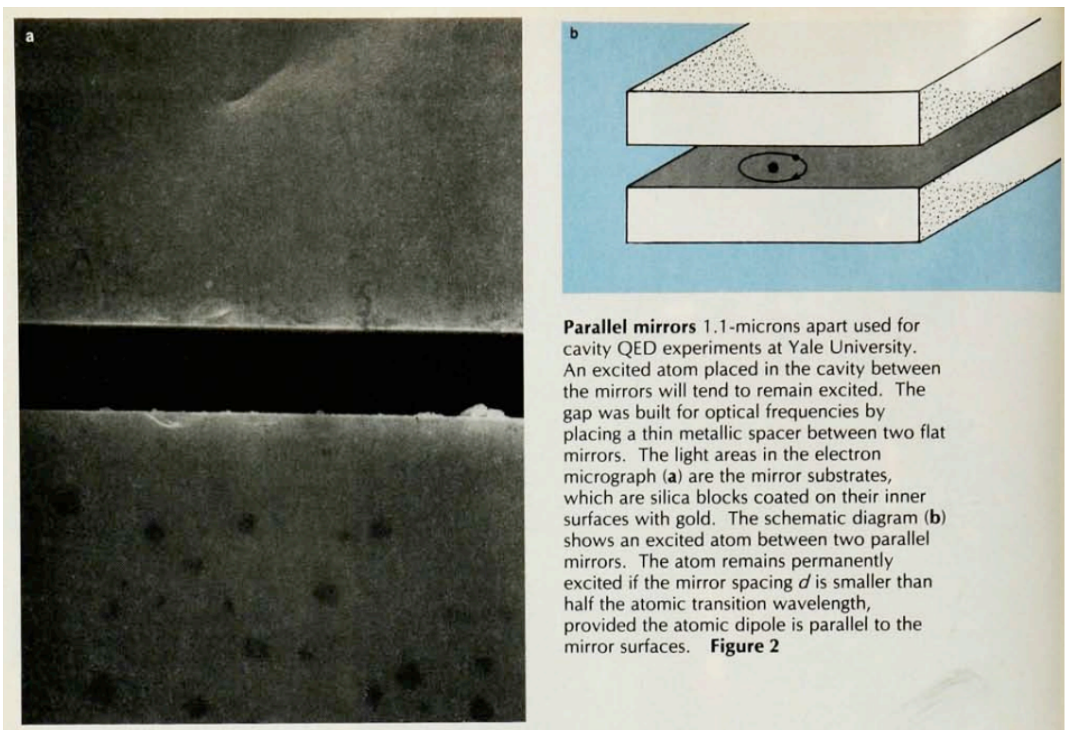

Figure 5: Image Source: Cavity Quantum Electrodynamics, Physics Today, January 1989, Fig. 2

An oscillating electric dipole radiates electromagnetic energy. In a purely semiclassical picture, where the atom is treated quantum mechanically but the electromagnetic field is classical, a stationary excited state has no oscillating dipole moment and therefore would not radiate. In such a description, an excited atom would remain indefinitely excited. The very existence of spontaneous emission thus signals the inadequacy of a purely classical treatment of the electromagnetic field and points toward the necessity of its quantization, with profound consequences for our understanding of the vacuum.

One might argue that spontaneous emission is almost too obvious to worry about. The notion that an excited atom could remain excited forever feels far-fetched; intuition suggests that something excited must de-excite, much like the saying, "What goes up, must come down." Yet what is truly striking is that this apparently inevitable process can be strongly suppressed or even effectively "turned off", simply by altering the electromagnetic environment in which the atom resides. In 1985, Hulet, Hilfer and Kleppner[5] (Hulet

[5] You may recognize this name from his famous introductory physics textbook co-authored with Kolenkow.

et al., 1985) from M.I.T. demonstrated "turning off" spontaneous emission, by being able to keep highly excited atoms in their excited state for approximately 20 times longer than usual.

The authors achieved this by confining highly excited Cesium atoms (excited to n=22, nearly sufficient to ionize the atom!) between reflective metallic plates about 230 μm apart. Analogous to how only certain wavelengths are allowed for standing waves on a string fixed at both ends, only certain wavelengths of light are allowed between the reflective plates, provided the polarization of the said radiation is parallel to the mirrors to observe the inhibited effect.

A group at Yale performed the experiment at an even smaller scale. They also showed that emission was not inhibited if the atomic dipole was rotated - the emitted radiation was no longer constrained by the boundary conditions imposed by the reflecting plates.

The cavity prevents the atom emitting a photon (think of it as quanta of energy referred to in Bohr's postulates), a phenomenon that might be called "no-photon interference".[6] De-excitation is not something purely dependent on the atom alone!

In 1925, Heisenberg published his *Umdeutung* paper and in 1927, proposed the 'uncertainty relation'.[7] The key idea is that there is a limit to the precision to which certain physical properties, such as position and momentum, or by analogy, as we will see soon, the electric and magnetic fields, can be simultaneously known.

This particular quantum feature implies that the fluctuations of the electric and magnetic fields cannot simultaneously vanish, not even in the darkest possible room—in the electromagnetic vacuum, in the absence of even a single photon.

Casimir Effect

Another phenomenon whose explanation is closely related to the feature above is the observation that two neutral, reflective plates feebly attract each other by a force other than the gravitational attraction between the two!

Controlling the Rate of Chemical Reactions

With the demonstration of inhibited spontaneous emission, it becomes interesting to ask whether other

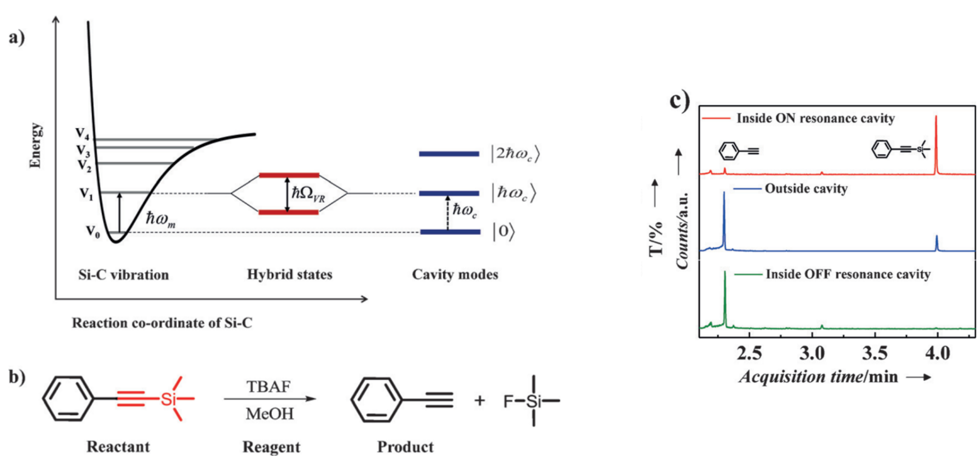

Figure 6: Image Source: Thomas et al. (2016), Fig. 1-3
(a) The cavity is tuned such that it is resonant with the Si-C vibrational transition in 1-phenyl-2-trimethylsilylacetylene (PTA) resulting in hybrid light-matter (polaritonic) states. (b) The silane deprotection reaction of PTA whose rate was controlled by the Ebbesen group. (c) GC-MS chromatograms of silane deprotection reactions carried out inside the cavity when it is ON resonance (red trace), OFF resonance (green trace) and outside the cavity (blue trace).

[6] The reader is referred to the excellent article by Nobel Prize winner Serge Haroche, who was among the scientists on the Yale team referred to in the main text. https://www.scientificamerican.com/article/cavity-quantum-electrodynamics/

[7] He received the Nobel Prize in 1933 for "the creation of quantum mechanics, the application for which has, inter alia, led to the discovery of the allotropic forms of hydrogen".

electronic or molecular transitions could be controlled. Would it be possible to carry out chemical reactions selectively at certain bonds in a molecule? Can we modify/ control the mechanisms by which molecules react?

The Ebbesen group submitted a paper in 2016, in which they studied the deprotection reaction of 1-phenyl-2-trimethylsilylacetylene (PTA) with tetra-*b*-butylammonium fluoride (TBAF). They injected liquid PTA into a cavity consisting of parallel mirrors separated by a distance of around 6 μm which was tuned precisely to be in resonance with the vibrational transitions of the Si-C bond in PTA.

The results of their experiment were dramatic (Figure 6 (c)). 20 minutes into the reaction, the ratio of the product to the reactant was evidently different! Coupling the vibrational mode of the Si-C bond had significantly altered the chemical reactivity of the molecule, resulting in much larger concentrations of the reactant than when the cavity was off-resonant, or when the reaction was carried out outside the cavity. This experiment showed that the 'strong-coupling' of the vibrational modes with the cavity could provide new possibilities for reaction control and to study reaction mechanisms!

Conclusion These experiments have brought to light[8] the "the inadequacy of concepts to supply us with a description of atomic events". They also provide a unique opportunity to control and study chemical reactions.

[8] sorry for the extremely bad pun.

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