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N68-19038 (ACCESSION NUMBER)
(THRU)
15 (PAGES)
1 (CODE)
23 (CATEGORY)
CR-93557 (NASA CR OR TMX OR AD NUMBER)
FACILITY FORM 602

GPO PRICE $ _____
CFSTI PRICE(S) $ _____
Hard copy (HC) 3.00
Microfiche (MF) .65
ff 653 July 65

February 1968

Center For Theoretical Studies
University of Miami/Coral Gables, Florida 33124

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* Work supported in part by the National Aeronautics and Space Administration and in part by the U. S. Air Force Office of Scientific Research.

** Work supported by the Advanced Research Projects Agency Contract SD-90.

A misconception which most physicists acquire in their formative years is that the photoelectric effect requires the quantization of the electromagnetic field for its explanation. The following quotation taken from a widely used physics text book[1] illustrates the point.

> "Einstein's photoelectric equation played an enormous part in the development of the modern quantum theory. But in spite of its generality and of the many successful applications that have been made of it in physical theories, the equation
>
> $$h\nu = E + \phi \tag{1}$$
>
> is, as we shall see presently, based on a concept of radiation - the concept of 'light quanta' - completely at variance with the most fundamental concepts of the classical electromagnetic theory of radiation".

In fact we shall see that the photoelectric effect may be completely explained <u>without</u> invoking the concept of "light quanta". To be sure, certain aspects of nature require quantization of the electromagnetic field for their explanation, for example:

1. Planck distribution law for black body radiation (1900),
2. Compton effect (1926),

3. Spontaneous emission (Dirac, 1927),

4. Electrodynamic level shifts (1947).

The photoelectric effect is definitely not included in the foregoing list. It is an historical accident that the photon concept should have acquired its strongest early support from Einstein's considerations on the photoelectric effect.

The physicists of the early years of this century deserve great credit for realizing that "something" had to be quantized. The very existence of atoms, (Bohr, 1913), requires the finiteness of Planck's constant to be taken into account for the behavior of the atomic electrons. However, once granted the existence of atoms, we shall see that all of the experimental photoelectric phenomena are described by a theory in which the electromagnetic field is treated classically while only the matter is treated quantum mechanically. These phenomena include (a) the Einstein photoelectric relation (1), (b) the linear relationship between photocurrent and light intensity and (c) observations at low radiation levels where photoelectrons are obtained after times of illumination insufficient for "accumulation" in an atom of enough energy to liberate an electron, i.e., $> \phi$.

A more detailed account of the theory of photoelectron emission, in which both the detector (atomic electrons) and the electromagnetic field (photons) are quantized, is published elsewhere.[2]

Our model for a photodetector consists of a collection of completely independent atoms. Each atom has one electron[3] and is bathed in a classical electromagnetic field, for which the electric field is

$$E(t) = E_o \cos \nu t \, . \tag{2}$$

As indicated in Fig. 1, the atom has a ground state $|g\rangle$, and a quasi-continuum of excited states $|k\rangle$ which are normalized in a length L very large compared to atomic dimensions, so that the k levels will approximate a continium when L is eventually allowed to become infinite. Photoelectron emission involves a transition from $|g\rangle$ to any of the $|k\rangle$ states. The Hamiltonian[4] for the electron as it interacts with the field is

$$H = H_o - eE(t)x, \tag{3}$$

where H_o is the Hamiltonian of the unperturbed atom, x is the atomic coordinate operator and e is the negative electronic charge. It is convenient to go into the interaction picture so that the interaction Hamiltonian becomes

$$V(t) = - eE(t)x(t), \tag{4}$$

where

$$x(t) = \exp\left\{iH_o t/\hbar\right\} x \exp\left\{-iH_o t/\hbar\right\} . \tag{5}$$

The nonvanishing matrix elements of (5) are of the form

$$\begin{aligned} \langle k|V(t)|g\rangle &= - ex_{k,g}\, E(t) \exp\left\{i\varepsilon_k t/\hbar\right\} , \\ \langle g|V(t)|k\rangle &= - ex_{g,k}\, E(t) \exp\left\{-i\varepsilon_k t/\hbar\right\} , \end{aligned} \tag{6}$$

where ε_k is the energy of the kth excited state measured relative to the ground state. We ignore transitions between excited states, i.e., we are interested in knowing if the atom is ionized, not in what happens to the electron once it is in the quasi-continuum. The photoelectron density matrix obeys the equation of motion

$$\frac{d\rho}{dt} = (-i/\hbar)\left[V(t),\rho(t)\right] \tag{7}$$

which has the formal solution

$$\rho(t) = \rho(0) - (i/\hbar)\int_0^t dt'\left[V(t'),\rho(t')\right] . \tag{8}$$

It is convenient to substitute Eq. (8) into (7) to obtain the alternative form for the time rate of change of the electronic density matrix

$$\frac{d\rho}{dt} = (-i/\hbar)\left[V(t),\ \rho(0)\right] + (-i/\hbar)^2\left[V(t),\ \int_0^t dt'\left[V(t'),\rho(t')\right]\right] \tag{9}$$

as in reference (2).

Let us now proceed to derive the relation

$$h\nu = E + \phi \ , \tag{10}$$

where E is the kinetic energy of the liberated electron and ϕ the work function of the detector. The energy distribution of the ejected electron is given by the diagonal elements of the electron density matrix, $\rho_{k,k}(t)$. The lowest order contribution to $\rho(t)$ is obtained by placing $\rho(0)$ in the right hand side of Eq. (8), using the V(t) given by (3), and noting that the only nonvanishing matrix element of $\rho(0)$ is $\rho_{g,g}(0) = 1$, we find

$$\rho_{k,k}(t) = (-i/\hbar)^2 \int_0^t dt' \int_0^{t'} dt'' \langle k| \left[V(t'), [V(t''), \rho(0)] \right] |k\rangle , \tag{11}$$

$$\rho_{k,k}(t) = \hbar^{-2} \int_0^t dt' \int_0^{t'} dt'' \Big[ex_{k,g} E_o \cos \nu t' \exp\left\{ i\varepsilon_k t'/\hbar \right\} \rho_{g,g}(0)$$

$$\times \, ex_{g,k} E_o \cos \nu t'' \exp\left\{ -i\varepsilon_k t''/\hbar \right\} \Big] + \text{c.c.} \tag{12}$$

Evaluation of the integral (12) with neglect of small non-resonant terms gives

$$\rho_{k,k}(t) \approx \frac{4 |ex_{k,g} E_o/2\hbar|^2 \sin^2\left\{ (\varepsilon_k \hbar^{-1} - \nu) t/2 \right\}}{\left\{ \varepsilon_k \hbar^{-1} - \nu \right\}^2} \ . \tag{13}$$

It is clear that an electron will be raised to the kth excited state with appreciable probability only if

$$\varepsilon_k \approx \hbar\nu, \tag{14}$$

with an energy spread of order

$$|\Delta\varepsilon_k| \approx \hbar/t, \tag{15}$$

which quickly becomes experimentally undetectable. We denote by $\phi = \varepsilon_1$ the energy of the first state of the quasi-continuous spectrum. This is the ionization energy of the atom, or work function of the photodetector. Measuring the energy $E > 0$ of the liberated electron from the ionization energy by setting

$$\varepsilon_k = \phi + E \ , \tag{16}$$

one has the desired Einstein photoelectric equation

$$\hbar\nu = \phi + E \ . \tag{17}$$

Equation (17) can only be satisfied if $\hbar\nu > \phi$, and we see that the energy dependence of the ejected photoelectrons obeys the Einstein relationship even for a <u>classical</u> radiation field illuminating <u>quantized</u> atoms. The concept of a photon is not needed.

The total probability $P(t)$ for finding a photoelectron is given by

$$P(t) = \sum_k \rho_{k,k}(t). \tag{18}$$

This may be evaluated for the lowest order expressions (13) by replacing the sum over k by an integral over ε

$$\sum_k \ldots. \rightarrow \int d\varepsilon\sigma(\varepsilon)\ldots., \tag{19}$$

where $\sigma(\varepsilon)$ is the number of states per unit range of ε. In the familiar manner, (13) becomes effectively

$$\rho_{k,k}(t) \approx 2\pi|ex_{k,g} E_o/2\hbar|^2 \delta(\varepsilon\hbar^{-1}-\nu)\, t \tag{20}$$

and (18) takes the time proportional form

$$P(t) = \gamma\, t, \tag{21}$$

where the constant γ is

$$\gamma = 2\pi\hbar\sigma(\hbar\nu)|ex_{k,g}/2\hbar|^2 E_o^{\,2}. \tag{22}$$

This formula implies a "rate" of transitions γ for each atom of a collection of independent atoms. This derivation provides a solution to an exercise proposed by Schiff[5]. It should be noted that (22) is proportional to the light intensity. Equation (21) certainly does not imply the "time delay" which some people used to expect for the photoelectrons produced by a classical e.m. field. The perturbation begins to mix the excited states into the electronic wave function as soon

as it is turned on. Of course, the calculation of P(t) refers to a probability for an ensemble in a typically quantum mechanical manner, and statistical fluctuations would be inevitable, but as shown elsewhere[2], are fully and satisfactorily describable by the theory.

In most time dependent problems one is contented with a result like (21), correct to lowest order perturbation theory. Because of the simplicity of the model for our photodetector, it is possible to carry out the calculation to all orders in the perturbation, and hence to have an example where rate equations are rigorously justified.

We begin by noting that, from Eq. (8), P(t) obeys the relations

$$\frac{dP(t)}{dt} = \frac{d}{dt} \sum_k \rho_{k,k}(t)$$

$$= (-i/\hbar)^2 \sum_k \langle k| \left[V(t), \int_0^t dt' \, [V(t'), \rho(t')] \right] |k\rangle, \tag{23}$$

or writing out the matrix product explicitly, observing (6)

$$\frac{dP(t)}{dt} = -(1/\hbar^2) \int_0^t dt' \sum_k \Big[V_{k,g}(t)\, V_{g,k}(t')\, \rho_{k,k}(t') + \rho_{k,k}(t')$$

$$\times V_{k,g}(t')\, V_{g,k}(t) \Big] + (1/\hbar^2) \int_0^t dt' \sum_k \Big[V_{k,g}(t')\, \rho_{g,g}(t')$$

$$\times V_{g,k}(t) + V_{k,g}(t)\, \rho_{g,g}(t')\, V_{g,k}(t') \Big] . \tag{24}$$

Since $\rho_{g,g}(t')$ and all $\rho_{k,k}(t')$ are positive and their sum is unity, it is clear that the $\rho_{k,k}(t')$ have an upper bound as functions of k. This may be estimated in the following fashion. It was seen from Eq. (15) that only the quasi-continuous states k in a range of energy

$$|\Delta\varepsilon_k| \approx \frac{\hbar}{t} \tag{25}$$

(given by an uncertainty principle) are appreciably excited. The number N of these states is about

$$N = (\hbar/t)\ \sigma(\hbar\nu). \tag{26}$$

At this stage in the calculation we might not be sure that the k dependence of $\rho_{k,k}(t')$ is given by the perturbation result (13), but the exact distribution[6] certainly cannot be appreciably sharper than given by (15). We may then estimate an upper bound for the $\rho_{k,k}(t')$ by

$$\rho_{k,k}(t') \lesssim N^{-1} \sum_k \rho_{k,k}(t') = \Big[1 - P(t')\Big]/N\ . \tag{27}$$

The density of states $\sigma(\hbar\nu)$ is proportional to the normalization length L, and hence as $L \to \infty$, we have $N \to \infty$ and all $\rho_{k,k} \to 0$, while

$$\rho_{g,g}(t') = 1 - P(t') \tag{28}$$

remains finite for any finite time t'. Then as $L \to \infty$ the terms in (24) involving $\rho_{k,k}(t')$ can be neglected compared to those involving $\rho_{g,g}(t')$ so Eq. (24) becomes

$$\frac{dP(t)}{dt} = \sum_k \int_0^t dt' \left| ex_{k,g} E_o/2\hbar \right|^2 \exp\left\{ i(\varepsilon_k \hbar^{-1} - \nu)(t-t') \right\} \rho_{g,g}(t') + c.c. \tag{29}$$

Replacing the sum over k by an integral over excited state energies ε, and using (28), we obtain

$$\frac{dP(t)}{dt} = \int d\varepsilon \; \sigma(\varepsilon) \int_0^t dt' \left| ex_{k,g} E_o /2\hbar \right|^2 \exp\left\{ i(\varepsilon\hbar^{-1} - \nu)(t-t') \right\} \left[1 - P(t') \right] + c.c. \tag{30}$$

The integral over ε leads to a delta function $2\pi\hbar\delta(t-t')$ multiplied by some slowly varying factors evaluated at resonance $\varepsilon = \hbar\nu$, and after doing the t integration we find the simple differential equation

$$\frac{dP(t)}{dt} = \gamma \left[1 - P(t) \right] , \tag{31}$$

where the rate constant γ has the value (22) indicated by the perturbative theory. The solution of this differential equation $P(t) = 1 - e^{-\gamma t}$ is intuitively obvious.

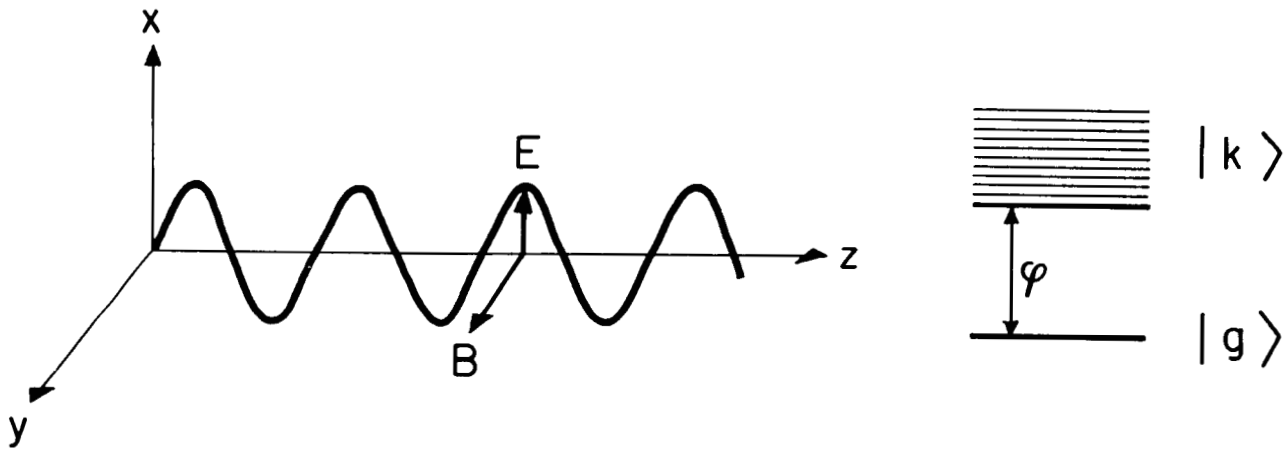
In conclusion, we understand the photoeffect as being the result of a classical field falling on a quantized atomic electron. The introduction of the photon concept is neither logically implied by nor necessary for the explanation of the photoelectric effect.

FOOTNOTES

1. F. K. Richtmyer, E. H. Kennard, T. Lauritsen, Introduction to Modern Physics, 5th ed. (McGraw Hill, New York 1955) p. 94.
2. M. O. Scully and W. E. Lamb, Jr., Phys. Rev. (to be published, 1968.)
3. For simplicity we consider the problem to be one dimensional with electric field and motion of the electron confined to the x axis.
4. Only the electric dipole part of the perturbation is taken, i.e., retardation and magnetic effects are neglected. This approximation is made only to simplify the equations.
5. L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1955), p. 220, problem 2.
6. This supposition can eventually be confirmed by examining equation (30).

FIGURE CAPTION

Classical field falling on atom having ground state $|g\rangle$ and continuum of excited states $|k\rangle$, lowest excited state energy is ϕ.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