Use of the Image Potential for the Surface Photoelectric Effect

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The surface photoelectric effect in metals is calculated taking account of the image force between electron and metal. The result is an increased number of slow electrons and a somewhat steeper maximum of the photoelectric effect as a function of the illuminating frequency. No agreement with experiment is obtained because the reflection and refraction of the light has not been taken into account.

QUANTUM mechanics affords a means for attacking the problem of the photoelectric effect. Near the threshold frequency the photoemission from metals arises because of the rapid change in the potential at the surface. Mitchell has given a convenient method for treating this surface photoelectric effect by means of stationary wave functions.[1] In this method the light is treated as a perturbation, which is found to add to the unperturbed solution of the wave equation a term representing outgoing waves or an electron emission. Mitchell has assumed a potential step at the surface of the metal, for it is then possible to express the solution with elementary functions. But it is only because of the change in the potential at the surface that there is any emission. It, therefore, is to be expected that the result is sensitive to the form of the potential assumed. For moderate distances from the surface of the metal the Schottky effect shows that the image potential is correct. It is also satisfactory with respect to reflection, since it has a very small reflection coefficient, thus giving the experimentally required Maxwellian velocities of thermionic electrons. The potential step fails in this respect since it gives rise to a large selective reflection of slow electrons. Further we do not need the exact form of the potential very near the surface as the wave function is no longer sensitive to the variations in the potential since the potential is already very low. Therefore the image potential seemed a suitable choice all the way from the metal to infinity.

The metal was treated essentially as an electron well containing free electrons. The wave-length of the light was assumed very long compared to that of the electrons, and refraction and reflection were neglected. Inside the metal the solution of the wave equation is given by plane waves. Sufficiently far outside the WKB solution is satisfactory because the potential variations are small compared to the potential. These solutions were joined by numerical integration from 1A to 10A. Continuity conditions and normalization to fit the Fermi-Dirac electron distribution in the metal determined all the constants, and hence the emission. The numerical work was carried out for potassium with a work function of 1.9 volts and a well of depth 3.8 volts.

The result of these calculations was compared with that obtained by using the potential step, and will be found in Table I. For a given fre-

TABLE I. *Comparison of calculations used in the image potential and that using the potential step.*

Initial State (volts)	Incident Light (cm^{-1})	Final State (volts)	Image Potential ($10^5 \times$electrons/quantum/volt*)	Potential Step ($10^5 \times$electrons/quantum/volt*)
−1.95	16500	.06	$5.28 \times \sin^2\theta/\cos\theta$	$3.60 \times \sin^2\theta/\cos\theta$
	20600	.57	2.43	3.45
	24600	1.07	1.26	2.16
	28700	1.58	.72	1.36
	32800	2.04	.42	.87
	37000	2.56	.30	.60
−2.46	20600	.06	21.10	14.85
	24600	.57	11.13	15.30
	28700	1.07	6.18	10.20
	32800	1.58	4.11	6.84
	37000	2.04	2.55	4.59
	41000	2.56	1.68	3.30
−2.96	24600	.06	16.92	12.36
	28700	.57	10.17	14.19
	32800	1.07	6.42	10.26
	37000	1.58	4.05	7.08
	41000	2.04	2.61	5.04
−3.56	28700	.06	9.66	7.14
	32800	.57	6.48	8.88
	37000	1.07	4.29	6.54
	41000	1.58	2.67	4.74

* i.e., to obtain the photoelectric yield integrate over the width of the electron band in volts.
θ = angle of incidence of the light.

[1] Mitchell, Proc. Roy. Soc. **A146**, 442 (1934).

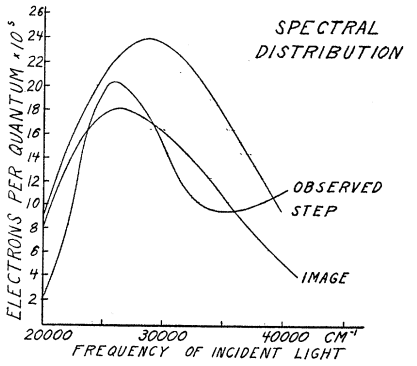

FIG. 1. Photoelectric current-observed values and values calculated from image forces and potential step.

quency it will be noticed that there is a larger percentage of slow electrons if one uses the image potential. For electrons of 0.1 volt energy the image potential gives a larger number, but for energies of 1 volt or more the potential step gives the larger. This comes about as the result of two opposing factors. Firstly the potential step gives rise to greater transition probabilities between the bound states and states with sufficient energy for the electron to escape from the metal. This results since the wave function oscillates less rapidly near the metal because the potential is higher than for the image potential and therefore contributes more to the matrix element. On the other hand considerable reflection occurs at the potential step especially for small energies. This second factor predominates when the energy of the electron is less than 0.1 volt, but becomes small when the energy is larger than this.

If one plots the total emission against frequency there results the curves shown in Fig. 1. As is to be expected from the above results one finds near the threshold frequency a greater yield of electrons. Also the maximum occurs at a slightly lower frequency and then falls off somewhat more rapidly than with the potential step. The reason is to be found in the fact that the rise in the curve occurs as it becomes possible to remove electrons from deeper lying levels. On reaching the lowest electron level the decreasing transition probability causes the emission to fall off except as the increasing transmission delays this, as it does for the potential step. Comparison with Suhrmann and Theissing's experimental curve[2] shows, however, that even the image potential yields a less rapid decline than experiment demands. To compare the absolute magnitude of the photoelectric yield the angle of incidence must be known. Suhrmann and Theissing do not give the angle of incidence they used; it was taken to be 60°. Other reasonable choices might change the emission by a factor of two.

So far no account has been taken of the reflection and refraction of the light occurring at the surface of the metal. If this is done, the vector potential of the light is no longer a constant, but fluctuates widely in the region where the photoelectric effect arises. To give a correct quantum mechanical treatment is an arduous task, even for the potential step, but Schiff and Thomas[3] have shown that above a certain frequency the photoelectric emission falls off. This critical frequency seems to be characterized by the fact that the vector potential of the light wave becomes infinite at some point in the metal. In a phenomenological description this would correspond to zero dielectric constant at that point. A reasonable estimate of the critical frequency leads to a value near the observed maximum of the photoelectric effect. The effect of the refraction and reflection introduces into the distribution curve a maximum sharper than that found by us and in better agreement with experiment.

Although the introduction of the image potential alone has failed to bring about complete agreement with experiment, the large changes introduced into the velocity distribution and the absolute magnitude of the yield, shows that a complete theory must consider the correct image force on the electron as well as the reflection and refraction of the light.

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[2] Suhrmann and Theissing, Zeits. f. Physik **52**, 453 (1928).
[3] Schiff and Thomas, Phys. Rev. **47**, 860 (1935).