

The following selenium compounds have been examined:—

TABLE VI.

Berzelianite, $Cu_2Se$ .	Strikerum Mine, Småland.
	White sublimate at $440^\circ$ .
Eucairite, $Cu_2S, Ag_2Se$ .	Loc. as above.
	Tr. of red subl. at $380^\circ$ .
	White subl. at $410^\circ$ .
Clausthalite, $PbSe$ .	Tilkerode; Harz.
	Tr. of red subl. at $340^\circ$ .
	White subl. at $600^\circ$ .

## LEAD.

The sublimate formed in air is  $PbO$ . It forms a yellowish sublimate which shows bluish-white where it thins out on the margins. The yellow colour intensifies upon heating. Owing to its high specific gravity much of it falls into the lower glass. Under the microscope it is finely granular. It is soluble in solution of  $KHO$  and in  $HCl$ .

The formation of this sublimate is at a higher temperature than that at which the mineral breaks up. Massicot, as an olive-yellow slag, first forms gradually on the hob as the mineral decomposes. This melts at about  $930^\circ$ , sublimation beginning at a temperature approximating to  $1000^\circ$ , when it progresses steadily. The sublimate is, therefore, obtained below the temperature of volatilization of  $Bi_2O_3$  and above that of  $TeO_2$ , but unless the temperature be carefully attended to there is risk of lead oxide volatilizing along with the latter sublimate.

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## II. On the Interaction between Radiation and Free Electrons.

By J. H. JEANS, M.A., F.R.S.\*

1. **T**HERE is now very general agreement that for a system of matter and æther to give Planck's formula for the radiation in its final steady state, the motion of the system must be in some way different from that predicted by the classical laws of dynamics as summarized in the principle of Least Action.

The problem of finding a new system of laws which shall lead to Planck's formula is as yet unsolved. In our present state of knowledge the problem is largely one of guessing, and the lucky guess has not yet been made. On the other

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hand, a problem which admits of scientific and ordered treatment is the following: to examine at what exact point or points it is necessary to break with the old dynamics in order to obtain Planck's formula for the final partition of radiant energy.

To begin with, there is nothing incompatible with Planck's formula in the classical laws of propagation of light in free æther. It is well known that the partition of energy is not changed by propagation in free æther—any law of partition persists indefinitely so long as no interaction between æther and matter occurs. Stated analytically, the argument runs as follows:—If  $F(\lambda, T)d\lambda$  is an initial partition of energy, then the final law is  $F(\lambda, T)d\lambda$  also, and since this is general enough to include Planck's law, no break need be made with the old dynamics as regards propagation in free æther.

Next, there is nothing incompatible with Planck's formula in the classical laws of thermodynamics as applied to radiant energy. For according to these laws, if  $F(\lambda, T)d\lambda$  is the initial partition of energy, the final law, after an infinite number of thermodynamical processes, can be shown to be of the form  $\phi(\lambda T)\lambda^{-5}d\lambda$  (Wien's law), in which  $\phi$  is a function which cannot be determined by purely thermodynamical reasoning. Since this final law is general enough to cover Planck's law, we may conclude that there is nothing in the thermodynamical theory of radiation which is incompatible with Planck's law. Thus Planck's law in no way compels us to abandon the classical laws of either propagation or of reflexion, compression, &c. of radiation, so long as these latter processes are effected by ideal walls such as are imagined in thermodynamics. The classical laws may stand for free æther and for ideal matter: it is when we come to real matter that the break with the classical laws must be made if we are to arrive at Planck's formula.

In the present paper an attempt is made to carry the investigation further along these lines. The simplest system of real matter which can be imagined is a single electron. I have tried to examine whether there is anything inconsistent with Planck's law in the classical laws of interaction between radiant energy and a single free electron. To answer this, it is necessary to investigate what would be the final law of partition of radiant energy in a system in which the radiant energy started from any initial law of partition, and had this law modified by encounters with a single free electron, the laws of interaction being assumed to be the classical laws. The question is: Will the final law be general enough to include Planck's law?

2. A single ray of light propagated parallel to the axis of  $x$  may be taken to be given by

$$\begin{aligned} X=0, \quad Y=A \cos \kappa(x+Vt), \quad Z=0, \\ \alpha=0, \quad \beta=0, \quad \gamma=-A \cos \kappa(x+Vt). \end{aligned}$$

The equations of an electron moving freely in this field according to the classical laws, will be

$$\begin{aligned} m\ddot{x} &= -eA \frac{\dot{y}}{V} \cos \kappa(x+Vt) + \left[ \frac{2}{3} \frac{e^2}{V^3} \ddot{x} + \dots \right] \\ m\ddot{y} &= eA \cos \kappa(x+Vt) + eA \frac{\dot{x}}{V} \cos \kappa(x+Vt) + \left[ \frac{2}{3} \frac{e^2}{V^3} \ddot{y} + \dots \right] \\ m\ddot{z} &= \left[ \frac{2}{3} \frac{e^2}{V^3} \ddot{z} + \dots \right], \quad \dots \dots \dots (1) \end{aligned}$$

in which the terms in square brackets represent the retarding force on the electron produced by its own emission of radiation. If the frequency of the light is  $p$ , so that  $p=\kappa V$ , the ratio of these terms to those on the left-hand sides of the equations is of the order of magnitude  $\frac{2}{3} \frac{e^2}{mV^3 p}$ . Giving to  $m$  its electromagnetic value  $\frac{2}{3} \frac{e^2}{aV^2}$ , this ratio is equal to  $pa/V$  or  $2\pi a/\lambda$ .

We are searching for the point of departure between the true laws and the classical laws, and this departure is known, from observation, to be most pronounced at low temperatures, at which all the radiation is of great wave-length, and the motion of free electrons is very slow. We may accordingly limit ourselves to the consideration of the problem for low temperatures, in the certainty that if a break with the classical laws is necessary, this special problem will disclose it. This limitation makes it legitimate to neglect  $a/\lambda$ , and therefore to omit all the terms in square brackets in the above equations. Further, it permits us to disregard variation of mass with velocity, and so to treat  $m$  as constant.

The equations simplified in this way become

$$\left. \begin{aligned} m\ddot{x} &= -eA \frac{\dot{y}}{V} \cos \kappa(x+Vt) \\ m\ddot{y} &= eA \cos \kappa(x+Vt) + eA \frac{\dot{x}}{V} \cos \kappa(x+Vt) \\ m\ddot{z} &= 0. \end{aligned} \right\} \dots \dots (2)$$

Put  $x+Vt=\xi$ , so that  $\dot{\xi}=\dot{x}+V$ ,  $\ddot{\xi}=\ddot{x}$ , and the equations become

$$\begin{cases} m\ddot{\xi} = -eA \frac{\dot{y}}{V} \cos \kappa\xi, \\ m\dot{y} = eA \frac{\dot{\xi}}{V} \cos \kappa\xi, \end{cases}$$

of which obvious first integrals are

$$\begin{aligned} \dot{\xi}^2 + \dot{y}^2 &= u^2 \\ \dot{y} &= \frac{eA}{\kappa m V} \sin \kappa\xi + v, \end{aligned}$$

where  $u, v$  are new constant velocities. Eliminating  $\dot{y}$ , we obtain as the equation for  $\xi$ ,

$$\dot{\xi}^2 = u^2 - \left( v + \frac{eA}{\kappa m V} \sin \kappa\xi \right)^2,$$

or putting  $\theta = \tan \frac{1}{2} \kappa\xi$ ,

$$\frac{4}{\kappa^2} \dot{\theta}^2 = (u^2 - v^2)(1 + \theta^2) - \frac{4eA}{\kappa m V} v\theta(1 + \theta^2) + \frac{4e^2 A^2}{\kappa^2 m^2 V^2} \theta^2.$$

From this the value of  $\theta$  may be written down as an elliptic function of the time, but the solution is of greater complexity than is either convenient or necessary for our purpose.

The same reason which enabled us to limit ourselves to low temperatures also permits us to consider only the case in which the light is of feeble intensity—we may neglect squares of  $A$ . The equation now becomes identical with

$$\frac{4}{\kappa^2} \dot{\theta}^2 = (u^2 - v^2) \left[ 1 + \theta^2 - \frac{2eAv\theta}{(u^2 - v^2)\kappa m V} \right]^2,$$

or, if  $u^2 - v^2 = w^2$ , so that  $w$  is another constant velocity,

$$\frac{2}{\kappa} \dot{\theta} = w \left( 1 - \frac{2eAv}{w^2 \kappa m V} \theta + \theta^2 \right),$$

leading to the integral

$$\tan \frac{1}{2} \kappa\xi = \tan \frac{1}{2} \kappa w t + \frac{eAv}{w^2 \kappa m V},$$

in which we avoid adding a constant of integration if we  
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suppose the origin from which  $t$  is measured to remain indefinite. We readily obtain

$$\xi = wt + \frac{eAv}{w^2 \kappa^2 m V} \cos \kappa wt,$$

and hence

$$\left. \begin{aligned} x &= (w - V)t + \frac{eAv}{w^2 \kappa^2 m V} \cos \kappa wt \\ y &= vt - \frac{eA}{w \kappa^2 m V} \cos \kappa wt \\ z &= w_0 t \end{aligned} \right\} \dots (3)$$

in which, strictly speaking, constants of integration must be added to  $x$ ,  $y$ ,  $z$ , and  $t$ .

It now appears that the motion of the electron may be regarded as compounded of

- (i.) a uniform velocity of translation,  $u_0, v_0, w_0$ ;
- (ii.) oscillations parallel to the axes of  $x$  and  $y$ , each of a purely harmonic nature, and of frequency  $\kappa w$ .

Since  $w = u_0 + V$ , the result is such as might have been anticipated from the Doppler theory, but it is not easy to give a rigorous proof without a detailed examination of the equations of motion.

3. The electron will, according to the classical dynamics, absorb light of frequency  $\kappa V$ ; it will emit light whose frequency will vary according to the direction of emission, the frequency in any direction being obtained by modifying the frequency of oscillation  $\kappa w$  in accordance with Doppler's principle.

Let polar coordinates  $r, \theta, \psi$  be taken, the axis of  $x$  being taken for  $\theta = 0$ , and the plane of  $xy$  for  $\psi = 0$ . The velocity of the electron has a component in the direction  $\theta, \psi$  equal to

$$u_0 \cos \theta + v_0 \sin \theta \cos \psi + w_0 \sin \theta \sin \psi,$$

so that the frequency, say  $q$ , of the radiation emitted in this direction will be given by

$$q = \frac{\kappa w}{V} (V - u_0 \cos \theta - v_0 \sin \theta \cos \psi - w_0 \sin \theta \sin \psi). \quad (4)$$

Let us assume the distribution in different directions of the radiation emitted by the electron to be

$$I(\theta, \psi) \sin \theta d\theta d\psi.$$

Let  $c_0^2$  stand for  $u_0^2 + v_0^2 + w_0^2$ , and let the mean-square velocity of the electron, averaged over a great length of time, be  $c^2$ . Let the proportion of the whole time during which the velocity components lie within a small range  $du_0 dv_0 dw_0$ , be

$$A f\left(\frac{u_0^2 + v_0^2 + w_0^2}{c^2}\right) du_0 dv_0 dw_0.$$

Then the total radiant energy emitted by the electron per unit time will, on the average, be

$$\iiint A f\left(\frac{u_0^2 + v_0^2 + w_0^2}{c^2}\right) I(\theta, \psi) \sin \theta d\theta d\psi du_0 dv_0 dw_0, \quad (5)$$

the integration being over all values of  $\theta, \psi, u_0, v_0$ , and  $w_0$ , and the frequency of any element of the light being given by equation (4).

To analyse this radiation according to frequency, we may change the variables from  $u_0, v_0, w_0, \theta$ , and  $\psi$  to  $u_0, w_0, \theta, \psi$ , and  $q$ . Writing  $q_0$  for  $\kappa V$ , the frequency of the incident light, we have

$$v_0 = \frac{1}{\sin \theta \cos \psi} \left\{ V - u_0 \cos \theta - w_0 \sin \theta \sin \psi - \frac{q}{q_0} \frac{V^2}{V + u_0} \right\}$$

$$\frac{\partial v_0}{\partial q} = -\frac{1}{q_0} \frac{V^2}{(V + u_0) \sin \theta \cos \psi},$$

whence integral (5) may be written in the form

$$\begin{aligned} A \int dq \iiint f \left\{ \frac{1}{c^2} (u_0^2 + w_0^2) + \frac{1}{c^2} \operatorname{cosec}^2 \theta \sec^2 \psi \right. \\ \left. \times \left( V - u_0 \cos \theta - w_0 \sin \theta \sin \psi - \frac{q V^2}{q_0 (V + u_0)} \right)^2 \right\} \\ \times I(\theta, \psi) \frac{1}{q_0} \frac{V^2}{(V + u_0)} \operatorname{cosec} \theta \sec \psi d\theta d\psi du_0 dw_0, \quad (6) \end{aligned}$$

of which the form after integration is

$$\int \frac{1}{q_0} \Phi\left(\frac{q}{q_0}, c^2\right) dq. \quad (7)$$

4. Suppose the electron is in a region of space in which the law of partition of radiant energy is  $\phi(q_0) dq_0$ , the energy being distributed at random as regards direction. Suppose that unit energy of frequency  $q$  is, as the result of interaction with the electron, after unit time replaced by energy  $\theta(q_0)$  of the original frequency  $q_0$ , and a spectrum  $\int F(q_0, q) dq$  of

scattered energy. By the result of § 3,  $F(q_0, q)$  must be of the form

$$F(q_0, q) = \frac{1}{q_0} \Phi\left(\frac{q}{q_0}, c^2\right), \quad \dots \quad (8)$$

and so, by the conservation of energy,

$$1 - \theta(q_0) = \int_0^\infty F(q_0, q) dq = \int_0^\infty \Phi\left(\frac{q}{q_0}, c^2\right) \frac{dq}{q_0}.$$

On integration this last is a function of  $c^2$  only, so that  $\theta(q_0)$  does not depend on  $q_0$ , and may be replaced by  $\theta$ .

The law of partition of the whole energy after unit time is

$$\int dq_0 \theta \phi(q_0) + \int dq \int_0^\infty \phi(q_0) F(q_0, q) dq_0,$$

or arranged according to frequency  $q$ ,

$$\int dq \left[ \theta \phi(q) + \int_0^\infty \phi(q_0) F(q_0, q) dq_0 \right]. \quad \dots \quad (9)$$

If the radiation in the space is to be in temperature equilibrium with the electron, the partition of energy must be unaltered by the interaction between the electron and the radiation. The final partition of energy (9) must accordingly be identical with the initial partition of energy  $\int dq \phi(q)$ . Thus we must have

$$\theta \phi(q) + \int_0^\infty \phi(q_0) F(q_0, q) dq_0 = \phi(q),$$

or by equation (8)

$$\phi(q) [1 - \theta] = \int_0^\infty \phi(q_0) \Phi\left(\frac{q}{q_0}, c^2\right) \frac{dq_0}{q_0}, \quad \dots \quad (10)$$

and the partition of energy required,  $\phi(q)$ , is the solution of this integral equation.

The equation may be written

$$\int_0^\infty \frac{\phi(q_0)}{\phi(q)} \left(\frac{q}{q_0}\right) \Phi\left(\frac{q}{q_0}, c^2\right) d\left(\frac{q_0}{q}\right) = 1 - \theta,$$

or, if  $q_0 = uq$ ,

$$\int_{u=0}^{u=\infty} \frac{\phi(uq)}{\phi(q)} \Phi\left(\frac{1}{u}, c^2\right) \frac{du}{u} = 1 - \theta,$$

so that the ratio of  $\phi(uq)$  to  $\phi(q)$  must be independent of  $q$ .

The solution is easily found to be

$$\phi(q) = Cq^n, \quad \dots \quad (11)$$

in which  $C$  and  $n$  are constants.

5. It is at once obvious that this form cannot include Planck's formula. Thus we have seen that there is nothing (so far as the evidence of the radiation formula goes) which is untrue in the ordinarily assumed laws for free æther, or in the ordinarily assumed thermodynamical laws, but it now appears that there must be something untrue in the equations which have been used as the basis of the analysis of §§ 2, 3. It is somewhere in these equations that the break between the classical dynamics and the true dynamics must occur.

6. Any attempt to localize still more definitely the exact point of failure of the classical equations must of necessity involve a detailed discussion of the equations of which we have made use.

In equations (1) it may first be noticed that the terms in square brackets, representing *emission*, have not been used at all—equations (1) were immediately replaced by equations (2) because it was found that the terms in equation (1) in square brackets were negligible for the particular crucial problem we were testing. Nothing, then, is to be gained by discussing whether the terms in square brackets are accurate or inaccurate. But two assumptions have been made about the emission—first that the emission terms in equation (1) may be neglected for the special problem under consideration, and, second, (in § 3), that a simple-harmonic motion of a free electron results in an emission of light of the same frequency. Both these assumptions must of course be regarded as being under suspicion.

For the rest, we have assumed the truth of equations (2), which are simply the equations of action of electric and magnetic forces on an electron as a whole. Experiments on electrons moving in electric and magnetic fields (*e. g.* determinations of  $e/m$ ) seem to indicate that these equations are at least true for steady fields, and, so long as we assume that the action on an electron at any instant depends solely on the field at that instant, it is hard to see how the equations can fail to be true for varying fields also.

One other assumption has been implied: namely, that a single free electron in a field of radiant energy is a possible dynamical system. It may be that the simplest system which can be considered is not a single free electron but a tube of force with an electron at one end and a positive charge at the other.



7. Apart from these speculations, the definite result seems to emerge, that the departure from the classical mechanics is to be looked for in the fundamental equations of æther and electricity. Nothing so complicated as the structure of matter appears to be involved. It is not a question of modifying our ideas (in so far as we have ideas) on the build of atoms or molecules: we are called on to revolutionize views which have long been regarded as well-established on the nature or meaning of electricity, æther, or radiation.

III. On Canonical Relations in General Dynamics.  
By Professor A. GRAY, F.R.S.\*

1. IN a paper on General Dynamics (Proc. R. S. E., Feb. 19, 1912) I have derived Hamilton's principal function S, and the parallel function S' [§ 5, (1) below], with the corresponding partial differential equations, by a direct process not involving the calculus of variations. Hamilton's Principle and the Principle of Least Action may, as exemplified below, be deduced from the functions S, S', and it will be seen that the use of the two functions facilitates the proof and discussion of various other theorems.

It may be recalled that the canonical equations of a system, unacted on by friction, and defined by k coordinates, q<sub>1</sub>, q<sub>2</sub>, ..., q<sub>k</sub>, that is the 2k equations of the type

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}, \quad \frac{dq}{dt} = \frac{\partial H}{\partial p} \dots \dots \dots (1)$$

can, as Jacobi proved, be replaced by finite equations, if the complete integral of the Hamiltonian differential equation

$$\frac{\partial S}{\partial t} + H\left(\frac{\partial S}{\partial q_1}, \frac{\partial S}{\partial q_2}, \dots, \frac{\partial S}{\partial q_k}, q_1, q_2, \dots, q_k, t\right) = 0 \dots (2)$$

can be found.

Here

$$H = \Sigma(p\dot{q}) - T + V, \dots \dots \dots (3)$$

and p(=∂T/∂q̇) is derived from T, the kinetic energy expressed as a function of the q's, q̇'s, and, it may be, of t. Since the solution of a dynamical problem consists in the expression of the values of the coordinates, the velocities (the q̇'s) [or the momenta (the p's)] in terms of t and initial

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values a<sub>1</sub>, a<sub>2</sub>, ..., a<sub>k</sub>, b<sub>1</sub>, b<sub>2</sub>, ..., b<sub>k</sub>, say, of the q's and p's, H can be expressed for time t in terms of the a's, the b's, t and τ, or, if we please, in terms of the p's, the q's, and t. It is desirable for clearness to state explicitly in all dynamical relations which are obtained what are the variables in terms of which the different quantities are supposed to be expressed.

2. It is not unusual to assume tacitly that the reciprocal relations discussed in §§ 6....11 below, when established, in form, as consequences of the fact that two successive partial differentiations of a certain function of the initial and final coordinates (or momenta) are commutative, hold also when the quantities of which derivatives are taken are quite differently expressed. For example from the relation

$$\frac{\partial S}{\partial a_i} = -b_i \dots \dots \dots (1)$$

where S is a function of the q's and the a's, and therefore so also is b<sub>i</sub>, we get, since ∂S/∂q = p,

$$\frac{\partial p}{\partial a_i} = -\frac{\partial b_i}{\partial q} \dots \dots \dots (2)$$

Now the dynamical relation which is of real practical importance is one of exactly the same form, which holds when p is expressed as a function of the initial coordinates and momenta and t, while b<sub>i</sub> is expressed as a function of the final coordinates and momenta and t. It is one of the objects of the present paper to supply the necessary proof of the permanence of form here exemplified by a particular case of a very general property of canonical relations.

3. The determination of the complete integral of (2) § 1, consists in finding S as a function of q<sub>1</sub>, q<sub>2</sub>, ..., q<sub>k</sub>, t, and k coordinates α<sub>1</sub>, α<sub>2</sub>, ..., α<sub>k</sub> (which may be the k initial coordinates, or any k independent functions of these) and τ, the initial value of the time, which, if it is convenient to do so, may be taken as zero. The finite equations are then

$$\frac{\partial S}{\partial \alpha_1} = \beta_1, \dots, \frac{\partial S}{\partial \alpha_k} = \beta_k \dots \dots \dots (1)$$

If a<sub>1</sub>, a<sub>2</sub>, ..., a<sub>k</sub>, the initial coordinates are used, the finite equations become, as is well known, and will be shown in what follows,

$$\frac{\partial S}{\partial a_1} = -b_1, \dots, \frac{\partial S}{\partial a_k} = -b_k \dots \dots \dots (2)$$