



XIII. The binding of electrons by atoms

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is steered with increasing velocity down towards the middle, where the cars can pass and repass without difficulty.

To avoid a deep hole in the sink in the middle, the profile can change to the parabola of a forced vortex, where

$$v = \mu x, \quad n = 2, \quad y = \frac{x^2}{2p}, \quad NG = p, \quad \lambda = \frac{1}{4}GV = \frac{1}{2}SP.$$

On a horizontal circle of this track of one lap to the mile, NP=840 feet; described in two minutes at 30 miles an hour, NV=60 feet, and $\cot \theta = \frac{NP}{NV} = 14$, a slope of 4° .

Raise the speed to 60 miles an hour on this track, NP=420, NV=270, feet, and the slope is nearly 30° , the circuit of two laps to the mile made in 30 seconds.

At a speed limit of 90 miles an hour, NP=280, NV=540, feet; round a circle of three laps to the mile, on a slope of over 62° . The surface could then change to a paraboloid; with a flat area in the middle, where a car could come to rest.

XIII. *The Binding of Electrons by Atoms.* By J. W. NICHOLSON, F.R.S., *Fellow of Balliol College, Oxford* *.

ACCORDING to the quantum theory of atomic structure and of the emission of line spectra, the paths of the electron in the atom vary according to the particular co-ordinates used in the process of quantizing the separate momenta. Thus in the simple case of a hydrogen atom, containing a nucleus and one electron, we may use either spherical polar or parabolic coordinates, and the admissible orbits are entirely different in the two cases. Yet the final values of the atomic energy are the same, and consequently each method yields the same theoretical spectrum. It has been suggested that there is in fact, in every case, only one type of coordinates which can be used, when all the modifying circumstances, such as the variation of the mass of the electron with speed, are taken into account. The only problems yet solved are those in which the separation of variables, after the manner of Jacobi, can be effected, and the contention is in fact that there is, in every case, only one set of coordinates which allows this separation, when non-degenerate cases of the motion are discussed.

But it is generally believed that the atomic energy is in all cases determinate and definite. We shall show, in the

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first place, that this conclusion requires modification when the path extends to infinity. The hyperbolic orbits of Epstein, which have been used extensively in the interpretation of certain groups of γ rays associated with many of the chemical atoms, constitute an instance, and we shall show that they rest on a mathematical error, and that in fact it is not possible to preserve finite phase-integrals in the process of quantizing the momenta. In fact, it appears that the whole process is only applicable to finite paths, and gives no clue to the phenomena taking place during the binding of an electron which comes from a considerable distance.

In another form, the question we propose is as to whether a hyperbolic path is possible in the same way as an elliptic one. Such would, of course, be characterized by a *positive* energy W . Certain available evidence of a simple kind, apparently not hitherto noticed, is in existence. For the existence of such paths involves the existence of parabolic paths, with $W=0$. In passage from a stationary state of energy W_1 (negative) to a parabolic path taking the electron outside the atom altogether, a quantity of energy W_1 should be involved. Spectral lines given by

$$h\nu = W_n,$$

where W_n corresponds to any one of the stationary states, should thus exist. In other words, the 'limits' of spectral series should themselves be spectral lines. But there are two reasons why evidence on these lines cannot be decisive, especially when it is negative evidence. For in the first place, the values of W_n determining the limits of series are of such magnitude that only for two or three, in any case, can the corresponding lines come into the visible spectrum, and with only hydrogen atoms and charged helium atoms to test, and enormous band spectra for both elements, the test cannot readily be applied. Moreover, the probability of an electron entering the atom in a parabolic rather than a hyperbolic path is so small that any resulting lines could hardly be expected to be of visible intensity under ordinary conditions. We consider, therefore, that the question whether limits of series are themselves spectral lines, on the principles of the quantum theory, cannot, at least at this juncture, be examined in the light of experiment, and that it must remain a matter of deduction from other phenomena.

We find it necessary, as stated, to disagree with the hypothesis, explicitly indicated several times by Sommerfeld and others, and implicitly assumed at least by the remaining

writers on the quantum theory of spectra, that the energy W is always completely determinate when all the momenta are quantized. This can be disproved not only for fictitious laws of force in an atom, but for laws which must actually occur in systems with an existence, if only a temporary one.

Consider, for example, a simple doublet and an electron in orbital motion about it. Regarding the doublet as stationary, and of moment M , its external potential is

$$V = \frac{M \cos \theta}{r^2}$$

when it is situated at the origin, with its axis along the axis of z , using spherical polar coordinates. The equation of energy for an electron moving in its presence is

$$\frac{1}{2}m \{ \dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \sin^2 \theta \dot{\phi}^2 \} + \frac{Me \cos \theta}{r^2} = -W.$$

The momenta are, in the usual notation,

$$p_1 = \frac{\partial T}{\partial \dot{r}} = m\dot{r}, \quad p_2 = \frac{\partial T}{\partial \dot{\theta}} = mr^2\dot{\theta},$$

$$p_3 = \frac{\partial T}{\partial \dot{\phi}} = mr^2 \sin^2 \theta \dot{\phi},$$

so that

$$\frac{1}{2}m \left\{ p_1^2 + \frac{p_2^2}{r^2} + \frac{p_3^2}{r^2 \sin^2 \theta} \right\} + \frac{Me \cos \theta}{r^2} = -W.$$

Now ϕ is a speed coordinate as usual, so that

$$p_3 = \text{const.} = n_1 h / 2\pi$$

when subjected to the quantum relation, n_1 being an integer.

For the Jacobi solution, we must also take, in separating variables,

$$p_2^2 + \frac{p_3^2}{\sin^2 \theta} + 2mMe \cos \theta = \beta$$

where β is constant, and

$$\frac{1}{2}m \left\{ p_1^2 + \frac{\beta}{r^2} \right\} = -W.$$

Thus

$$p_1 = \sqrt{-2mW - \frac{\beta}{r^2}}.$$

With a positive W , the motion is not real. Thus W must be negative and the path necessarily extends to infinity. A critical value of r is $\sqrt{\frac{\beta}{-2mW}}$, and the other is infinity.

The phase-integral for p_1 is

$$2 \int_{\sqrt{\frac{\beta}{-2mW}}}^{\infty} p_1 dr$$

which is infinite, but nevertheless independent of W . For writing

$$r = \sqrt{\frac{\beta}{-2mW}} \cdot \sigma, \quad \text{it becomes}$$

$$\begin{aligned} 2 \int_1^{\infty} \sqrt{-2mW} \left(1 - \frac{1}{\sigma^2}\right)^{\frac{1}{2}} \sqrt{\frac{\beta}{-2mW}} d\sigma \\ = 2 \sqrt{\beta} \int_1^{\infty} d\sigma \left(1 - \frac{1}{\sigma^2}\right)^{\frac{1}{2}} \end{aligned}$$

A finite integral is secured,—Epstein's procedure, for instance,—by using the phase-integral not for p_1 , but for $p_1 - (p_1)_{r=\infty}$, which in the same way yields

$$2 \sqrt{\beta} \int_1^{\infty} d\sigma \left\{ \left(1 - \frac{1}{\sigma^2}\right)^{\frac{1}{2}} - 1 \right\} = 2 \sqrt{\beta} \left(1 - \frac{\pi}{2}\right),$$

again independent of W . Now β is quantized, or expressed definitely in terms of integers already, from the phase-integral for the momentum p_2 . The phase integral for p_1 can only, in this case, lead to another expression of similar type for β , but to no expression for W . It is not at all clear that the two expressions for β , also, can both be valid simultaneously.

This possibility has hitherto apparently been overlooked by authors in this subject.

No case has, however, been noticed in which W is indeterminate for a *finite* path. One very important conclusion is that the whole investigation is valid for a negatively charged atom with a distant electron.

We proceed now to discuss the possible existence of definite paths with a positive total energy and infinite extent, for a single electron around a nucleus of charge νe , situated at the origin. This is Epstein's problem, which he treats as only two-dimensional. The energy equation is

$$\frac{1}{2}m \left\{ p_1^2 + \frac{p_2^2}{r^2} + \frac{p_3^2}{r^2 \sin^2 \theta} \right\} - \frac{\nu e^2}{r} = W,$$

where W is positive, and represents the total energy, and the p 's are the momenta.

We have thus

$$p_3 = \text{const.} = \frac{n_1 h}{2\pi},$$

$$p_2^2 + \frac{p_3^2}{\sin^2 \theta} = \beta^2,$$

being clearly positive,

$$\frac{1}{2} m \left\{ p_1^2 + \frac{\beta^2}{r^2} \right\} - \frac{ve^2}{r} = W.$$

The phase-integral for p_2 is

$$n_2 h = \int p_2 d\theta = 2 \int d\theta \cdot \sqrt{\beta^2 - \frac{p_3^2}{\sin^2 \theta}},$$

the limits being the suitable values of θ for which $p_2 = 0$. The factor 2 represents the double journey in this co-ordinate,

$$\sin \psi = \frac{p_3}{\beta},$$

where ψ is one of the limits, and the other admissible value, for a real integral, is $\pi - \psi$. Thus

$$\begin{aligned} n_2 h &= 2 \int_{\psi}^{\pi-\psi} d\theta \sqrt{\beta^2 - p_3^2 / \sin^2 \theta} \\ &= 2\beta \int_1^{\frac{\beta}{p_3}} \frac{dw}{w} \sqrt{\frac{w-1}{\frac{\beta}{p_3} - w}} \quad \left(\text{with } \sin \theta = \frac{p_3}{\beta} \sqrt{w} \right). \end{aligned}$$

Write

$$w = \sin^2 \omega + \frac{\beta^2}{p_3^2} \cos^2 \omega,$$

and we have

$$n_2 h = 4\beta \cdot \frac{\beta^2 - p_3^2}{p_3^2} \int_0^{\pi/2} \frac{\cos^2 \omega d\omega}{\sin^2 \omega + \frac{\beta^2}{p_3^2} \cos^2 \omega},$$

or with $\tan \omega = t$,

$$n_2 h = \frac{4\beta}{p_3^2} (\beta^2 - p_3^2) \int_0^{\infty} \frac{dt}{(1+t^2) \left(\frac{\beta^2}{p_3^2} + t^2 \right)}$$

$$\begin{aligned} &= 4\beta \left\{ \tan^{-1} t - \frac{p_3}{\beta} \tan^{-1} \frac{p_3 t}{\beta} \right\}_0 \\ &= 2\pi\beta \left\{ 1 - \frac{p_3}{\beta} \right\} = 2\pi(\beta - p_3), \end{aligned}$$

whence

$$\beta = \frac{n_2 h}{2\pi} + p_3 = (n_1 + n_2) \frac{h}{2\pi},$$

these integers being thus additive, in the usual way.

The phase-integral for p_1 is

$$n_2 h = \int dr \sqrt{2mW + \frac{2mve^2}{r} - \frac{\beta^2}{r^2}},$$

if we seek to quantize p_1 as it stands. The limits would then be a positive value of r and infinity, for half the path, and the integral would be infinite. But it is clearly necessary to suppose that when the electron is at infinity, out of range of action of the nucleus, it should not be subject to a quantum relation, so that $(p_1)_{r=\infty}$ is not affected by the rule, and only the variable part

$$p_1 - (p_1)_\infty$$

is so affected. Yet this question of quantizing p_1 presents some difficulties in whatever way it is suggested that it should be effected, and we consider that Epstein's discussion of the matter is very incomplete and not logically justifiable in its mathematical procedure. We shall thus consider various alternatives which may give a finite phase-integral.

Now the actual r -path is not a passage from $r=\alpha$ (say) to $r=\infty$ and back, and the phase-integral is not twice the definite integral between these limits. The electron goes from a limiting radius to infinity, and back to the same radius elsewhere, and the passage through infinity distinguishes this phase-integral from those which occur in the other coordinates.

We must, of course, also remember that the sign of p_1 depends upon the part of the path concerned,—whether the electron is departing or returning. The critical value of r is the positive root of

$$2mW + \frac{2mve^2}{r} - \frac{\beta^2}{r^2}$$

$$\text{or} \quad \frac{1}{r} = \frac{mve^2 + \sqrt{m^2 v^2 e^4 + 2mW\beta^2}}{\beta^2} = \frac{1}{\alpha} \text{ (say).}$$

Writing, generally, with a new variable ϕ ,

$$\frac{1}{r} - \frac{mve^2}{\beta^2} = \sqrt{\frac{m^2 v^2 e^4 + 2mW\beta^2}{\beta^4}} \cos \phi,$$

we have $\phi=0$ in the critical position (perihelion, in the usual terminology), and

$$\cos \phi = -\frac{mve^2}{\beta^2} \bigg/ \sqrt{\frac{m^2v^2e^4 + 2mW\beta^2}{\beta^4}} = \cos \eta \text{ (say),}$$

when $r=\infty$.

What is required for the correct evaluation of the phase-integral is a *continuous* variable which shall change in one direction,—and thus give a definite integral,—as r goes to infinity and returns, the sign of p_1 being automatically taken into account,—or the sign of $p_1 - (p_1)_\infty$ when $(p_1)_\infty$ is not zero as in a parabolic path. The new variable ϕ has this property, and ranges from zero to 2π as r goes through its changes. We have denoted its value, when $r=\infty$, by η above, where η is evidently an obtuse angle.

The phase-integral for p_1 alone would be

$$n_3h = \int_{\phi=0}^{2\pi} dr \sqrt{2mW + \frac{2mve^2}{r} - \frac{\beta^2}{r^2}}$$

(the square root being properly interpreted in different regions) where

$$\frac{1}{r} = \frac{mve^2}{\beta^2} + \frac{1}{\beta^2} \sqrt{m^2v^2e^4 + 2mW\beta^2} \cos \phi$$

$$0 = \frac{mve^2}{\beta^2} + \frac{1}{\beta^2} \sqrt{m^2v^2e^4 + 2mW\beta^2} \cos \eta,$$

and we find

$$dr = \frac{\sin \phi \, d\phi}{(\cos \phi - \cos \eta)^2} \frac{\beta^2}{q}, \quad q = \sqrt{2mW + m^2v^2e^4},$$

$$\sqrt{2mW + \frac{2mve^2}{r} - \frac{\beta^2}{r^2}} = \frac{q}{\beta} \sin \phi.$$

If the integration were continuous throughout,—as assumed by Epstein,—we should thus have

$$\begin{aligned} n_3h &= \beta \int_0^{2\pi} \frac{\sin^2 \phi \, d\phi}{(\cos \phi - \cos \eta)^2} \\ &= 2\beta \int_0^\pi \frac{\sin^2 \phi \, d\phi}{(\cos \phi - \cos \eta)^2}, \end{aligned}$$

which is an infinite integral, as would be expected.

If we merely quantized over the finite part of the hyperbola,—another possible suggestion,—we should have

$$\begin{aligned} n_3 h &= \beta \left\{ \int_0^\eta + \int_{2\pi-\eta}^{2\pi} \right\} \frac{\sin^2 \phi}{(\cos \phi - \cos \eta)^2} d\phi \\ &= 2\beta \int_0^\eta \frac{\sin^2 \phi d\phi}{(\cos \phi - \cos \eta)^2}, \end{aligned}$$

which is again infinite.

The nature of the first infinity merits a remark, however, for it is independent of η and therefore of W . For

$$\begin{aligned} 1 &= \int_0^\pi \frac{\sin^2 \phi d\phi}{(\cos \phi - \cos \eta)^2} = \left[\frac{\sin \phi}{\cos \phi - \cos \eta} \right] - \int_0^\pi \frac{\cos \phi d\phi}{\cos \phi - \cos \eta} \\ &= \left[\frac{\sin \phi}{\cos \phi - \cos \eta} \right] - \pi - \cos \eta \int_0^\pi \frac{d\phi}{\cos \phi - \cos \eta}. \end{aligned}$$

The principal value of the last integral is well known to be zero, for all values of η , so that the last term is zero. Our equation would be

$$n_3 h = -2\pi\beta + \left[\frac{\sin \phi}{\cos \phi - \cos \eta} \right],$$

where the principal value of the bracket must be taken, *i. e.* it is to be interpreted as

$$\text{Lt}_{\epsilon \rightarrow 0} \left\{ \left[\frac{\sin \phi}{\cos \phi - \cos \eta} \right]_0^{\eta-\epsilon} + \left[\frac{\sin \phi}{\cos \phi - \cos \eta} \right]_{\eta+\epsilon}^\pi \right\}.$$

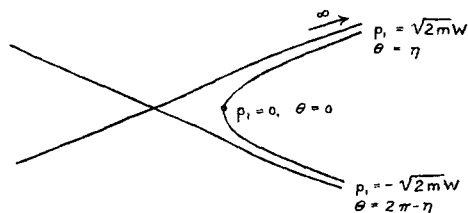
This becomes

$$\text{Lt}_{\epsilon \rightarrow 0} \left\{ \frac{\sin \eta}{\epsilon \sin \eta} + \frac{\sin \eta}{\epsilon \sin \eta} \right\} = \text{Lt} \cdot \frac{1}{2\epsilon},$$

which, though infinite, is an infinity independent of η and therefore of W . We have another aspect of the indeterminateness of W for such paths.

Our fundamental objection to Epstein's mode of integration may now be introduced. He integrates $p_1 - (p_1)_\infty$, and not p_1 , but this fact does not affect the question. For as ϕ ranges between 0 and 2π , if $p_1 = f(\phi)$, we have p_1 varying continuously with θ , and remaining positive, till $\theta = \eta$. Then p_1 becomes $-f(\phi_1)$ when $\phi = 2\pi - \phi_1$ on the return journey after $\phi = 2\pi - \eta$. Between $\phi = \eta$ and $\phi = 2\pi - \eta$, the value of r should be infinite, and p_1 changes from $\sqrt{2mW}$ to $-\sqrt{2mW}$, as in the figure.

The variation of p_1 between $\pm \sqrt{2mW}$ at infinity is the source of trouble, and it takes place while $\frac{1}{r}=0$.



Epstein takes twice the integral from $\phi=0$ to $\phi=\pi$, but according to the substitution formula, r is *negative* when ϕ goes from η to π , and negative values of r are clearly not permissible. A suitable integration for the infinite region cannot in fact be effected, and any supposition of a suitable variable in place of ϕ , for the change of p_1 at ∞ from $\sqrt{2mW}$ to $-\sqrt{2mW}$, would be entirely arbitrary,—but as it could not lead to a finite phase-integral, we pursue the matter no further.

These considerations, nevertheless, have considerable force when, thrown back as we now are upon the necessity, if the quantum theory is applicable, of using $p_1 - (p_1)_\infty$, we attempt to quantize this.

We have, when $\theta=\eta$

$$\begin{aligned}(p_1)_\infty &= \sqrt{2mW} \\ &= \frac{q}{\beta} \sin \eta,\end{aligned}$$

where $q = \sqrt{m^2 v^2 e^4 + 2mW\beta^2}$ as before.

And when $\phi=2\pi-\eta$,

$$(p_1)_\infty = \frac{q_1}{\beta} \sin (2\pi - \eta) = -\frac{q}{\beta} \sin \eta.$$

From $\phi=0$ to $\phi=\eta$,

$$p_1 - (p_1)_\infty = \frac{q}{\beta} (\sin \phi - \sin \eta).$$

From $\phi=2\pi-\eta$ to $\phi=2\pi$,

$$p_1 - (p_1)_\infty = +\frac{q}{\beta} (\sin \phi + \sin \eta),$$

and from $\phi=\eta$ to $\phi=2\pi-\eta$,

$$p_1 - (p_1)_\infty = 0.$$

With the value of dr , the phase-integral

$$n_3 h = \int_{\theta=0}^{2\pi} dr(p_1 - (p_1)_\infty)$$

breaks into three parts, thus

$$\begin{aligned} n_3 h &= \beta \int_0^\eta \frac{\sin \phi (\sin \phi - \sin \eta) d\phi}{(\cos \phi - \cos \eta)^2} + \beta \int_\eta^{2\pi-\eta} 0 \cdot d\phi \\ &\quad + \beta \int_{2\pi-\eta}^{2\pi} \frac{\sin \phi (\sin \phi + \sin \eta) d\phi}{(\cos \phi - \cos \eta)^2} \\ &= 2\beta \int_0^\eta \frac{\sin \phi (\sin \phi - \sin \eta) d\phi}{(\cos \phi - \cos \eta)^2} + 2\beta \int_\eta^\pi 0 \cdot d\phi \end{aligned}$$

by a simple transformation.

Finally, the only accurate phase-integral is

$$n_3 h = 2\beta \int_0^\eta \frac{\sin \phi (\sin \phi - \sin \eta) d\phi}{(\cos \phi - \cos \eta)^2},$$

while Epstein gives, in our notation,

$$n_3 h = 2\beta \int_0^\pi \frac{\sin \phi (\sin \phi - \sin \eta) d\phi}{(\cos \phi - \cos \eta)^2},$$

the part of his range from η to π involving a meaningless negative value of r , and violating $p_1 = (p_1)_\infty$ though the moving electron is at infinity. The principal value of Epstein's integral is, using the indefinite integral for the function in the form, readily obtained by parts,

$$\begin{aligned} &\int \frac{\sin \phi (\sin \phi - \sin \eta) d\phi}{(\cos \phi - \cos \eta)^2} \\ &= \frac{\sin \phi - \sin \eta}{\cos \phi - \cos \eta} - \phi + \cot \eta \cdot \log_e \left\{ \frac{\sin \frac{\eta - \phi}{2}}{\sin \frac{\eta + \phi}{2}} \right\} \end{aligned}$$

of the type

$$n_3 h = 2\beta \pi \left\{ -1 + \frac{2}{\pi \sin \eta} \right\}$$

or

$$\frac{2}{\pi \sin \eta} = \frac{(n_1 + n_2 + n_3)}{n_1 + n_2},$$

and ultimately

$$W = \frac{2\pi^2 m e^4 v^2}{h^2} \cdot \frac{1}{\frac{\pi}{4} (n_1 + n_2 + n_3)^2 - (n_1 + n_2)^2},$$

—generalized from his value which relates only to a *plane*

hyperbola. We have the sum $n_1 + n_2$ of the angular quanta in place of his single integer.

But this formula, with all the applications he makes to characteristic γ radiation, is not tenable, as resting on a mathematical error. Its apparent success appeared at one time to the writer to justify it as an empirical formula, in spite of his independent investigation, outlined above, indicating the impossibility of quantizing such orbits. Close examination, however, of the calculations of γ radiation and so forth made it clear that they were in several cases illusory, and determined more by order of magnitude than by the nature of the formula.

There is one convincing argument against the formula, however. It should give an emission spectrum for all values of n_1, n_2, n_3 and m_1, m_2, m_3 making

$$-W(m_1, m_2, m_3) + W(n_1, n_2, n_3)$$

positive. This can be tested in great numerical detail on the spectrum of a hydrogen atom, and the test fails entirely. No spectrum line is found,—in the secondary hydrogen spectrum,—in any of the assigned positions. Thus the formula really fails as an empirical one.

We have seen above that it must be replaced by

$$\begin{aligned} n_3 h &= 2\beta \int_0^\eta \frac{\sin \phi (\sin \phi - \sin \eta)}{(\cos \phi - \cos \eta)^2} d\phi \\ &= 2\beta \left[\frac{\sin \phi - \sin \eta}{\cos \phi - \cos \eta} - \phi + \cot \eta \log_e \left\{ \frac{\sin \frac{\eta - \phi}{2}}{\sin \frac{\eta + \phi}{2}} \right\} \right]_0^\eta \end{aligned}$$

which is logarithmically infinite.

The attempt to obtain a finite phase-integral, in this manner, in fact fails, and we must give up the hypothesis that even the variable part of p_1 can be quantized for the infinite path.

It is not difficult to see that this conclusion is general for any infinite path which is possible for an electron about a physically existent atom, whose nucleus can always be regarded, for the present purpose, as a superposition of free charges and a set of doublets. We have demonstrated the result for a single free charge, and previously for sets of doublets. Further analysis of the more general case does not seem necessary, and could readily be supplied by the reader.

Our conclusion must be as follows:—

A determinate and finite value of W cannot be obtained for an electron moving about any atomic nucleus, if the path involved takes the electron to infinity.