An approximation to the motion of two rotating electrical doublets in a plane. By P. A. TAYLOR, B.A., Emmanuel College.

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§ 1. *Introduction.* This problem was suggested by an article of Debye's* in which he considers the effect on a free electron of an electrical doublet constrained to rotate uniformly about a line through itself perpendicular to its own axis. Assuming that the free electron is initially at rest, he shows that to a first approximation it performs simple harmonic vibrations about its initial position. Proceeding to a second approximation, he shows that the free electron appears to be repelled by the rotating doublet. In this paper, instead of considering an electron and a rotating doublet, we consider two rotating doublets. In order to simplify the calculations we suppose that the two doublets are constrained to lie in a plane, but are otherwise free. The principal results of the calculations will be found collected in the summary at the end.

The problem is of interest as it might give a clue to the origin of forces between atoms. For Debye shows that the field due to a hydrogen atom at any distance greater than about ten times its radius is to a close approximation the same as the field of the equivalent rotating doublet†. We shall find that two rotating doublets behave as if they acted on each other with a force of the same general type as the interatomic forces found empirically by Lennard-Jones and the present author‡. Comparison can only be made as regards order of magnitude for three reasons. We have constrained our doublets to lie in a plane. Secondly, we shall consider the moment of inertia and the electrical moment of a doublet as constant, whereas in an encounter between two hydrogen atoms the radius vector from the proton to the electron of the same atom might suffer perturbations, so that the moment of inertia and the electrical moment may be variable. Thirdly, no gas so simple as a gas of hydrogen atoms exists.

§ 2. The plane of the paper is the plane in which the doublets are constrained to lie.

G is the centre of gravity of the two doublets O_1 and O_2.

* P. Debye, "Molekularkräfte und ihre elektrische Deutung, § 6," *Phys. Zeit.*, vol. XXII, p. 306 (1921).

† P. Debye, *loc. cit.*

‡ J. E. Jones, *Proc. Roy. Soc.* A, vol. CVI, pp. 441, 463, 709 (1924); vol. CVII, p. 157 (1925); J. E. Lennard-Jones and P. A. Taylor, *Proc. Roy. Soc.* A, vol. CIX, p. 476 (1925).

m_1 and m_2 are the masses of the two doublets O_1 and O_2 respectively.

μ_1 and μ_2 are the electrical moments of the two doublets O_1 and O_2 respectively.

I_1 and I_2 are the moments of inertia of the two doublets O_1 and O_2 respectively.

Gx and Gy are rectangular axes through G parallel to directions fixed in space.

The rest of the notation is as in the figure.

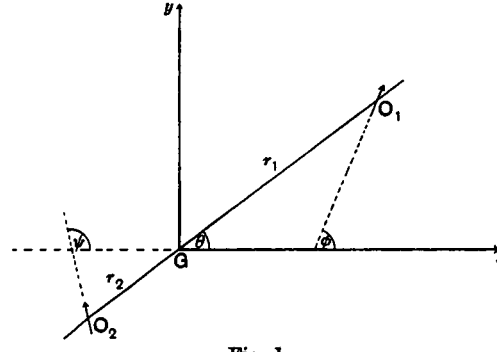

Fig. 1

We write also $\epsilon = \psi - \phi,$

$$r = r_1 + r_2.$$

Then, if T is the kinetic energy of the motion relative to G, and if V is the potential energy, we find

$$2T = M(\dot{r}^2 + r^2\dot{\theta}^2) + I_1\dot{\phi}^2 + I_2\dot{\psi}^2 \qquad \ldots\ldots(2{\cdot}0),$$

$$2V = \frac{2\mu_1\mu_2}{r^3}\{\cos\epsilon - 3\cos(\phi - \theta)\cos(\psi - \theta)\}$$

$$= -\frac{\mu_1\mu_2}{r^3}\{3\cos(\phi + \psi - 2\theta) + \cos(\phi - \psi)\} \quad \ldots(2{\cdot}1),$$

where $$M = \frac{m_1 m_2}{m_1 + m_2} \qquad \ldots\ldots(2{\cdot}2),$$

and we have at once Lagrange's equations of motion.

Suppose now that the doublets are at such a great distance apart that the coupling (i.e. the influence of one doublet on the motion of the other) is small. If there were no coupling each doublet would move with uniform velocity in a straight line and would

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rotate with constant angular velocity. Thus, neglecting the coupling, we have as an approximate solution

$$\left.\begin{aligned} r\cos\theta &= ut + \alpha \\ r\sin\theta &= vt + \beta \\ \phi &= \phi_1 t + \phi_0 \\ \psi &= \psi_1 t + \psi_0 \end{aligned}\right\} \quad \ldots\ldots(2{\cdot}3).$$

The arbitrary constants α, β, ϕ_0, ψ_0, u, v, ϕ_1, ψ_1 may be so chosen that the equations (2·3) determine the exact values of r, θ, ϕ, ψ, $\dot{r}$, $\dot{\theta}$, $\dot{\phi}$, $\dot{\psi}$ at any given instant of time (say $t = 0$). Now let u, v, ϕ_1, ψ_1 be chosen in this manner, i.e. the vector $[u, v]$ is the relative linear velocity of the two doublets, and ϕ_1 and ψ_1 the angular velocities of the doublets at time $t = 0$. Then α, β, ϕ_0, ψ_0 may be taken as new variables, defined in terms of r, θ, ϕ, ψ, t by equations (2·3). We have seen that an approximate solution of the equations of motion is given by $\alpha = \text{const.}, \beta = \text{const.}, \phi_0 = \text{const.}, \psi_0 = \text{const.}$ Therefore in the exact solution $\dot{\alpha}, \dot{\beta}, \dot{\phi}_0, \dot{\psi}_0$ will be small, and so also will be $\ddot{\alpha}$, $\ddot{\beta}$, $\ddot{\phi}_0$, $\ddot{\psi}_0$. (Also from the way in which u, v, ϕ_0, ψ_0 were chosen, at time $t = 0$ we have $\dot{\alpha} = 0$, $\dot{\beta} = 0$, $\dot{\phi}_0 = 0$, $\dot{\psi}_0 = 0$ accurately.)

We may express the equations of motion after some algebraic reduction in the following form:

$$\left.\begin{aligned} \ddot{\alpha} &= A\cos(\phi_1+\psi_1)t + B\sin(\phi_1+\psi_1)t \\ &\qquad + C\cos(\phi_1-\psi_1)t + D\sin(\phi_1-\psi_1)t \\ \ddot{\beta} &= A'\cos(\phi_1+\psi_1)t + B'\sin(\phi_1+\psi_1)t + \ldots \\ \ddot{\phi} &= A''\cos(\phi_1+\psi_1)t + \ldots \\ \ddot{\psi} &= A'''\cos(\phi_1+\psi_1)t + \ldots \end{aligned}\right\} \quad (2{\cdot}4).$$

The A's, B's, etc. are expressions of which the following are typical:

$$\left.\begin{aligned} A &= -\frac{15\mu_1\mu_2}{4Mr^4}\cos(\phi_0+\psi_0-3\theta) - \frac{3\mu_1\mu_2}{4Mr^4}\cos(\phi_0+\psi_0-\theta) \\ B &= \frac{15\mu_1\mu_2}{4Mr^4}\sin(\phi_0+\psi_0-3\theta) + \frac{3\mu_1\mu_2}{4Mr^4}\sin(\phi_0+\psi_0-\theta) \\ C'' &= -\frac{\mu_1\mu_2}{2I_1r^3}\sin(\phi_0-\psi_0) \\ D'' &= -\frac{\mu_1\mu_2}{2I_1r^3}\cos(\phi_0-\psi_0) \end{aligned}\right\} \quad (2{\cdot}5).$$

The right-hand sides of equations (2·4) are functions of t, both directly and *via* the A's, B's, C's, D's, which are given as functions of $r, \theta, \phi_0, \psi_0$ by equations (2·5) and other equations of similar form.

The two variables r and θ are given by equations (2·3) as functions of t, both directly and *via* α and β. To a first approximation we may neglect the variation of the four quantities α, β, ϕ_0, ψ_0, as we have shown that they are approximately constant. If the angular velocities of the doublets are large compared with the ratio of their linear relative velocity to their distance apart, we can consider r and θ as approximately constant. Thus for a first approximation we can consider the A's, B's etc. as constant, i.e. their variations are slow compared with the variations of

$$\begin{matrix}\cos\\ \sin\end{matrix}(\phi_1 \pm \psi_1)\, t.$$

We can now integrate equations (2·4) and obtain equations like

$$\begin{aligned}\alpha - \alpha_0 = {} & \frac{A}{(\phi_1+\psi_1)^2}[1-\cos(\phi_1+\psi_1)t] \\ & + \frac{B}{(\phi_1+\psi_1)^2}[(\phi_1+\psi_1)t - \sin(\phi_1+\psi_1)t] \\ & + \frac{C}{(\phi_1-\psi_1)^2}[1-\cos(\phi_1-\psi_1)t] \\ & + \frac{D}{(\phi_1-\psi_1)^2}[(\phi_1-\psi_1)t - \sin(\phi_1-\psi_1)t] \quad \ldots(2\cdot6),\end{aligned}$$

where α_0, β_0, ϕ_{00}, ψ_{00} are the values of α, β, ϕ_0, ψ_0 respectively when $t = 0$.

For a second approximation we must no longer consider the A's, B's, etc. as constants. Let r_0, r_1, θ_0, θ_1 be the values at time $t = 0$ of r, $\dot{r}$, θ, $\dot{\theta}$ respectively. Then since we have already assumed that the linear relative velocity of the doublets is small, we may write, for a few periods of revolution of the doublets at least

$$\begin{aligned} r &= r_0 + r_1 t, \\ \theta &= \theta_0 + \theta_1 t. \end{aligned}$$

Expanding the A's etc. to the first order in r_1, θ_1, and also in $(\alpha - \alpha_0)$, $(\beta - \beta_0)$, etc., we have (letting the suffix 0 denote the values at time $t = 0$)

$$\begin{aligned} A = {} & A_0 + \left(\frac{\partial A}{\partial r}\right)_0 r_1 t + \left(\frac{\partial A}{\partial \theta}\right)_0 \theta_1 t + \left(\frac{\partial A}{\partial \alpha}\right)_0 (\alpha - \alpha_0) + \left(\frac{\partial A}{\partial \beta}\right)_0 (\beta - \beta_0) \\ & + \left(\frac{\partial A}{\partial \phi_0}\right)_0 (\phi_0 - \phi_{00}) + \left(\frac{\partial A}{\partial \psi_0}\right)_0 (\psi_0 - \psi_{00}) \quad (2\cdot70) \\ = {} & E_a + F_a t + G_a \cos(\phi_1+\psi_1)t + H_a \sin(\phi_1+\psi_1)t \\ & + K_a \cos(\phi_1-\psi_1)t + L_a \sin(\phi_1-\psi_1)t \\ & \qquad \ldots\ldots(2\cdot71). \end{aligned}$$

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The E_a's, F_a's, etc. are constants whose values may be found by substituting in equation (2·70) from (2·6) and similar equations and comparing the result with equation (2·71). Similarly

$$B' = E'_b + F'_b t + \ldots.$$

Substituting in equations (2·4) from equations (2·71) we have

$$\begin{aligned}\ddot{\alpha} = \{&E_a + F_a t + G_a \cos(\phi_1+\psi_1)t + H_a \sin(\phi_1+\psi_1)t + K_a \cos(\phi_1-\psi_1)t \\ &+ L_a \sin(\phi_1-\psi_1)t\} \cos(\phi_1+\psi_1)t \\ + \{&E_b + F_b t + \ldots \quad + L_b \sin(\phi_1-\psi_1)t\} \sin(\phi_1+\psi_1)t \\ + \{&E_c + F_c t + \ldots \quad + L_c \sin(\phi_1-\psi_1)t\} \cos(\phi_1-\psi_1)t \\ + \{&E_d + F_d t + \ldots \quad + L_d \sin(\phi_1-\psi_1)t\} \sin(\phi_1-\psi_1)t \\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \ldots\ldots(2\cdot8).\end{aligned}$$

§ 3. We will first suppose that neither $(\phi_1+\psi_1)$ nor $(\phi_1-\psi_1)$ is small, i.e. $(\phi_1+\psi_1)$ and $(\phi_1-\psi_1)$ are to be considered as large and of the same order of magnitude as ϕ_1 and ψ_1. We will find the average relative acceleration of the doublets over a time $t=-\tau$ to $t=+\tau$, where the time 2τ is sufficiently large to contain a large number of periods of

$$\begin{matrix}\cos\\ \sin\end{matrix}(\phi_1+\psi_1)t \text{ and } \begin{matrix}\cos\\ \sin\end{matrix}(\phi_1-\psi_1)t,$$

and yet sufficiently small for r and θ to be effectively constant*. Letting a bar denote the average value with respect to t over the time $-\tau$ to $+\tau$ we have

$$\overline{t \begin{matrix}\cos\\ \sin\end{matrix} \omega t} = 0,$$

where ω denotes either $(\phi_1+\psi_1)$ or $(\phi_1-\psi_1)$.

$$\overline{t \sin \omega t} = \frac{1}{\omega}\cos\omega\tau + \frac{1}{\tau\omega^2}\sin\omega\tau.$$

The first term in this expression fluctuates, going through a cycle of values, equally positive and negative, in the time of one period of $\begin{matrix}\cos\\ \sin\end{matrix}\omega t$. We are trying to compare the actual motion with one in which the effects of individual rotations are smoothed out; and this term $(-\cos\omega\tau/\omega)$ contributes nothing permanent to the

* This is possible as regards $(\phi_1+\psi_1)t$, but not as regards $(\phi_1-\psi_1)t$, when the doublets represent normal Bohr hydrogen atoms, rotating in the same sense, and whose relative velocity is the kinetic theory velocity appropriate to a temperature of 0°C. For then the distance travelled in 30 periods of revolution of the doublets is about $\frac{1}{10}$ of the radius of a hydrogen atom, and hence a considerably smaller fraction of the distance apart of the two doublets. To make a suitable choice of τ possible as regards both $(\phi_1+\psi_1)t$ and $(\phi_1-\psi_1)t$ we should have to make our doublets correspond to hydrogen atoms with different quantum numbers.

averaged acceleration. Besides, owing to the factor $1/\omega$, the extreme values of $(-\cos\omega\tau/\omega)$ would be small compared with $\overline{\cos^2\omega t}$ (i.e. $\frac{1}{2}$). A fortiori, the term $(\sin\omega\tau/\tau\omega^2)$, which also fluctuates through positive and negative values, tends to zero as τ increases, and contains a factor $1/\omega^2$, contributes nothing permanent to the averaged acceleration. So we write

$$\overline{t\sin\omega t} = 0.$$

Similarly

$$\overline{\begin{matrix}\cos\\ \sin\end{matrix}\omega t} = 0, \qquad \overline{\cos\omega t\sin\omega t} = 0, \qquad \overline{\begin{matrix}\cos^2\\ \sin^2\end{matrix}\omega t} = \tfrac{1}{2},$$

$$\overline{\begin{matrix}\cos\\ \sin\end{matrix}(\phi_1+\psi_1)\,t\,\begin{matrix}\cos\\ \sin\end{matrix}(\phi_1-\psi_1)\,t} = 0.$$

Applying these results to equation (2·8) we have

$$\bar{\bar{\alpha}} = \tfrac{1}{2}(G_a + H_b + K_c + L_d) \qquad \text{.....(3·0).}$$

We can evaluate the constants occurring in this equation by somewhat lengthy algebra, and we find

$$\bar{\bar{\alpha}} = \frac{9\mu_1^2\mu_2^2}{2M^2r^9}\left\{\frac{13}{(\phi_1+\psi_1)^2}+\frac{1}{(\phi_1-\psi_1)^2}\right\}\cos\theta + \frac{3\mu_1^2\mu_2^2(I_1+I_2)}{8MI_1I_2r^7}\left\{\frac{9}{(\phi_1+\psi_1)^2}+\frac{1}{(\phi_1-\psi_1)^2}\right\}\cos\theta.$$

Also

$$\bar{\bar{\alpha}} = \rho\cos\theta - \tau\sin\theta,$$

where ρ and τ are the radial and transverse averaged relative accelerations respectively in the directions of r and θ increasing. Therefore

$$\left.\begin{aligned} R = M\rho &= \frac{9\mu_1^2\mu_2^2}{2Mr^9}\left\{\frac{13}{(\phi_1+\psi_1)^2}+\frac{1}{(\phi_1-\psi_1)^2}\right\} \\ &\quad + \frac{3\mu_1^2\mu_2^2(I_1+I_2)}{8I_1I_2r^7}\left\{\frac{9}{(\phi_1+\psi_1)^2}+\frac{1}{(\phi_1-\psi_1)^2}\right\} \\ T = M\tau &= 0 \end{aligned}\right\} \quad (3\cdot1),$$

where R and T are the apparent forces corresponding to the accelerations ρ and τ. Thus we see that the doublets repel each other with a force $(\lambda r^{-7} + \mu r^{-9})$, where λ and μ are positive constants which may be found by comparison with equation (3·1).

We now have to consider what is the influence of one doublet on the angular velocity of the other. Similarly to equation (3·0) we find

$$\bar{\bar{\dot{\phi}}} = \bar{\bar{\dot{\phi}}}_0 = \tfrac{1}{2}(G_a'' + H_b'' + K_c'' + L_d'') \qquad \text{.....(3·2).}$$

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When we evaluate explicitly the constants occurring on the right-hand side of this equation we find

$$\left.\begin{aligned} G_a'' + H_b'' &= 0 \\ K_c'' + L_d'' &= 0 \end{aligned}\right\} \quad \ldots\ldots(3{\cdot}21),$$

and so

$$\ddot{\bar{\phi}} = 0 \quad \ldots\ldots(3{\cdot}22).$$

Thus to our order of approximation the angular velocities of the two doublets remain constant throughout the interaction; and the coefficients λ and μ remain constant, their values depending on the constant values (ϕ_1 and ψ_1) of the angular velocities of the doublets. That is to say, during the whole of an encounter (provided the doublets do not approach each other too closely), the doublets appear to repel each other with a force $(\lambda r^{-7} + \mu r^{-9})$, where λ and μ are constants, given by

$$\left.\begin{aligned} \lambda &= \frac{3\mu_1^2\mu_2^2\,(I_1+I_2)}{8I_1I_2}\left\{\frac{9}{(\phi_1+\psi_1)^2}+\frac{1}{(\phi_1-\psi_1)^2}\right\} \\ \mu &= \frac{9\mu_1^2\mu_2^2}{2M}\left\{\frac{13}{(\phi_1+\psi_1)^2}+\frac{1}{(\phi_1-\psi_1)^2}\right\} \end{aligned}\right\} \quad \ldots(3{\cdot}3).$$

§ 4. So far we have assumed that neither $(\phi_1 + \psi_1)$ nor $(\phi_1 - \psi_1)$ is small. We now consider the state of affairs when $(\phi_1 - \psi_1)$ is small. Let $\phi_1 - \psi_1 = \xi$, where ξ is small. We also write $\phi_1 + \psi_1 = \eta$. Then, since

$$\frac{1-\cos\xi t}{\xi^2} = \tfrac{1}{2}t^2 - \tfrac{1}{24}\xi^2t^4 \text{ approx.}^*$$

and

$$\frac{\xi t - \sin\xi t}{\xi^2} = \tfrac{1}{6}\xi t^3 \text{ approx.}^*,$$

the equations (2·6) take the form

$$\alpha - \alpha_0 = \frac{A}{\eta^2}(1-\cos\eta t) + \frac{B}{\eta^2}(\eta t - \sin\eta t) + \tfrac{1}{2}Ct^2 + \tfrac{1}{6}D\xi t^3 - \tfrac{1}{24}C\xi^2t^4 \quad \ldots\ldots(4{\cdot}0).$$

Corresponding to equations (2·71) we shall have

$$A = \mathrm{E}_a + \mathrm{F}_a t + G_a\cos\eta t + H_a\sin\eta t + \tfrac{1}{2}M_at^2 + \tfrac{1}{6}N_a\xi t^3 - \tfrac{1}{24}M_a\xi^2t^4 \quad \ldots\ldots(4{\cdot}1).$$

The new coefficients M_a, N_a, E_a, F_a, etc., may be found by substituting in (2·70) from (4·0) and comparing the result with (4·1). Thus corresponding to equation (2·8) we have

$$\begin{aligned} \ddot{\alpha} = {} & \{\mathrm{E}_a + \mathrm{F}_a t + G_a\cos\eta t + H_a\sin\eta t + \tfrac{1}{2}M_at^2 + \tfrac{1}{6}N_a\xi t^3 \\ & \qquad - \tfrac{1}{24}M_a\xi^2t^4\}\cos\eta t \\ & + \{\mathrm{E}_b + \mathrm{F}_b t + \ldots \qquad - \tfrac{1}{24}M_b\xi^2t^4\}\sin\eta t \\ & + \{\mathrm{E}_c + \mathrm{F}_c t + \ldots \qquad - \tfrac{1}{24}M_c\xi^2t^4\}(1 - \tfrac{1}{2}\xi^2t^2) \\ & + \{\mathrm{E}_d + \mathrm{F}_d t + \ldots \qquad - \tfrac{1}{24}M_d\xi^2t^4\}\,\xi \end{aligned} \quad \ldots\ldots(4{\cdot}2).$$

* For justification of these approximations see footnote on p. 281.

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We now require to take some new averages. As in § 3 we choose the time 2τ to be sufficiently large to contain a large number of periods of $\begin{matrix}\cos\\ \sin\end{matrix} \omega t$ and yet sufficiently small for r and θ to be effectively constant, and we then average over the time $t = -\tau$ to $t = +\tau$*. Now we are comparing the actual motion with a comparison motion in which the effects of individual rotations are smoothed out. In this comparison motion the average acceleration during the time $t = -\tau$ to $t = +\tau$ is the sum of two terms:

(i) the actual acceleration (in the comparison motion) at time $t = 0$.

(ii) a term which tends to zero as τ tends to zero.

We are trying to find the actual acceleration at time $t = 0$ in the comparison smoothed out motion. Consequently terms in our average which tend to zero as τ tends to zero are to be identified with (ii) and hence omitted. Terms which fluctuate equally positive and negative disappear as before in the smoothing out process, e.g.

$$\overline{t^2 \cos \eta t} = \frac{1}{2\tau}\int_{-\tau}^{\tau} t^2 \cos \eta t\, dt = \frac{\tau}{\eta}\sin \eta\tau + \frac{2}{\eta^2}\cos \eta\tau - \frac{2\sin \eta\tau}{\eta^3\tau}.$$

We may either say that each term in this expression fluctuates equally positive and negative and is therefore to be omitted; or we may say that $\overline{t^2 \cos \eta t} \to 0$ as $\tau \to 0$ (as is clear without integration) and hence $\overline{t^2 \cos \eta t}$ is to be omitted. Hence we write

$$\overline{t^2 \cos \eta t} = 0.$$

Similarly we put

$$\overline{t^2 \sin \eta t} = 0,$$

$$\overline{t^3 \begin{matrix}\cos\\ \sin\end{matrix} \eta t} = 0,$$

$$\overline{t^n} = 0, \qquad n = 1, 2, 3, 4.$$

Applying these results to equation (4·2) we have

$$\ddot{\bar{\alpha}} = \tfrac{1}{2}(G_a + H_b) + \mathrm{E}_c \qquad \text{.....(4·3).}$$

Evaluating the right-hand side of this equation explicitly we find

$$\begin{aligned}\ddot{\bar{\alpha}} = {} & \left\{\frac{117\mu_1^2\mu_2^2}{2M^2\eta^2\gamma^9} + \frac{27\mu_1^2\mu_2^2(I_1 + I_2)}{8MI_1I_2\eta^2\gamma^7} - \frac{3\mu_1\mu_2\cos\epsilon_0}{2M\gamma^4}\right\}\cos\theta \\ & - \frac{27\mu_1^2\mu_2^2}{2M^2\eta^2\gamma^9}\cos(\epsilon_0 + 2\chi_0)\{\cos(\epsilon_0 + \theta) + \cos(\epsilon_0 - \theta)\} \\ & + \frac{9\mu_1^2\mu_2^2}{2M^2\eta^2\gamma^9}\sin(\epsilon_0 + 2\chi_0)\{\sin(\epsilon_0 + \theta) - \sin(\epsilon_0 - \theta)\} \\ & + \frac{9\mu_1^2\mu_2^2(I_1 - I_2)}{8MI_1I_2\eta^2\gamma^7}\sin(\epsilon_0 + 2\chi_0)\{\sin(\epsilon_0 + \theta) + \sin(\epsilon_0 - \theta)\} \\ & \qquad \text{.....(4·4),}\end{aligned}$$

* We have already seen that this choice of τ is possible when the doublets represent normal hydrogen atoms.

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where $\epsilon_0 = \phi_0 - \psi_0$, and $\chi_0 = \psi_0 - \theta$ ...(4·41), (4·42).

Now the terms in $\begin{matrix}\cos\\ \sin\end{matrix}(\epsilon_0 + 2\chi_0)$ change sign in every quarter revolution of either doublet, the periods of revolution of the two doublets being the same. That is, these terms change sign whenever the centre ($t = 0$ in previous work) of the time over which the average is taken is made earlier or later by a quarter of the period of revolution of either doublet. Thus on the average the terms in $\begin{matrix}\cos\\ \sin\end{matrix}(\epsilon_0 + 2\chi_0)$ contribute nothing permanent to $\bar{\bar{\alpha}}$*. Therefore we write

$$\bar{\bar{\alpha}} = \left\{\frac{117\mu_1^2\mu_2^2}{2M^2\eta^2r^9} + \frac{27\mu_1^2\mu_2^2(I_1+I_2)}{8MI_1I_2\eta^2r^7} - \frac{3\mu_1\mu_2\cos\epsilon_0}{2Mr^4}\right\}\cos\theta.$$

Also, as before, $\bar{\bar{\alpha}} = \rho\cos\theta - \tau\sin\theta$,

and therefore

$$\left.\begin{aligned} R = M\rho &= -\frac{3\mu_1\mu_2\cos\epsilon_0}{2r^4} + \frac{27\mu_1^2\mu_2^2(I_1+I_2)}{8I_1I_2\eta^2r^7} + \frac{117\mu_1^2\mu_2^2}{2M\eta^2r^9}\\ T = M\tau &= 0 \end{aligned}\right\} \quad (4\cdot5).$$

Now similarly to equation (4·3) we have

$$\bar{\bar{\phi}} = \bar{\bar{\phi}}_0 = \tfrac{1}{2}(G_a'' + H_b'') + E_c'' \qquad \ldots\ldots(4\cdot6).$$

By the first of equations (3·21) and an explicit evaluation of E_c'' this becomes

$$\begin{aligned}\bar{\bar{\phi}} = E_c'' &= -\frac{\mu_1\mu_2}{2I_1r^3}\sin\epsilon_0 - \frac{27\mu_1^2\mu_2^2\sin\epsilon_0\cos(\epsilon_0+2\chi_0)}{4MI_1\eta^2r^8}\\ &\quad - \frac{3\mu_1^2\mu_2^2(I_1-I_2)\cos\epsilon_0\sin(\epsilon_0+2\chi_0)}{4I_1^2I_2\eta^2r^6}\\ &= -\frac{\mu_1\mu_2}{2I_1r^3}\sin\epsilon_0 \qquad \ldots\ldots(4\cdot7)\end{aligned}$$

by the same argument as before. Hence we cannot now say that the angular velocities of the doublets remain constant and equal to their initial values; and if $(\phi_1 - \psi_1)$ is small initially, we do not know that it will remain small.

§ 5. In order to discuss this case more fully we make the additional assumption that the two doublets have the same

* If the average value of $\begin{matrix}\cos\\ \sin\end{matrix}(\epsilon_0+2\chi_0)$ is not exactly zero, it will be very small compared with unity, and the coefficient of $r^{-n}\begin{matrix}\cos\\ \sin\end{matrix}(\epsilon_0+2\chi_0)$ in equation (4·4) is only about $\frac{1}{3}$ or $\frac{1}{4}$ of the corresponding coefficient of r^{-n} in the terms independent of $\begin{matrix}\cos\\ \sin\end{matrix}(\epsilon_0+2\chi_0)$.

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moment of inertia, $I_1 = I_2 = I$ (say)*. Using Lagrange's equations of motion in ϕ and ψ, deduced from equations (2·0) and (2·1), we obtain the accurate (unaveraged) equation

$$\ddot{\epsilon} + \frac{\mu_1\mu_2}{Ir^3}\sin\epsilon = 0,$$

where $$\epsilon = \phi - \psi.$$

Or $$\ddot{\epsilon} + n^2 \sin\epsilon = 0 \qquad \text{.....(5·0)},$$

where $$n = \sqrt{\mu_1\mu_2/Ir^3} \qquad \text{.....(5·01)}.$$

Thus there is a pendulum motion in ϵ, in which the length of the simple equivalent pendulum is a function of the distance apart of the doublets. Thus the motion in ϵ is analogous to the motion of a pendulum of variable length.

We now want to compare the motion in ϵ with the motion of a pendulum of slowly varying length. We assume that the length of the equivalent simple pendulum only changes by a very small fraction of itself during one period in ϵ, and that there is no resonance between the vibrations in ϵ and the rotations of the doublets. We proceed to investigate whether these assumptions are fulfilled when the doublets represent hydrogen atoms in their principal quantum orbits. If $(-e)$ and m are the charge and mass respectively of an electron, and a the radius of the principal quantum orbit in the hydrogen atom, we have $\mu = \mu' = ea$, $I = ma^2$. Therefore

$$n^2 = e^2/mr^3 \qquad \text{.....(5·1)}.$$

We find that if τ_1 is the period of vibration in ϵ for small amplitudes, and τ' the period of revolution of a doublet,

$$\tau_1 = 3{\cdot}95\,.\,10^{-4}\,.\,r^{\frac{3}{2}} \text{ secs.}, \quad \tau' = 1{\cdot}52\,.\,10^{-16} \text{ secs.} \quad (5{\cdot}20),\ (5{\cdot}21),$$

therefore $$\tau_1/\tau' \fallingdotseq 2{\cdot}6\,.\,x^{\frac{3}{2}}\dagger \qquad \text{.....(5·22)},$$

where $r = x\,.\,10^{-8}$, so that x is the measure of r in Ångstrom units.

Now our work is based on the assumption that r is large compared with a, i.e. x is large compared with $\frac{1}{2}$‡. Hence τ_1 is large compared with τ'. Thus the period in ϵ contains many periods of revolution of the doublets, and there is no resonance between the vibrations in ϵ and the rotations of the doublets.

Let us suppose now that the relative velocity of the doublets is such that during the time $\tau_1\ \delta r/r$ is very small, where δr denotes

* This condition is always fulfilled when the doublets represent hydrogen atoms, for two hydrogen atoms would only have the same initial angular velocities if they had the same quantum numbers, and then they would have the same moments of inertia.

† Numerical results are calculated from formulae and data given by Sommerfeld, *Atomic Structure and Spectral Lines* (transl. Brose), and Jeans, *Dynamical Theory of Gases* (3rd ed.).

‡ $a = 0{\cdot}532$ Å. Even if r were only $10a$, τ_1 would be $30\tau'$.

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the change in r during one period in ϵ. Then by equation (5·1) $\delta n/n = -\frac{3}{2}\delta r/r$, and is very small, i.e. the length of the simple equivalent pendulum changes by a very small fraction of itself during one of its own oscillations.

The conditions are now satisfied for the motion in ϵ to be analogous to the motion of a pendulum of slowly varying length and for Ehrenfest's invariant to apply. The energy integral of equation (5·0) is

$$\tfrac{1}{2}\dot{\epsilon}^2 = n^2(\cos\epsilon - \cos\gamma) \qquad \ldots\ldots(5\cdot3),$$

where γ is the amplitude in ϵ*; and Ehrenfest's invariant is

$$\oint \dot{\epsilon} d\epsilon = \text{const.} \qquad \ldots\ldots(5\cdot4).$$

Equations (5·1), (5·3), (5·4) can easily be shown to lead to the equation

$$r = \lambda y^{\frac{3}{2}} \qquad \ldots\ldots(5\cdot5),$$

where λ is an arbitrary constant and

$$y = \sin^2\tfrac{1}{2}\gamma \int_0^{\frac{\pi}{2}} \frac{\cos^2\phi\, d\phi}{\sqrt{1 - \sin^2\tfrac{1}{2}\gamma \sin^2\phi}} \qquad \ldots\ldots(5\cdot51)$$

$$= E - K\cos^2\tfrac{1}{2}\gamma \qquad \ldots\ldots(5\cdot52),$$

K and E being the complete elliptic integrals of the first and second kind respectively to the modulus $\sin\frac{1}{2}\gamma$. By considering the integral in equation (5·51) we can show that r/λ or $y^{\frac{3}{2}}$ steadily increases from 0 to 1 as γ increases from 0 to π. From tables of elliptic functions we easily calculate the following values:

γ	20°	40°	80°	120°	160°
$\frac{r}{\lambda}$	0·083	0·205	0·491	0·768	0·963

Hence the curve giving r/λ as a function of γ is as shown in Fig. 2.

When we are given the value of γ corresponding to any given value of r, we can determine λ from the curve and then read off the value of γ for any value of r smaller than λ. γ and r increase and decrease together. If γ is real for any given value of r, γ is real for any smaller value of r.

Now before two rotating doublets with the same moment of inertia enter each other's fields their angular velocities will be the same if they have the same quantum number. That is, when r is

* The case of one doublet gaining complete revolutions on the other, corresponding to the equivalent pendulum swinging right round, would be represented in the analysis by γ imaginary or $|\cos\gamma| > 1$.

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infinite, $\dot{\epsilon} = 0$. Now γ is the value of $|\epsilon|$* when $\dot{\epsilon} = 0$. Therefore, when r is infinite, γ is the angle between the doublets and is therefore real. Therefore r/λ is finite. Therefore λ is infinite. Therefore when r is finite, $r/\lambda = 0$, $\gamma = 0$, and $\epsilon = 0$. This conclusion is only true if the preceding work is valid for all values of r greater than some definite finite value. We now investigate the limits of validity of our work.

When the doublets correspond to hydrogen atoms in their principal quantum orbits, we must have $r > r_1$, where r_1 is moderately large compared with a, the radius of a hydrogen atom.

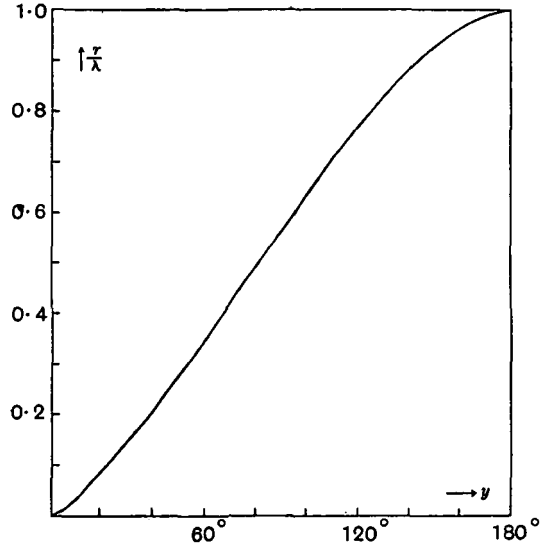

Fig. 2

Suppose for definiteness we take $r_1 = 10a = 5$ Å. This satisfies Debye's condition mentioned in § 1 for considering the field of a hydrogen atom as due to a rotating doublet. The force on an electron due to an electron or proton at a distance of $10a$ is only $\frac{1}{100}$ of the force on it due to its own proton. Hence the "coupling" is small. The distance travelled in one revolution of either doublet, when the doublets have the kinetic theory velocity appropriate to hydrogen atoms at 0° C. is $3{\cdot}8.10^{-11}$ cm., or less than $\frac{1}{1000}$ of their distance apart. Thus the condition mentioned just before equation (2·6) is satisfied. Also a choice of τ is possible for averaging purposes; and the condition that τ_1/τ' is large is satisfied.

Also the condition that $\delta r/r$ is to be small leads to the condition

* I.e. the absolute value of ϵ, when ϵ is taken to satisfy $-\pi < \epsilon \leqslant \pi$.

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$r < R_1$, where R_1 is small compared with 10,000 Å., $R_1 = 500$ Å. (say). Then our treatment of the motion is valid when $r_1 < r < R_1$.

Now we can see from Fig. 2 that whatever value γ had when $r = R_1$, when $r < \frac{1}{10}R_1$, $\gamma <$ about 24°, i.e. $1 \geqslant \cos\gamma \geqslant 0{\cdot}9$. Now $\cos\epsilon$ varies between $\cos\gamma$ and 1, hence very little error will result from putting $\cos\epsilon = 1$ for that part of the motion for which $r < \frac{1}{10}R_1$.

Thus, if $r_1 < r < \frac{1}{10}R_1$, or 5 Å. $< r <$ 50 Å., the two rotating doublets move as if there were a force of repulsion (R) between them given by

$$R = -\lambda_4 r^{-4} + \lambda_7 r^{-7} + \lambda_9 r^{-9} \qquad \text{.....(5·6),}$$

where

$$\lambda_4 = \tfrac{3}{2}\mu_1\mu_2, \quad \lambda_7 = 27\mu_1^2\mu_2^2/4I\eta^2, \quad \lambda_9 = 117\mu_1^2\mu_2^2/2M\eta^2$$
$$\text{.....(5·61), (5·62), (5·63),}$$

obtained by putting $I_1 = I_2 = I$ and $\cos\epsilon = 1$ in equation (4·5).

From equation (4·7) and the similar one for $\bar{\psi}$ we see that when $I_1 = I_2$, $\ddot{\bar{\phi}} + \ddot{\bar{\psi}} = 0$. Also the relative angular velocity is so small that one doublet gains an angle γ ($< \pi$) on the other only in the course of a large number of revolutions of either (since τ_1/τ' is large)*. Hence the angular velocities of the two doublets remain approximately constant and equal to their initial values, which are, of course, equal. Hence the λ's in equation (5·6) are constants, their numerical values being $\lambda_4 = 9{\cdot}68.10^{-36}$, $\lambda_7 = 1{\cdot}62.10^{-60}$, $\lambda_9 = 4{\cdot}34.10^{-79}$. We notice that when $r = 1$ Å. ($= 10^{-8}$ cm.) the repulsive term varying as r^{-9} is very small compared with the repulsive term varying as r^{-7} (the ratio being about $\frac{1}{370}$); the term in r^{-9} diminishes more rapidly with increasing distance than the term in r^{-7}. Thus at the distances for which our work is valid, we may write without sensible error

$$R = -9{\cdot}68.10^{-36}r^{-4} + 1{\cdot}62.10^{-60}r^{-7} \qquad \text{.....(5·7).}$$

This is a law of force of the same form as that obtained empirically by Lennard-Jones for helium, argon, and neon.

The attractive force in R just balances the repulsive force (i.e. $R = 0$) if $r \fallingdotseq 0{\cdot}55$ Å. This distance is much less than the minimum distance for which our work is valid. All we can deduce is that at distances for which our work is valid the attractive force preponderates. This excessive attractive force is not in accordance with the empirical results of Lennard-Jones. There are two possibilities, it may be due to the specialization of the mathematical

* This statement justifies the expansions of $\begin{matrix}\cos\\ \sin\end{matrix}\xi t$ in § 4 in the case when the rotating doublets represent normal Bohr hydrogen atoms, for we only require these expansions to be true for moderately few periods of revolution of each atom including the time $t = 0$; hence ξt is small compared with γ, itself less than π.

model; or, as a gas of hydrogen atoms is unstable and forms into a gas of ordinary hydrogen, it may be that the attractive force is greater in the case of hydrogen than in the case of the three monatomic gases helium, argon, and neon.

A useful way of comparing repulsive fields is by means of "diameters" as defined by Lennard-Jones*. If σ is the "diameter" corresponding to a repulsive force $\lambda_n r^{-n}$, we have

$$\sigma = \{\lambda_n/2{\cdot}06\,.\,10^{-16}\,(n-1)\}^{1/(n-1)}.$$

Applying this conception to the repulsive term in equation (5·7), we find $\sigma = 3{\cdot}31$ Å. This is of the same order of magnitude as the values obtained empirically by Lennard-Jones for helium ($\sigma = 3{\cdot}124$ Å.), neon ($\sigma = 4{\cdot}300$ Å.), and argon ($\sigma = 7{\cdot}053$ Å.). The value of n ($n = 7$) is rather smaller than those obtained empirically by Lennard-Jones for helium ($n = 14$), neon ($n = 11$), and argon ($n = 9$). It is to be noticed that the hydrogen atom is very much more unsymmetrical than the atoms of the three inert gases mentioned; on this account we should expect the index n to have a smaller value than in the case of these three inert gases. The agreement between the calculated and observed repulsive forces is quite good in view of the model chosen.

§ 6. *Summary.* We may summarize our conclusions as follows. If the rotating doublets have quite different angular velocities initially, then they repel each other with a force (R) given by

$$R = \lambda r^{-7} + \mu r^{-9} \qquad \text{.....(6·0),}$$

where
$$\lambda = \frac{3\mu_1^2\mu_2^2\,(I_1+I_2)}{8I_1I_2}\left\{\frac{9}{(\phi_1+\psi_1)^2}+\frac{1}{(\phi_1-\psi_1)^2}\right\} \qquad \text{...(6·01),}$$

and
$$\mu = \frac{9\mu_1^2\mu_2^2}{M}\left\{\frac{13}{(\phi_1+\psi_1)^2}+\frac{1}{(\phi_1-\psi_1)^2}\right\} \qquad \text{.....(6·02),}$$

ϕ_1 and ψ_1 being the (constant) angular velocities of the two doublets.

If the doublets have the same angular velocities initially, and the same moments of inertia, then over a certain range of r we have

$$R = -\lambda_4 r^{-4} + \lambda_7 r^{-7} + \lambda_9 r^{-9} \qquad \text{.....(6·1),}$$

where

$$\lambda_4 = \tfrac{3}{2}\mu_1\mu_2, \quad \lambda_7 = 27\mu_1^2\mu_2^2/16I\omega^2, \quad \lambda_9 = 117\mu_1^2\mu_2^2/8M\omega^2$$
$$\text{.....(6·11), (6·12), (6·13),}$$

and ω is the common value of the angular velocities of the doublets. When the doublets correspond to hydrogen atoms in their principal

* J. E. Jones, *Proc. Roy. Soc.* A, vol. CVI, pp. 452 *et seq.* (1924).

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quantum orbits, the range of distance becomes 5 Å. to 50 Å. and the formula for R reduces to

$$R = -9{\cdot}68.10^{-36}r^{-4} + 1{\cdot}62.10^{-60}r^{-7} \quad \ldots\ldots(6{\cdot}2).$$

This is a law of force of the type found empirically by Lennard-Jones for helium, neon, and argon. The attractive term in this formula is larger than the attractive terms found by Lennard-Jones. The repulsive term, however, which leads to a "diameter" of 3·31 Å., is in very satisfactory agreement with the repulsive terms found by Lennard-Jones.

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