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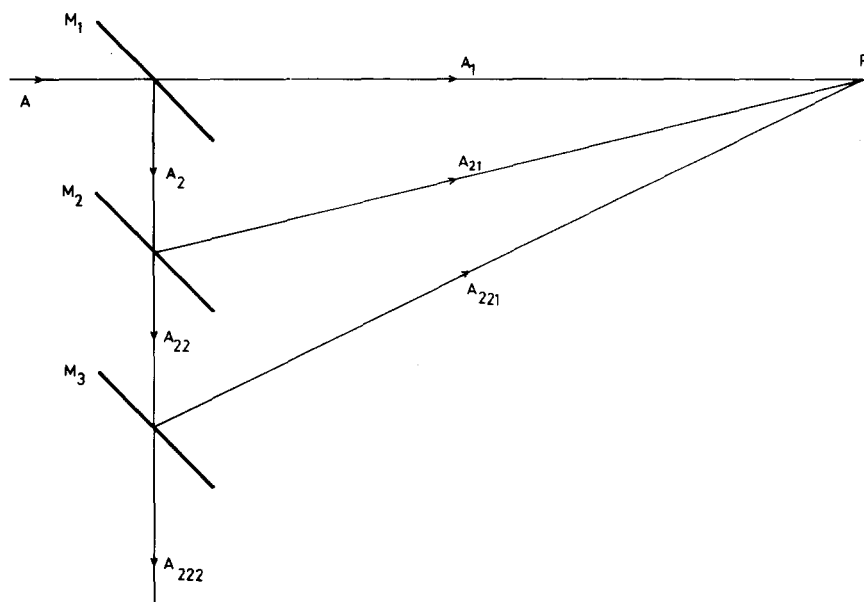View Online

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Fig. 1. Wave division at three partially transmitting mirrors M_1, M_2, and M_3. The complex amplitude A of the incident wave is split by M_1 into two parts A_1 and A_2; subsequently A_2 is split into A_{21} and A_{22} by M_2 and A_{22} is split into A_{221} and A_{222} by M_3. Waves of amplitude A_1, A_{21}, and A_{221} interfere at P.

graph of this article arose because we took seriously the predictions of a simple theory in a limiting case for which it was inadequate.

Finally, a simple example is given illustrating the principle involved when a wave of relatively high intensity undergoes complete cancellation by a wave of low intensity, after the latter has undergone two amplitude divisions. In Fig. 1, M_1, M_2, and M_3 represent partially transmitting mirrors and A is the amplitude of the wave incident upon M_1. A_1, A_2 are the amplitudes of the waves into which A is divided by M_1; similarly, A_2 is divided by M_2 into A_{21} and A_{22}, and A_{22} is divided by M_3 into A_{221} and A_{222}. The three waves of amplitude A_1, A_{21}, and A_{221} interfere at P, which may be regarded as a distant point such that the angle $M_1 \widehat{P} M_3$ is negligibly small so that the propagation vectors may be regarded as parallel. Conservation of energy requires

$$|A|^2 = |A_1|^2 + |A_2|^2, \quad |A_2|^2 = |A_{21}|^2 + |A_{22}|^2,$$
$$|A_{22}|^2 = |A_{221}|^2 + |A_{222}|^2.$$

In order to produce zero disturbance at P the amplitudes must satisfy $-A_1 = A_{21} + A_{221}$; simultaneous solutions of these equations may easily be found which also satisfy $|A_2|^2 < |A_1|^2$, i.e., which correspond to a wave of relatively high intensity undergoing complete cancellation by a wave of low intensity, after the latter has undergone two amplitude divisions. A numerical example of such a solution is

$$|A| = 1; \quad |A_1| = \tfrac{4}{5}, \quad |A_2| = \tfrac{3}{5};$$
$$|A_{21}| = 2/5, \quad |A_{22}| = \sqrt{5}/5;$$
$$|A_{221}| = \tfrac{2}{5}, \quad |A_{222}| = \tfrac{1}{5};$$

when the resultant disturbance at P may, with appropriate choice of phase, be made zero.

[1]M. Born and E. Wolf, *Principles of Optics* (Pergamon, Oxford, 1970), p. 323.

The classical polarizability of the hydrogen atom

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The electric polarizability of a "classical" hydrogen atom is calculated and found to have the value $\alpha = (21/4)a_0^3$ for an energy equal to the known quantum-mechanical ground state energy, as compared with the quantum-mechanical value of $(18/4)a_0^3$.

I. INTRODUCTION

The topic given in the title came to my attention recently by way of a well-known example often given in introduc-

tory or intermediate electromagnetism classes: Find the polarizability of an atom, using the simple model of a positive point charge nucleus surrounded by an equal negative charge cloud uniformly distributed throughout a sphere of

radius R. An elementary argument,[1] which begins by using Gauss' law to show that the field of such a uniform charge is proportional to the distance from the center, continues by showing that in the presence of an external field E the nucleus will be in equilibrium at a distance from the center which yields a dipole moment $M = R^3E$ (in cgs units), so that the polarizability is $\alpha = R^3$. Often one argues that a plausible choice of R for the hydrogen atom would be $R = a_0$, the Bohr radius; then we have $\alpha = a_0^3$, which is indeed of the right order of magnitude.

If, in a misguided attempt to "do better," one argues that, after all, the charge distribution is known from quantum mechanics to be exponential in r rather than uniform,[2] one easily obtians by the same method the slightly different result $\alpha = 3/4\,a_0^3$, owing to the fact that for the exponential distribution the electronic charge density at the origin is higher by a factor $\frac{4}{3}$ than it is for the uniform distribution. Unfortunately, as a conscientious but puzzled student knocking on my door had realized, this is *farther away* from, rather than closer to, the experimental value![3] The quantum mechanical value is well known[4] to be 4.5 a_0^3, which is six times larger than the "static" value quoted above. It was the effort to explain this discrepancy to my students (and, of course, to myself!) which led me to the considerations described below.

II. EFFECT OF FIELD ON PARTICULAR ORBITS

The "classical" value found as described above need not, of course, have any relation (except as to order of magnitude) to the correct quantum-mechanical value, since it is a "static" calculation which totally ignores the real dynamics of the electron. Nothing is said, for example, of the forces which would be needed to *keep* the uniform sphere of charge in place, or of the distortion which the external field would produce in that uniform distribution. But, after all, one *should* be able to do a proper classical calculation in the following sense: Given an electron in a Kepler orbit of fixed energy, investigate how that orbit is affected by an external field, and in particular, what average dipole moment is induced. The fact that classically orbits of *any* energy are allowed, whereas quantum mechanics instructs us that only particular ones are realized, can be "tacked on" afterward by looking at the classical result for the particular allowed energies (most importantly, the ground state energy) stipulated by quantum mechanics.

Thinking along these lines, it is natural to look first at some simple possible orbits. The simplest of all is the case of a circular orbit whose plane is perpendicular to the applied field. Clearly a circular orbit, with the nucleus displaced by a distance d normal to the plane of the orbit from the center, is possible; the component of the Coulomb force e^2/R^2 perpendicular to the plane must just balance the force due to the external field E: so $(e^2/R^2)(d/R) = eE$, and this gives $ed = R^3E$, so that $\alpha = R^3$. If we choose $R = a_0$, corresponding to the known ground state energy, which is $(-e^2/2a_0)$, of the hydrogen atom, we again have the result $\alpha = a_0^3$, just as for the static "sphere" distribution.

For other possible orbits the effect of the external field becomes harder to calculate. One reasonably simple case, which is in a certain sense at the opposite extreme from the circular one (which is characterized by *zero* eccentricity), is the degenerate ellipse of *maximum* eccentricity, i.e., a "straight line" orbit. Suppose the electron moves along the x axis, with the nucleus at the origin, and the electric field is

also along the x axis. The potenial energy of the electron is given by

$$V(x) = -e^2/x + eEx,$$

and the motion takes place between $x = 0$ and $x = x_0$, where x_0 is the classical "turning point" defined by $V(x_0) = \epsilon = -|\epsilon|$. Here ϵ is the energy of the electron, which is negative for a bound state. For weak fields $(E \ll e/x_0^2)$, solving for x_0 gives

$$x_0 = (e^2/|\epsilon|)(1 - \beta\cdots),$$

where

$$\beta = e^3E/|\epsilon|^2 \cong E/(e/x_0^2) \ll 1.$$

The expectation value of x may be calculated as the time average:

$$\langle x \rangle = \left(\frac{2}{T}\right)\int_0^{T/2} x(t)dt$$

and the period T is given by $T = 2\int_0^{T/2} dt$, so that we may write

$$\langle x \rangle = \int_0^{T/2} x(t)dt \Big/ \int_0^{T/2} dt = \int_0^{x_0} x\left(\frac{dx}{v}\right)\Big/ \int_0^{x_0}\frac{dx}{v}.$$

Here v, the velocity of the electron, is given by energy conservation:

$$\tfrac{1}{2}mv^2 = \epsilon - V(x) = e^2/x - eEx - |\epsilon|.$$

Thus we may write, after slight rearrangement,

$$\langle x \rangle = \int_0^{x_0} x^{3/2}[Q(x)]^{-1/2}dx \Big/ \int_0^{x_0} x^{1/2}[Q(x)]^{-1/2}dx,$$

with $Q(x) = 1 - (|\epsilon|/e^2)x - (|\epsilon|/e^2)^2\beta x^2$. The integrals can be done to first order in β (hence E) easily (see Appendix I), and the result is

$$\langle x \rangle = \frac{3}{4}\left(\frac{e^2}{|\epsilon|}\right) - \left(\frac{25}{32}\right)\left(\frac{e^5E}{|\epsilon|^3}\right).$$

It is the second term, which represents the *shift* of $\langle x \rangle$ induced by the external field E, which we want; the first term, $\langle x \rangle_0$, will average to zero if we remember that our "linear" atom could have been oriented *either* to the left *or* to the right of the origin with equal probability. Hence the induced dipole moment is, on average,

$$-e(\langle x \rangle - \langle x \rangle_0) = (25/32)(e^6/|\epsilon|^3)E,$$

which yields a polarizability

$$\alpha = (25/32)(e^6/|\epsilon|^3).$$

Now for the ground state of hydrogen, $|\epsilon| = e^2/2a_0$, so

$$\alpha = (25/32)e^6/(e^2/2a_0)^3 = (25/4)a_0^3.$$

This result is very interesting, inasmuch as it is over six times as great as the value (a_0^3) obtained for the circular orbit; furthermore, it is actually *greater* than the quantum-mechanical value of $(\frac{9}{2})a_0^3$. But we should not be too surprised at this, for on reflection we realize that the "straight line" orbit corresponds to *zero* angular momentum, whereas the circular orbit corresponds to the *maximum* angular momentum consistent with a given energy (which is, of course, $\hbar$ in the case of an orbit of energy $-e^2/2a_0$). Since we know that the quantum-mechanical ground state has angular momentum zero, a satisfactory correspondence has emerged; indeed we may suspect that a classical treatment which averaged over all possible angular momenta (i.e., orbits of all possible eccentricities and orientations

relative to the external field), might yield a value of the polarizability, surely intermediate between the extremes of a_0^3 and $(25/4)a_0^3$, which might be fairly close to the quantum-mechanical value.

III. GENERAL TREATMENT

In order to carry out this program, we may use the fundamental principle of statistical mechanics: A system is equally likely to be found (*a priori*) in equal volumes of its phase space, consistent with whatever restrictions or constraints are present. Here our only restriction is on the energy, so we are dealing with a "microcanonical" ensemble.[5] Then the prescription for finding the average of any function $F(q, p)$ of the coordinates and momenta of the system is given by

$$\langle F \rangle = \int F(q, p)\delta(H - \epsilon)d\Gamma \Big/ \int \delta(H - \epsilon)d\Gamma.$$

Here H is the Hamiltonian of the system, ϵ is the energy value, and $d\Gamma$ is the appropriate element of phase space. The delta function enforces the restriction to a constant-energy hypersurface in the phase space. In our case we have

$$H = p^2/2m - e^2/r + e\mathbf{E} \cdot \mathbf{r}$$

as the Hamiltonian of the electron in the field of the nucleus (assumed at the origin) and the external field $\mathbf{E}$; we will take $\epsilon = -|\epsilon|$ to be a negative energy corresponding to a bound state. We want to find the expectation value of the electron's dipole moment $\mathbf{M} = -e\mathbf{r}$. Clearly the only nonvanishing component of $\mathbf{M}$ will be the one in the direction of $\mathbf{E}$; so if we choose the z axis of a polar coordinate system in the direction of the external field $\mathbf{E}$, we may rewrite the Hamiltonian as

$$H = p^2/2m - e^2/r + eEr \cos \theta$$

and the desired dipole moment as

$$\langle M \rangle = \langle -er \cos \theta \rangle.$$

The phase space element is

$$d\Gamma = dx\, dy\, dz\, dp_x\, dp_y\, dp_z,$$

where x, y, z and p_x, p_y, p_z are the electron's Cartesian position and momentum components; but, since H depends only on the squared magnitude p^2 of the momentum and on r and θ, clearly a "polar" volume element in both the space and momentum parts of the phase space is suggested:

$$d\Gamma = (2\pi r^2 \sin \theta\, d\theta\, dr)(4\pi p^2\, dp),$$

where the integration over the solid angle in $\mathbf{p}$ space and over the azimuth angle in $\mathbf{r}$ space has been carried out. The required average therefore reduces to

$$\langle r \cos \theta \rangle$$

$$= \left(\int_0^\infty \int_0^\infty \int_0^\pi r \cos \theta \delta(H - \epsilon)p^2\, dp r^2\, dr \sin \theta\, d\theta \right)$$

$$\left(\int_0^\infty \int_0^\infty \int_0^\pi \delta(H - \epsilon)p^2\, dp r^2 \sin \theta\, d\theta \right)^{-1}.$$

The delta-function factor in the integrand can be used to carry out the p integration; with the help of some standard delta-function algebra it may be rewritten as

$$\delta(H - \epsilon) = \delta(p^2/2m - e^2/r + eEr \cos \theta - \epsilon)$$

$$= 2m\delta[p^2 - 2m(e^2/r - eEr \cos \theta + \epsilon)]$$

$$= 2m\delta[p^2 - P^2(r, \theta)]$$

$$= (m/P)\{\delta[p - P(r, \theta)] + \delta[p + P(r, \theta)]\},$$

with $P(r, \theta)$ defined by

$$P^2(r, \theta) = 2m(e^2/r - eEr \cos \theta - |\epsilon|).$$

Since the range of the p integration is from 0 to ∞, only the term $\delta(p - P)$ in the integrand gives a nonvanishing contribution, and then only if the condition $P^2(r, \theta) > 0$ is satisfied. Hence we have

$$\int_0^\infty p^2 \delta(H - \epsilon)dp = \frac{m}{P} \int_0^\infty p^2 \delta(p - P)dp$$

$$= \begin{cases} mP(r, \theta), & \text{if } P^2(r, \theta) \geqslant 0, \\ 0, & \text{otherwise.} \end{cases}$$

Then the required averge reduces to

$$\langle r \cos \theta \rangle = \frac{\iint_R r \cos \theta P(r, \theta)r^2 \sin \theta\, dr\, d\theta}{\iint_R P(r, \theta)r^2 \sin \theta\, dr\, d\theta},$$

where the region of integration R for both numerator and denominator is defined by the condition

$$e^2/r - eEr \cos \theta - |\epsilon| \geqslant 0.$$

Here again the required integrals can be done to first order in the field E without great difficulty (see Appendix II) with the result

$$\langle r \cos \theta \rangle = -[21/32(e^5 E / |\epsilon|^3].$$

Hence the induced dipole moment is

$$\langle M \rangle = \langle -er \cos \theta \rangle = +(21/32)(e^6 E / |\epsilon|^3)$$

and for $|\epsilon| = e^2/2a_0$, the hydrogen ground state energy, we obtain

$$\langle M \rangle = (21/4)a_0^3 E,$$

so that the polarizability is

$$\alpha = (21/4)a_0^3.$$

This lies, as we suspected, between the extremes for the "circular" and the "straight line" orbits, although considerably closer to the latter. Furthermore, it is fairly close to the quantum-mechanical result, exceeding it by a factor 7/6.

IV. SUMMARY

We have shown that the polarizability of hydrogen may be found in a "semiclassical" fashion and that the result is considerably closer to the quantum-mechanical value than is the static "charge-cloud" value with which the whole discussion started. The calculation is, we believe, understandable at the junior/senior level, and is instructive in that ideas from electromagnetism, classical mechanics, and statistical mechanics are all drawn upon. The result is one that we have not found in a casual search of the literature (nor in responses to random queries addressed to knowledgeable colleagues!) and it may therefore be of some interest in its own right as well as *qua* pedagogical example.

Professor Sir Sam Edwards and to Professor Volker Heine for their kind hospitality at the Cavendish. I also thank Professor Eugen Merzbacher for helpful discussions and Professor Neil Ashcroft and Dr. Tricia Reeves for comments on the first draft of the paper.

APPENDIX A

The integrals to be done are of the form

$$J_n = \int_0^{x_0} x^n [Q(x)]^{-1/2} dx, \quad \text{for } n = \frac{1}{2}, \frac{3}{2},$$

where $Q(x) = [1 - x/d - \beta(x^2/d^2)]$, with $d = e^2/|\epsilon|$ and $\beta = Ed^2/e \ll 1$, and with $x_0 =$ the root of $Q(x)$ which is near $x = d$:

$$x_0 = d(1 - \beta...).$$

Rewriting $Q(x) = (1 - x/x_0)[1 + \beta x_0/d^2)x]$, we may expand the integrand for small β as

$$[Q(x)]^{-1/2} = (1 - x/x_0)^{-1/2}[1 - (\beta x_0/2d^2)x...],$$

so that

$$J_n = \int_0^{x_0} x^n \left(1 - \frac{x}{x_0}\right)^{-1/2} \left(1 - \frac{\beta x_0}{2d^2} x + \cdots\right) dx.$$

Then changing variables by the substitution $x = x_0 \sin^2 \psi$, we have

$$J_n = 2x_0^{n+1} \int_0^{\pi/2} \sin^{2n+1} \psi \left(1 - \frac{\beta x_0^2}{2d^2} \sin^2 \psi + \cdots\right) d\psi.$$

For the required values of n the integrals are elementary, and give

$$J_{1/2} = (\pi d^{3/2}/2)[1 - (15/8)\beta...]$$

and

$$J_{3/2} = (3\pi d^{5/2}/8)[1 - (35/12)\beta...].$$

Hence

$$\langle x \rangle = \frac{J_{3/2}}{J_{1/2}} = \frac{3d}{4} - \frac{25\beta d}{32}... = \frac{3}{4}\frac{e^2}{|\epsilon|} - \frac{25}{32}\frac{e^5 E}{|\epsilon|^3}....$$

APPENDIX B

The integrals to be calculated are I_1 and I_2, where

$$I_1 = \int_R \int P(r, \theta) r^2 \sin \theta \, dr \, d\theta$$

and

$$I_2 = \int_R \int r \cos \theta \, P(r, \theta) r^2 \sin \theta \, dr \, d\theta.$$

Here $P^2(r, \theta) = e^2/r - eEr \cos \theta - |\epsilon|$ and the region R is defined by the condition $P^2(r, \theta) \geqslant 0$. It is convenient to use $u = \cos \theta$ as the integration variable; then we have

$$I_1 = \int_{-1}^1 du \int_0^{r_0} P(r, u) r^2 \, dr$$

and

$$I_2 = \int_{-1}^1 u \, du \int_0^{r_0} P(r, u) r^3 \, dr,$$

where r_0 is the root of $P^2(r, u) = 0$, which is close to $d = e^2/|\epsilon|$, and is given to first order in the field E by

$r_0 = d(1 - \beta u...)$ with β defined as in Appendix A. Apart from a constant which cancels on taking the ratio I_2/I_1, we may then write

$$I_1 = \int_{-1}^1 du \int_0^{r_0} r^{3/2}[Q(r, u)]^{1/2} \, dr$$

and

$$I_2 = \int_{-1}^1 u \, du \int_0^{r_0} r^{5/2}[Q(r, u)]^{1/2} \, dr,$$

where

$$Q(r, u) = 1 - \frac{r}{d} - \beta u \frac{r^2}{d^2} = \left(1 - \frac{r}{r_0}\right)\left(1 + \frac{\beta u r_0 r}{d^2}\right).$$

then to first order in β, the integrals become

$$I_1 = \int_{-1}^1 du \int_0^{r_0} r^{3/2} \sqrt{1 - \frac{r}{r_0}} \left(1 + \frac{\beta r_0 u}{2d^2} r...\right) dr$$

and

$$I_2 = \int_{-1}^1 u \, du \int_0^{r_0} r^{5/2} \sqrt{1 - \frac{r}{r_0}} \left(1 + \frac{\beta r_0 u}{2d^2} r...\right) dr,$$

and the same change of variable as used in Appendix A is appropriate: $r = r_0 \sin^2 \psi$. Then

$$I_1 = 2r_0^{5/2} \int_{-1}^1 du \int_0^{\pi/2} \sin^4 \psi \cos^2 \psi$$
$$\times \left(1 + \frac{\beta r_0^2 u}{2d^2} \sin^2 \psi...\right) d\psi$$

and

$$I_2 = 2r_0^{7/2} \int_{-1}^1 u \, du \int_0^{\pi/2} \sin^6 \psi \cos^2 \psi$$
$$\times \left(1 + \frac{\beta r_0^2 u}{2d^2} \sin^2 \psi...\right) d\psi.$$

Since it is clear that the first nonvanishing term in I_2 is the term linear in β, only the zero-order term in I_1 is required, and the results are

$$I_1 = \pi d^{5/2}/8$$

and

$$I_2 = -(21/256)\beta d^{7/2}.$$

so that

$$\langle r \cos \theta \rangle = \frac{I_2}{I_1} = -\frac{21}{32}\beta d = -\frac{21}{32}\frac{e^5 E}{|\epsilon|^3}.$$

[1] This argument is given in many texts; for example, D. J. Griffiths, *Introduction to Electrodynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1981), pp. 139 and 140. (note that, in SI units, a factor $4\pi\epsilon_0$ is present in expressions for the polarizability, which is absent in cgs units.)

[2] As suggested, e.g., in Ref. 1 Problem 2, p. 141.

[3] A. M. Portis [*Electromagnetic Fields* (Wiley, New York, 1978), p. 80] lists an experimental value which corresponds to $\alpha = 4.4a_0^3$.

[4] E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1970), p. 424.

[5] That is, we contemplate a collection of hydrogen atoms, all having the same energy, but with "random" values of eccentricities of their orbits and orientations of the planes of their orbits. The correct specification of this "randomness" lies in attributing equal probabilities to equal volumes of the phase space of the electron in the atom.