The Electromagnetic Shift of Energy Levels

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(Received June 27, 1947)

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Reprinted in "Quantum Electrodynamics", edited by Julian Schwinger

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B very beautiful experiments, Lamb and Retherford[1] have shown that the fine structure of the second quantum state of hydrogen does not agree with the prediction of the Dirac theory. The $2s$ level, which according to Dirac's theory should coincide with the $2p_{\frac{1}{2}}$ level, is actually higher than the latter by an amount of about 0.033 cm^{-1} or 1000 megacycles. This discrepancy had long been suspected from spectroscopic measurements.[2][3] However, so far no satisfactory theoretical explanation has been given. Kemble and Present, and Pasternack[4] have shown that the shift of the Is level cannot be explained by a nuclear interaction of reasonable magnitude, and Uehling[5] has investigated the effect of the "polarization of the vacuum" in the Dirac hole theory, and has found that this effect also is much too small and has, in addition, the wrong sign.

Schwinger and Weisskopf, and Oppenheimer have suggested that a possible explanation might be the shift of energy levels by the interaction of the

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[1]Phys. Rev. **72,** 241 (1947).

[2]W. V. Houston, Phys. Rev. **51,** 446 (1937).

[3]R. C. Williams, Phys. Rev. **54,** 558 (1938).

[4]E. C. Kemble and R. D. Present, Phys. Rev. **44,** 1031 (1932); S. Pasternack, Phys. Rev. **54,** 1113 (1938).

[5]E. A. Uehling, Phys. Rev. **48,** 55 (1935).

electron with the radiation field. This shift comes out infinite in all existing theories, and has therefore always been ignored. However, it is possible to identify the most strongly (linearly) divergent term in the level shift with an electromagnetic mass effect which must exist for a bound as well as for a free electron. This effect should properly be regarded as already included in the observed mass of the electron, and we must therefore subtract from the theoretical expression, the corresponding expression for a free electron of the same average kinetic energy. The result then diverges only logarithmically (instead of linearly) in non-relativistic theory: Accordingly, it may be expected that in the hole theory, in which the main term (self-energy of the electron) diverges only logarithmically, the result will be convergent after subtraction of the free electron expression.[6] This would set an effective upper limit of the order of mc^2 to the frequencies of light which effectively contribute to the shift of the level of a bound electron. I have not carried out the relativistic calculations, but I shall assume that such an effective relativistic limit exists.

The ordinary radiation theory gives the following result for the self-energy of an electron in a quantum state m, due to its interaction with transverse electromagnetic waves:

$$W = -(2e^2/3\pi hc^3) \times \int_0^K kdk \sum_n |\mathbf{v}_{mn}|^2/(E_n - E_m + k), \qquad (1)$$

where $k = h\omega$ is the energy of the quantum and v is the velocity of the electron which, in non-relativistic theory, is given by

$$\mathbf{v} = \mathbf{p}/m = (h/im)\nabla. \qquad (2)$$

Relativistically, $\mathbf{v}$ should be replaced by $c\alpha$ where α is the Dirac operator. Retardation has been neglected and can actually be shown to make no substantial difference. The sum in (1) goes over all atomic states n, the integral over all quantum energies k up to some maximum K to be discussed later.

For a free electron, $\mathbf{v}$ has only diagonal elements and (1) is replaced by

$$W_0 = -(2e^2/3\pi hc^3) \int kdk\mathbf{v}^2/k. \qquad (3)$$

This expression represents the change of the kinetic energy of the electron for fixed momentum, due to the fact that electromagnetic mass is added to

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[6]It was first suggested by Schwinger and Weisskopf that hole theory must be used to obtain convergence in this problem.

the mass of the electron. This electromagnetic mass is already contained in the experimental electron mass; the contribution (3) to the energy should therefore be disregarded. For a bound electron, $\mathbf{v}^2$ should be replaced by its expectation value, $(\mathbf{v}^2)_{mm}$ But the matrix elements of $\mathbf{v}$ satisfy the sum rule

$$\sum_n |\mathbf{v}_{mn}|^2 = (\mathbf{v}^2)_{mm}. \tag{4}$$

Therefore the relevant part of the self-energy becomes

$$W' = W - W_0 = +\frac{2e^2}{3\pi hc^3} \times \int\limits_0^K dk \sum_n \frac{|\mathbf{v}_{mn}|^2(E_n - E_m)}{E_n - E_m + k}. \tag{5}$$

This we shall consider as a true shift of the levels due to radiation interaction.

It is convenient to integrate (5) first over k. Assuming K to be large compared with all energy differences $E_n - E_m$ in the atom,

$$W' = \frac{2e^2}{3\pi hc^3} \sum_n |\mathbf{v}_{mn}|^2(E_n - E_m) \ln \frac{K}{|E_n - E_m|}. \tag{6}$$

(If $E_n - E_m$ is negative, it is easily seen that the principal value of the integral must be taken, as was done in (6).) Since we expect that relativity theory will provide a natural cut-off for the frequency k, we shall assume that in (6)

$$K \approx mc^2. \tag{7}$$

(This does not imply the same limit in Eqs. (2) and (3).) The argument in the logarithm in (6) is therefore very large; accordingly, it seems permissible to consider the logarithm as constant (independent of n) in first approximation. We therefore should calculate

$$A = \sum_n A_{nm} = \sum_n |\mathbf{p}_{nm}|^2(E_n - E_m). \tag{8}$$

This sum is well known; it is

$$a = \Sigma|\mathbf{p}_{nm}|^2(E_n - E_m) = -h^2 \int \psi_m^* \nabla V \cdot \nabla \psi_m dr$$

$$= \tfrac{1}{2}h^2 \int \nabla^2 V \psi_m^2 dr = 2\pi h^2 e^2 Z \psi_m^2(0). \tag{9}$$

for a nuclear charge Z. For any electron with angular momentum $l \neq 0$ the wave function vanishes at the nucleus; therefore, the sum $A = 0$. For example, for the $2p$ level the negative contribution $A_{1S,2P}$ balances the positive

contributions from all other transitions. For a state with $l = 0$, however,

$$\psi_m^2(0) = (Z/na)^2/\pi, \tag{10}$$

where n is the principal quantum number and a is the Bohr radius.

Inserting (10) and (9) into (6) and using relations between atomic constants, we get for an S state

$$W_{ns}' = \frac{8}{3\pi} \left(\frac{e^2}{hc}\right)^3 Ry \frac{Z^4}{n^3} \ln \frac{K}{(E_n - E_m)_{A\mathbf{v}}}, \tag{11}$$

where Ry is the ionization energy of the ground state of hydrogen. The shift for the $2p$ state is negligible; the logarithm in (11) is replaced by a value of about -0.04. The average excitation energy $(E_n - E_m)_{A\mathbf{v}}$ for the $2s$ state of hydrogen has been calculated numerically[7] and found to be 17.8 Ry, an amazingly high value. Using this figure and $K = mc^2$, the logarithm has the value 7.63, and we find

$$W_{ns}' = 136 \ln[K/(E_n - E_m)] = 1040 \text{ megacycles.} \tag{12}$$

This is in excellent agreement with the observed value of 1000 megacycles.

A relativistic calculation to establish the limit K is in progress. Even without exact knowledge of K, however, the agreement is sufficiently good to give confidence in the basic theory. This shows

(1) that the level shift due to interaction with radiation is a real effect and is of finite magnitude,

(2) that the effect of the infinite electromagnetic mass of a point electron can be eliminated by proper identification of terms in the Dirac radiation theory.

(3) that an accurate experimental and theoretical investigation of the level shift may establish relativistic effects (e.g., Dirac hole theory). These effects will be of the order of unity in comparison with the logarithm in Eq. (11).

If the present theory is correct, the level shift should increase roughly as Z^4 but not quite so rapidly, because of the variation of $(E_n - E_m)_{A\mathbf{v}}$ in the logarithm. For example, for He$^+$ the shift of the es level should be about 13 times its value for hydrogen, giving 0.43 cm^{-1}, and that of the $3s$ level about 0.13 cm^{-1}. For the x-ray levels LI ind LII, this effect should be superposed upon the effect of screening which it partly compensates. An accurate theoretical calculation of the screening is being undertaken to establish this point.

This paper grew out of extensive discussions at the Theoretical Physics Conference on Shelter Island, June 2 to 4, 1947. The author wishes to

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[7] I am indebted to Dr. Stehn and Miss Steward for the numerical calculations.

express his appreciation to the National Academy of Science which sponsored this stimulating conference.