PHYSICAL REVIEW VOLUME 75, NUMBER 3 FEBRUARY 1, 1949

On the Self-Energy of a Bound Electron*

NORMAN M. KROLL** AND WILLIS E. LAMB, JR.
Columbia University, New York, New York

(Received October 7, 1948)

The electromagnetic shift of the energy levels of a bound electron has been calculated on the basis of the usual formulation of relativistic quantum electrodynamics and positron theory. The theory gives a finite result of 1052 megacycles per second for the shift $2^2S_{\frac{1}{2}}-2^2P_{\frac{1}{2}}$ in hydrogen, in close agreement with the non-relativistic calculation by Bethe.

I. INTRODUCTION

BETHE[1] has recently discussed the anomalous fine structure[2] in hydrogen on the basis of non-relativistic quantum electrodynamics. His result for the $2^2S_{\frac{1}{2}}-2^2P_{\frac{1}{2}}$ displacement was

$$\Delta W = W(2^2S_{\frac{1}{2}}) - W(2^2P_{\frac{1}{2}}) = (\alpha^3 Ry/3\pi)\log(K/\bar{\epsilon}), \quad (1)$$

where $\alpha = e^2/\hbar c \sim 1/137$ the fine structure constant, Ry the Rydberg energy $\alpha^2mc^2/2$, and $\bar{\epsilon}$ an average excitation energy of the atom, calculated to be $17.8Ry$. As Bethe's calculation diverged logarithmically, it was necessary for him to introduce a cut-off energy K for the light quanta which could be emitted and reabsorbed by the atom. On the basis of speculations as to the improved convergence of a relativistic calculation which included positron theoretic effects, Bethe took K equal to mc^2. This led to a value of $\Delta W/h = 1040$ megacycles per second, which was in very good agreement with the then available observation[3] of 1000 Mc/sec.

The purpose of this paper is to show that a relativistic calculation of ΔW does, in fact, give a convergent answer, and to present the results and some details of a calculation based on the 1927–1934 formulation of quantum electrodynamics due to Dirac, Heisenberg, Pauli, and Weisskopf. It will appear from this that the formal relativistic invariance of the present theory is to some degree illusory in that all self-energies diverge logarithmically, so that the difference of two energies such as $W(2^2S_{\frac{1}{2}})$ and $W(2^2P_{\frac{1}{2}})$, although finite, is not necessarily unique. The method we have used has a certain simplicity in its motivation, however, and the results are surprisingly plausible in their mathematical appearance. In any case, the calculations may serve as an illustration of the extent to which physical results may be derived from a divergent field theory.

The calculation is incomplete in several well defined respects. It is only made to order α in the coupling between the electron and the electromagnetic field, and to fourth order in the ratio of the velocity of the atomic electron to the velocity of light. It is expected that these deficiencies will be made up elsewhere. We will make no effort to improve on the low frequency part of the calculation as done by Bethe, for this is essentially a non-relativistic problem.

II. DERIVATION OF EQUATIONS FOR SELF-ENERGY

We start from the Hamiltonian for a system of N electrons moving in an external static electric potential energy field V and interacting with the radiation field. After elimination of the longitudinal and scalar photons in the usual way, we obtain the Hamiltonian

$$H = H_{\text{rad}} + H_{\text{mat}} + H_{\text{int}}, \quad (2)$$

$$H_{\text{rad}} = \int d\mathbf{k} \sum_{\lambda=1}^{2} N_{\mathbf{k}\lambda}\hbar c|\mathbf{k}|, \quad (3)$$

---

* Work supported by the Signal Corps.

** Now National Research Fellow at The Institute for Advanced Study.

[1] H. A. Bethe, Phys. Rev. 72, 339 (1947). It may be of some interest to observe that if the non-relativistic theory is taken seriously to such an extent that retardation and the recoil energy in the energy denominators are retained, the dynamic self-energy diverges only *logarithmically*, and the $S-P_{\frac{1}{2}}$ level shift *converges*, and, in fact, with K determined to be $K=2mc^2$. The resulting shift of 1134 Mc is in disagreement with the observations.

[2] W. E. Lamb, Jr. and R. C. Retherford, Phys. Rev. 72, 241 (1947).

[3] A later tentative value reported at the April 1948 Washington Physical Society meeting was 1065±20 Mc/sec.

$$H_{\text{mat}}=\sum_{i=1}^{N}\left[c\boldsymbol{\alpha}_i\cdot\mathbf{p}_i+\beta_i mc^2+V(\mathbf{r}_i)\right],\tag{4}$$

$$H_{\text{int}}=-\sum_{i=1}^{N}e\boldsymbol{\alpha}_i\cdot\mathbf{A}(\mathbf{r}_i)+\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}e^2/r_{ij}.\tag{5}$$

Here e is the (negative) charge on the electron; $\boldsymbol{\alpha}$, β are the Dirac matrices in the form

$$\boldsymbol{\alpha}=\begin{pmatrix}0 & \boldsymbol{\sigma}\\ \boldsymbol{\sigma} & 0\end{pmatrix},\quad \beta=\begin{pmatrix}I & 0\\ 0 & -I\end{pmatrix},\tag{6}$$

where $\boldsymbol{\sigma}$ are the usual two-component Pauli matrices. The vector potential of the radiation field is expanded in plane waves normalized in the continuous spectrum as

$$\mathbf{A}(\mathbf{r})=-(i/2\pi)\int d\mathbf{k}\sum_{\lambda=1}^{2}(\hbar c/k)^{\frac{1}{2}}\mathbf{b}_{\mathbf{k}\lambda}\mathbf{e}_{\mathbf{k}\lambda}\times\exp(i\mathbf{k}\cdot\mathbf{r})+\text{conj.},\tag{7}$$

where $\mathbf{b}_{\mathbf{k}\lambda}{}^{+}$, $\mathbf{b}_{\mathbf{k}\lambda}$ are the creation and destruction operators for a light quantum of wave vector $\mathbf{k}$ and polarization type $\lambda=1, 2$.

In position theory, because of the indefiniteness of the number of electrons, it is convenient to use second quantization for the electrons as well as for the light quanta. Then

$$H_{\text{mat}}\rightarrow\int d\mathbf{x}\psi^{+}(\mathbf{x})\{c\boldsymbol{\alpha}\cdot\mathbf{p}+\beta mc^2+V(\mathbf{x})\}\psi(\mathbf{x}),\tag{8}$$

$$H_{\text{int}}\rightarrow-\int d\mathbf{x}\psi^{+}(\mathbf{x})e\boldsymbol{\alpha}\cdot\mathbf{A}(\mathbf{x})\psi(\mathbf{x})+\int\int d\mathbf{x}d\mathbf{x}'\psi^{+}(\mathbf{x})\psi(\mathbf{x})(e^2/|\mathbf{x}-\mathbf{x}'|)\times\psi^{+}(\mathbf{x}')\psi(\mathbf{x}')=\mathbf{H}_1+\mathbf{H}_C,\tag{9}$$

where $\psi^{+}(\mathbf{x})$ and $\psi(\mathbf{x})$ are, respectively, creation and destruction operators for an electron. We will expand $\psi(\mathbf{x})$ in terms of the eigenfunctions $u_n(\mathbf{x})$ of the potential field V

$$\psi(\mathbf{x})=\sum_n \mathbf{a}_n u_n(\mathbf{x}),\tag{10}$$

where the coefficients $\mathbf{a}_n$ are operators corresponding to the destruction of an electron in state n, etc.

We are concerned with the self-energy of a "single" electron bound in some stationary state $u_a(\mathbf{r})$ in the potential field V. In positron theory, this is taken to mean "self-energy of one electron in state a plus the vacuum electrons" minus "self-energy of the vacuum electrons alone." The highly divergent interaction of the extra electron with the infinite charge density of the vacuum electrons must still be removed. This is done by the process of symmetrization[4, 5] in which the calculation is also made using the equally justified picture that all the electrons in existence are positively charged, so that the observance of a negatively charged electron in state a corresponds to a vacancy in the sea of negative energy states otherwise filled with positively charged particles. Then the results of the two methods of calculation are averaged. Since in the first picture there is one particle present in addition to the vacuum particles, and in the second picture one particle fewer, the self-term $i=j$ in the electrostatic energy cancels out as does the direct Coulomb interaction between the bound electron and the vacuum electrons, insofar as the latter are not polarized by an external electric field. The result is an avoidance of all singularities worse than logarithmic, and these may be plausibly discarded by renormalization of charge[6] and mass.

The self-energy to order α consists of the first-order Coulomb self-energy W_C and the second-order electrodynamic self-energy W_D. The former will split naturally into a direct or vacuum polarization term W_P and a static exchange term W_S. The static and dynamic terms W_S and W_D were first calculated by Weisskopf[5] in 1934 for the case of a free electron.

To calculate W_C we need the expectation values of the operator

$$H_C=\frac{1}{2}\int\int d\mathbf{x}d\mathbf{x}'\psi^{+}(\mathbf{x})\psi(\mathbf{x})\times(e^2/|\mathbf{x}-\mathbf{x}'|)\psi^{+}(\mathbf{x}')\psi(\mathbf{x}')\tag{11}$$
$$=\sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta}A_{\alpha\beta\gamma\delta}\mathbf{a}_{\alpha}{}^{+}\mathbf{a}_{\beta}\mathbf{a}_{\gamma}{}^{+}\mathbf{a}_{\delta},$$

where

$$A_{\alpha\beta\gamma\delta}=\frac{1}{2}\int\int d\mathbf{x}d\mathbf{x}'u_{\alpha}{}^{*}(\mathbf{x})u_{\beta}(\mathbf{x})\times(e^2/|\mathbf{x}-\mathbf{x}'|)u_{\gamma}{}^{*}(\mathbf{x}')u_{\delta}(\mathbf{x}'),\tag{12}$$

---

[4] W. Heisenberg, Zeits. f. Physik 90, 209 (1934).

[5] V. F. Weisskopf, Zeits. f. Physik 90, 817 (1934).

[6] P. A. M. Dirac, Solvay Congress, 1933.

for the states represented by the Schrödinger functionals

$$\Phi(1_a 0_{r'} 1_\rho),\ \Phi(0_r 1_\rho),\ \text{first picture,} \tag{13a}$$

$$\Phi(0_{(\rho)} 0_{(a)} 1_{(r')}),\ \Phi(0_{(\rho)} 1_{(r)}),\ \text{second picture.} \tag{13b}$$

Here r denotes any positive energy state, while a prime indicates the exclusion of the state a occupied by the bound electron. The letters ρ, σ denote any negative energy state, while the indices n, α, β, γ, and δ are to be used for a complete set of states of any energy whatever. In the alternate picture, a positive energy state of a positive particle is represented by (ρ) and a negative energy state by (r), (s). The state whose vacancy constitutes our electron is denoted by (a).

Consider the expectation value

$$\Phi^*(1_a 0_{r'} 1_\rho) \sum_{\alpha\beta\gamma\delta} a_\alpha{}^+ a_\beta a_\gamma{}^+ a_\delta A_{\alpha\beta\gamma\delta}\, \Phi(1_a 0_{r'} 1_\rho).$$

Using the matrix elements[5] for the destruction and creation operators, we obtain

$$\sum_r A_{arra} + \sum_\rho A_{\rho\rho aa} + \sum_\rho A_{aa\rho\rho} + \sum_\rho \sum_\sigma A_{\sigma\sigma\rho\rho} + \sum_\rho \sum_{r'} A_{\rho r' r' \rho}.$$

Subtracting the vacuum terms

$$\sum_\rho \sum_\sigma A_{\sigma\sigma\rho\rho} + \sum_\rho \sum_r A_{\rho r r \rho},$$

the self-energy of the electron in state a on the basis of the negative particle picture is

$$\sum_r A_{arra} + 2\sum_\rho A_{aa\rho\rho} - \sum_\rho A_{a\rho\rho a} = \sum_n \pm A_{anna} + 2\sum_\rho A_{aa\rho\rho},$$

where the upper or lower sign is to be taken for a positive or negative energy state, respectively. The first term represents an exchange term and diverges only logarithmically. The last term is the direct Coulomb energy of the electron in state a interacting with the sea of negative energy electrons and diverges quadratically. As mentioned above, the worst part of this divergence is removed by the process of symmetrization. On the basis of the alternate picture, we therefore calculate the expectation value

$$\Phi^*(0_\rho 0_a 1_{r'}) \sum_{(\alpha)(\beta)(\gamma)(\delta)} a_{(\alpha)}{}^+ a_{(\beta)} a_{(\gamma)}{}^+ a_{(\delta)} A_{(\alpha)(\beta)(\gamma)(\delta)}\, \Phi(0_{(\rho)} 0_{(a)} 1_{(r')}),$$

and obtain

$$\sum_{(r')} \sum_{(s')} A_{(r')(r')(s')(s')} + \sum_{(\rho)} \sum_{(r')} A_{(r')(\rho)(\rho)(r')} + \sum_{(r')} A_{(r')(a)(a)(r')}.$$

The vacuum term is

$$\sum_{(r)} \sum_{(s)} A_{(r)(r)(s)(s)} + \sum_{(r)} \sum_{(\rho)} A_{(r)(\rho)(\rho)(r)},$$

and the difference

$$\sum_{(r)} A_{(a)(r)(r)(a)} - \sum_{(\rho)} A_{(a)(\rho)(\rho)(a)} - 2\sum_{(r)} A_{(a)(a)(r)(r)} = \sum_{(n)} \pm A_{(a)(n)(n)(a)} - 2\sum_{(r)} A_{(a)(a)(r)(r)},$$

represents the self-energy of the electron in state a as calculated on the basis of the positive particle picture. The wave functions u_n and $u_{(n)}$ are identical for physical reasons, so that we may now drop the parentheses. Averaging the two results, we obtain

$$\sum_n \pm A_{anna} + \sum_n \mp A_{aann} = W_S + W_P. \tag{14}$$

The static term W_S is

$$W_S = \sum_n \pm A_{anna} = \tfrac{1}{2} \sum_n \pm \int\int d\mathbf{x} d\mathbf{x}' u_a^*(\mathbf{x}) u_n(\mathbf{x}) \times (e^2/|\mathbf{x}-\mathbf{x}'|) u_n^*(\mathbf{x}') u_a(\mathbf{x}'), \tag{15}$$

and by use of a Fourier representation for $1/|\mathbf{x}-\mathbf{x}'|$

$$\frac{1}{|\mathbf{x}-\mathbf{x}'|} = (1/2\pi^2) \int d\mathbf{k} \exp(i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}'))/\mathbf{k}^2, \tag{16}$$

may be written as

$$W_S = (e^2/4\pi^2) \int \frac{d\mathbf{k}}{k^2} \sum_n \pm \int d\mathbf{x} u_a^*(\mathbf{x}) \times \exp(i\mathbf{k}\cdot\mathbf{x}) u_n(\mathbf{x}) \int dx' u_n^*(\mathbf{x}') \times \exp(-i\mathbf{k}\cdot\mathbf{x}') u_a(\mathbf{x}'). \tag{17}$$

The polarization term $W_P(a)$

$$W_P(a) = \sum_n \mp A_{aann} = \frac{e^2}{2} \int d\mathbf{x} |u_a(\mathbf{x})|^2 \times \int \frac{d\mathbf{x}'}{|\mathbf{x}-\mathbf{x}'|} \sum_n \mp |u_n(\mathbf{x}')|^2, \tag{18}$$

may be written as

$$W_P(a) = \int d\mathbf{x} |u_a(\mathbf{x})|^2 ev(\mathbf{x}), \tag{19}$$

where the function $v(\mathbf{x})$ is the potential due to a charge density[7–9]

$$\rho(\mathbf{x}) = (e/2) \sum_n \mp |u_n(\mathbf{x})|^2, \tag{20}$$

induced in the vacuum by the external electrostatic field. The energy W_P vanishes for a free electron.

The second-order electrodynamic self-energy $W_D(a)$ of the electron in state a, according to the electron picture, is given by the difference of the energy $W_D(1_a0_{r'}1_\rho)$ for the electron in state a plus the vacuum electrons and the energy $W_D(0_r1_\rho)$ of the vacuum electrons alone. The vacuum energy $W_D(0_r1_\rho)$ is given by second-order perturbation theory, and involves the virtual emission and re-absorption of a light quantum of wave vector $\mathbf{k}$ and polarization type λ. There are two types of terms, represented by the following transition schemes:

$$\begin{pmatrix} \rho \rightarrow r+\mathbf{k} \\ r+\mathbf{k} \rightarrow \rho \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \rho \rightarrow \rho+\mathbf{k} \\ \sigma+\mathbf{k} \rightarrow \sigma \end{pmatrix}.$$

In the case of the energy $W_D(1_a0_{r'}1_\rho)$, there are some additional transitions which the added electron can make, and some of the previously allowed transitions are prevented by the presence of the atomic electron in state a. One has then the following types of transitions:

$$\begin{pmatrix} \rho \rightarrow r'+\mathbf{k} \\ r'+\mathbf{k} \rightarrow \rho \end{pmatrix}, \quad \begin{pmatrix} a \rightarrow r+\mathbf{k} \\ r+\mathbf{k} \rightarrow a \end{pmatrix},$$

$$\begin{pmatrix} \rho \rightarrow \rho+\mathbf{k} \\ \sigma+\mathbf{k} \rightarrow \sigma \end{pmatrix}, \quad \begin{pmatrix} \rho \rightarrow \rho+\mathbf{k} \\ a+\mathbf{k} \rightarrow a \end{pmatrix},$$

$$\begin{pmatrix} a \rightarrow a+\mathbf{k} \\ \rho+\mathbf{k} \rightarrow \rho \end{pmatrix}.$$

The difference of the two corresponding energies is

$$-\int d\mathbf{k} \sum_{\lambda=1}^{2} \Big[\sum_r (|(r\mathbf{k}|\mathbf{H}_1|a)|^2/(E_r+\hbar ck-E_a))$$

$$-\sum_\rho (|(a\mathbf{k}|\mathbf{H}_1|\rho)|^2/(E_a+\hbar ck+E_a))$$

$$+2\sum_\rho ((a|\mathbf{H}_1|a\mathbf{k})(\rho\mathbf{k}|\mathbf{H}_1|\rho)/\hbar ck)\Big],$$

which may be written as

$$-\int d\mathbf{k} \sum_{\lambda=1}^{2} \Big[\sum_n (\pm|(n\mathbf{k}|\mathbf{H}_1|a)|^2/$$

$$(|E_n|+\hbar ck \mp E_a))+2\sum_\rho ((a|\mathbf{H}_1|a\mathbf{k})$$

$$\times(\rho\mathbf{k}|\mathbf{H}_1|\rho)/\hbar ck)\Big].$$

Symmetrization affects only the second term, and gives

$$W_D(a) = -\int d\mathbf{k} \sum_{\lambda=1}^{2} \sum_n$$

$$\times(\pm|(n\mathbf{k}|\mathbf{H}_1|a)|^2/(|E_n|+\hbar ck \mp E_a))$$

$$+\int d\mathbf{k} \sum_{\lambda=1}^{2} \sum_n$$

$$\times(\pm(a|\mathbf{H}_1|a\mathbf{k})(n\mathbf{k}|\mathbf{H}_1|n)/\hbar ck). \tag{21}$$

The last term can be written as

$$\int (d\mathbf{k}/k^2) \sum_{\lambda=1}^{2} \sum_n$$

$$\pm \int\int d\mathbf{x}d\mathbf{x}' u_a^*(\mathbf{x}) \alpha \cdot \mathbf{e}_{\mathbf{k}\lambda} u_a(\mathbf{x})$$

$$\times \exp(i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')) u_n^*(\mathbf{x}') \alpha \cdot \mathbf{e}_{\mathbf{k}\lambda} u_n(\mathbf{x}'),$$

which will be zero if the polarization current[7–9]

$$\mathbf{j}(\mathbf{x}') = e \sum_n \mp u_n^*(\mathbf{x}') \alpha u_n(\mathbf{x}') \tag{22}$$

is zero. In the absence of an external vector potential, this current is in fact zero, so that the last term in Eq. (21) will henceforth be dropped. It should be noted that two physically different **k**-spaces are involved in the expressions Eq. (17) and Eq. (21) for W_S and W_D.

---

[7] See reference 4, Eq. (40).

[8] E. A. Uehling, Phys. Rev. **48**, 55 (1935), W. Pauli and M. Rose, Phys. Rev. **49**, 462 (1936), and V. F. Weisskopf, Kgl. Danske Vid. Sels. Math.-Fys. Medd **14**, No. 6 (1936).

[9] R. Serber, Phys. Rev. **48**, 49 (1935).

III. COMPUTATION OF THE SELF-ENERGIES

We turn now to the evaluation of the expressions W_S, W_D, W_P for the self-energy. We shall pay particular attention to the static and dynamic terms W_S and W_D, as the polarization (Uehling) term W_P is directly related to the polarization charge density which has been computed by others.[7–9]

In the calculations to follow, relativistic units will be used throughout, in which $\hbar$, m, and c are taken equal to unity.

Our main interest, of course, is in the case of an electron moving in a Coulomb field for which $V=-e^2/r$. The integrals like

$$(n\mathbf{k}|\mathbf{H}_1|a)=-(ie/2\pi k^{\frac{1}{2}})\int d\mathbf{x}u_n^*(\mathbf{x})\boldsymbol{\alpha}\cdot\mathbf{e}_{\mathbf{k}\lambda}\times\exp(-i\mathbf{k}\cdot\mathbf{x})u_a(\mathbf{x})$$

occur in the theory of the relativistic photoelectric effect and have been studied extensively by Hall.[10] Because of their complexity, it seems hardly likely that we could perform the necessary further operations on them to evaluate such expressions as W_D. Even more must such a direct attack be ruled out for the case of an electron moving in a general potential field $V(\mathbf{x})$, for which the relativistic eigenfunctions $u_n(\mathbf{x})$ are not known. The only remaining method of approach seems to be to make an expansion of some kind. We observe that if the electron is free, the evaluation of the sums is a comparatively simple matter. Thus, if $u_a(\mathbf{x})$ is a plane wave of momentum $\mathbf{p}$, then

$$\int d\mathbf{x}u_n^*\boldsymbol{\alpha}\cdot\mathbf{e}\exp(-i\mathbf{k}\cdot\mathbf{x})u_a$$

is different from zero only if the momentum of the state n is $\mathbf{k}+\mathbf{p}$, and there are only four such states. In the case of a "weakly" bound electron, i.e., for

$$k\gg(a||\mathbf{p}||a),$$

one might expect that the matrix element above would have an appreciable value only when $|E_n|$ is of the order $E_k=+(1+k^2)^{\frac{1}{2}}$. We take advantage of this fact in the method of calculation used.

The sums over n can be performed, at least formally, by making use of the completeness of the solutions of the Dirac equation. Thus W_S can be written in the form

$$W_S=(e^2/4\pi^2)\int(d\mathbf{k}/k^2)\sum_n\int d\mathbf{x}u_a^*(\mathbf{x})\times\exp(i\mathbf{k}\cdot\mathbf{x})(H/|H|)u_n(\mathbf{x})\int d\mathbf{x}'u_n^*(\mathbf{x}')\times\exp(-i\mathbf{k}\cdot\mathbf{x}')u_a(\mathbf{x}'),\quad(23)$$

where

$$H=\boldsymbol{\alpha}\cdot\mathbf{p}+\beta+V\quad(24)$$

is the Hamiltonian of the unperturbed electronic motion, and $|H|$ the absolute value of the Hamiltonian, by which we mean an operator having the same eigenstates and spectrum as the Hamiltonian, except that its eigenvalues are taken to be positive. It can most conveniently be computed by representing it as $+(H^2)^{\frac{1}{2}}$. The equivalence of Eqs. (17) and (23) follows from the fact that $H/|H|$ is $+1$ when operating on a positive energy state and -1 when operating on a negative energy state. Using the completeness of the $u_n(\mathbf{x})$, we now find

$$W_S=(e^2/4\pi^2)\int(d\mathbf{k}/k^2)\int d\mathbf{x}u_a^*(\mathbf{x})\times\exp(i\mathbf{k}\cdot\mathbf{x})(H/|H|)\exp(-i\mathbf{k}\cdot\mathbf{x})u_a(\mathbf{x}),\quad(25)$$

so that the problem of computing W_S is reduced to that of finding the expectation value of the operator

$$(e^2/4\pi^2)\int(d\mathbf{k}/k^2)\times\exp(-i\mathbf{k}\cdot\mathbf{x})(H/|H|)\exp(+i\mathbf{k}\cdot\mathbf{x})$$

for the state a. We first note that for any polynomial function $f(\mathbf{p},V)$

$$f(\mathbf{p},V)\exp(+i\mathbf{k}\cdot\mathbf{x})u_a(\mathbf{x})=\exp(+i\mathbf{k}\cdot\mathbf{x})f(\mathbf{k}+\mathbf{p},V)u_a(\mathbf{x}).$$

This theorem may then be used for any function $f(\mathbf{p},V)$ such as $H/|H|$, for which a series expansion in $\mathbf{p}$ and V is valid. We therefore write

$$(H/|H|)\exp(i\mathbf{k}\cdot\mathbf{x})u_a(\mathbf{x})=\exp(i\mathbf{k}\cdot\mathbf{x})(H/|H|)_{\mathbf{k}+\mathbf{p}}u_a(\mathbf{x}),$$

---

[10] H. Hall, Rev. Mod. Phys. 8, 358 (1936).

where the notation

$$(\quad)_{\mathbf{k}+\mathbf{p}}$$

means that the operator $\mathbf{p}$ is to be replaced by $\mathbf{k}+\mathbf{p}$ everywhere it appears within the brackets. One then has

$$W_S=(e^2/4\pi^2)\left(a\left|\int\frac{d\mathbf{k}}{k^2}(H/|H|)_{\mathbf{k}+\mathbf{p}}\right|a\right). \quad (26)$$

In an entirely similar manner, one can show that

$$W_D=-(e^2/4\pi^2)\left(a\left|\int(d\mathbf{k}/k)\sum_{\lambda=1}^{2}\boldsymbol{\alpha}\cdot\mathbf{e}_{\mathbf{k}\lambda}\right.\right.$$
$$\times\left\{\left(\frac{H}{|H|}+1\right)\Big/(|H|+k-E_a)\right.$$
$$\left.\left.\left.+\left(\frac{H}{|H|}-1\right)\Big/(|H|+k+E_a)\right\}_{\mathbf{k}+\mathbf{p}}\boldsymbol{\alpha}\cdot\mathbf{e}_{\mathbf{k}\lambda}\right|a\right). \quad (27)$$

The evaluation of the terms W_S and W_D thus hinges on the expression of the operators

$$(1/|H|)_{\mathbf{k}+\mathbf{p}} \quad \text{and} \quad (1/(|H|+k\mp E_a))_{\mathbf{k}+\mathbf{p}}$$

in terms of operators whose expectation values can be readily obtained.

Turning now to this task, we write

$$\begin{aligned}(|H|)_{\mathbf{k}+\mathbf{p}}&=((H^2)^{\frac{1}{2}})_{\mathbf{k}+\mathbf{p}}=(((\boldsymbol{\alpha}\cdot\mathbf{p}+\beta+V)^2)^{\frac{1}{2}})_{\mathbf{k}+\mathbf{p}}\\&=((1+\mathbf{p}^2+\boldsymbol{\alpha}\cdot\mathbf{p}V+V\boldsymbol{\alpha}\cdot\mathbf{p}+2\beta V+V^2)^{\frac{1}{2}})_{\mathbf{k}+\mathbf{p}}\\&=(1+k^2+2\mathbf{k}\cdot\mathbf{p}+\mathbf{p}^2+2V(\boldsymbol{\alpha}\cdot\mathbf{k}+\boldsymbol{\alpha}\cdot\mathbf{p}+\beta)\\&\qquad+\boldsymbol{\alpha}\cdot\boldsymbol{\pi}V+V^2)^{\frac{1}{2}},\end{aligned} \quad (28)$$

where $\boldsymbol{\pi}$ denotes an operator $\mathbf{p}$ which operates only on the quantity immediately following it (e.g., $\boldsymbol{\alpha}\cdot\mathbf{p}V=V\boldsymbol{\alpha}\cdot\mathbf{p}+\boldsymbol{\alpha}\cdot\boldsymbol{\pi}V$).

It is clear that the ratio of $(|H|)_{\mathbf{k}+\mathbf{p}}$ to $(1+k^2)^{\frac{1}{2}}$ approaches unity as k becomes large, which corresponds to our previous statement regarding the relationship between the magnitude of the matrix elements and the energy of the state n. Thus we expand

$$(1/|H|)_{\mathbf{k}+\mathbf{p}} \quad \text{and} \quad (1/|H|+k\mp E_a)_{\mathbf{k}+\mathbf{p}}$$

as follows:

$$\begin{aligned}(1/|H|)_{\mathbf{k}+\mathbf{p}}&=1/(E_k+\Delta_k)\\&=1/E_k-\Delta_k/E_k^2+\Delta_k^2/E_k^3-\cdots,\end{aligned} \quad (29)$$

$$\begin{aligned}(1/(|H|+k\mp E_a))_{\mathbf{k}+\mathbf{p}}&\\=1/(D_k^{\pm}+\Delta_k\mp w_a)&=1/D_k^{\pm}\\&-(\Delta_k\mp w_a)/(D_k^{\pm})^2+\cdots,\end{aligned} \quad (30)$$

where

$$E_k=(1+k^2)^{\frac{1}{2}}, \quad (31)$$

$$\Delta_k=|H|-E_k, \quad (32)$$

$$D_k^{\pm}=E_k+k\mp 1, \quad (33)$$

$$w_a=E_a-1. \quad (34)$$

It is, of course, also necessary to evaluate Δ_k by applying the binomial expansion

$$\begin{aligned}\Delta_k=|H|_{\mathbf{p}+\mathbf{k}}-E_k&=(E_k^2+\delta_{\mathbf{k}})^{\frac{1}{2}}-E_k\\&=\tfrac{1}{2}\delta_{\mathbf{k}}-\tfrac{1}{8}(\delta_{\mathbf{k}}^2/E_k)+\tfrac{1}{16}(\delta_{\mathbf{k}}^3/E_k^2)+\cdots,\end{aligned} \quad (35)$$

where

$$\begin{aligned}\delta_{\mathbf{k}}=2\mathbf{k}\cdot\mathbf{p}+\mathbf{p}^2+2V(\boldsymbol{\alpha}\cdot\mathbf{k}+\boldsymbol{\alpha}\cdot\mathbf{p}+\beta)&\\+\boldsymbol{\alpha}\cdot\boldsymbol{\pi}V+V^2.&\end{aligned} \quad (36)$$

All expansions indicated are to be carried to sufficiently high order so as to include all terms which are effectively of the fourth or lower order in v/c. The operator $\mathbf{p}$ is obviously of first order in v/c, V is of second order because of the virial theorem, while $\mathbf{k}$, β are of zeroth order. Since $\alpha_x^2=\alpha_y^2=\alpha_z^2=1$, $\boldsymbol{\alpha}$ must be regarded as a zero-order quantity until the expansion has been fully worked out.

The expansion of the operators in the manner indicated and the summation over the polarization direction $\lambda=1$, 2 is a straightforward but lengthy matter. This being completed, one is left with a sum of expectation values of various operators

$$\begin{aligned}&1,\ \beta,\ \boldsymbol{\alpha}\cdot\mathbf{p},\ \beta\boldsymbol{\alpha}\cdot\mathbf{p},\ \mathbf{p}^2,\ \beta\mathbf{p}^2,\ V,\ \beta V,\\&\boldsymbol{\sigma}\cdot\boldsymbol{\pi}V\times\mathbf{p},\ \boldsymbol{\alpha}\cdot\boldsymbol{\pi}V,\ \beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi}V,\ \boldsymbol{\pi}^2V,\ V\mathbf{p}^2,\ \mathbf{p}^2V,\ \boldsymbol{\pi}V\cdot\mathbf{p},\\&\mathbf{p}^4,\ \beta\mathbf{p}^4,\ V^2,\ \beta V^2,\ V\boldsymbol{\alpha}\cdot\mathbf{p},\ \beta V\boldsymbol{\alpha}\cdot\mathbf{p},\\&\boldsymbol{\alpha}\cdot\mathbf{p}\mathbf{p}^2,\ w=E-1=\boldsymbol{\alpha}\cdot\mathbf{p}+\beta+V-1,\ w^2,\ \beta w,\end{aligned}$$

each multiplied by a combination of some fifty elementary integrals over k. The result of this calculation is given in Eq. (73) below. Before coming to it, we shall first discuss briefly the validity of the expansion used and the form in which the self-energy is expressed.

Assuming for the moment that $\mathbf{p}$ and V can be regarded as numbers less than unity (in relativistic units), then the expansions of

$$(1/|H|)_{\mathbf{k}+\mathbf{p}} \quad \text{and} \quad (1/(|H|+k+E_a))_{\mathbf{k}+\mathbf{p}},$$

(if carried far enough) are valid for all values of k, since E_k approaches unity and D_k^- approaches two as k goes to zero. On the other hand, D_k^+

approaches zero in this limit, so that one should examine the low k behavior for this case. It turns out that that part of

$$\Delta_k - w_a,$$

which does not approach zero as k approaches zero is of the order $(v/c)^2$. Therefore, in the term involving $D_k{}^+$ we shall carry our integrals down only to some intermediate wave number k_i, which, for convenience, we take to be of order $\alpha^{\frac{1}{2}}$. This term must then be given a separate treatment for the low k region $0 \leqslant k \leqslant k_i$. One would expect that the result is independent of the precise value of k_i, and this is indeed the case.

The assumption that $\mathbf{p}$ and V are always numbers less than unity is, of course, not valid. For example, in the case of the Coulomb field $V(\mathbf{x})$ becomes infinite at the origin. The region over which V is large, however, is small, so that the contribution to the expectation value from the region in which the expansion is invalid should be small. Again, in the case of the Coulomb field, $\mathbf{p}^2 u_a(\mathbf{x})$ becomes large compared to $u_a(\mathbf{x})$ for small $\mathbf{x}$. It should be observed that in the case of the Coulomb field this circumstance limits the expansion to the power of v/c here used, as the expected values of V^3, $\mathbf{p}^6$, $\boldsymbol{\pi}^4 V$, etc., diverge for S states of the Coulomb field. Although the error introduced by this phenomenon is believed to be small, a numerical estimate would be desirable. We shall not, however, make such an estimate here, as the problem is a purely non-relativistic one.

In order to simplify the appearance and physical interpretation of our results, we have found it convenient to make use of various relationships between the expectation values of the Dirac operators which are valid to the order of v/c required. Thus one can write any solution of the Dirac equation as

$$u = \begin{pmatrix} \phi \\ \omega \end{pmatrix}, \tag{37}$$

where ϕ and ω are two-component wave functions satisfying

$$(\boldsymbol{\sigma}\cdot\mathbf{p}(1/(1+E-V))\boldsymbol{\sigma}\cdot\mathbf{p} + V + 1 - E)\phi = 0, \tag{38}$$

$$\omega = (1/(1+E-V))\boldsymbol{\sigma}\cdot\mathbf{p}\phi, \tag{39}$$

so that for a positive energy state ω is of order v/c with respect to ϕ, which apart from terms of order $(v/c)^2$ is just a non-relativistic two-component Pauli-Schrödinger wave function. One can then see, for example, that

$$\begin{aligned}(a|\mathbf{p}^2 - \beta\mathbf{p}^2|a) &= 2\int d\mathbf{x}((1/(1+E-V)) \\ &\quad \times \boldsymbol{\sigma}\cdot\mathbf{p}\phi_a)^* \mathbf{p}^2 (1/(1+E-V))\boldsymbol{\sigma}\cdot\mathbf{p}\phi_a \\ &\simeq \frac{1}{2}\int d\mathbf{x}\phi_a{}^* \mathbf{p}^4 \phi_a \\ &\simeq \tfrac{1}{2}(a|\mathbf{p}^4|a),\end{aligned} \tag{40}$$

since $1-E$ and V are of order $(v/c)^2$, and $\int d\mathbf{x}\phi_a \mathbf{p}^4 \phi_a$ and $(a|\mathbf{p}^4|a)$ differ only by a quantity of order $(v/c)^6$. One can therefore simplify the final result Eq. (73) by expressing all operators in terms of certain arbitrarily chosen ones which we have taken to be

$$\beta,\ \boldsymbol{\alpha}\cdot\mathbf{p},\ V,\ \boldsymbol{\pi}^2 V,\ \beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi} V,$$
$$V\mathbf{p}^2,\ \mathbf{p}^4, \text{ and } V^2.$$

Our reduction is obtained by using the following relations between expectation values

$$1 \rightarrow \beta + \tfrac{1}{2}\boldsymbol{\alpha}\cdot\mathbf{p} - \tfrac{1}{8}\mathbf{p}^4 + \tfrac{1}{4}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi} V, \tag{41}$$

$$\mathbf{p}^2 \rightarrow \boldsymbol{\alpha}\cdot\mathbf{p} + \tfrac{1}{2}\mathbf{p}^4 + \tfrac{1}{2}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi} V, \tag{42}$$

$$\mathbf{p}^2 \rightarrow \boldsymbol{\alpha}\cdot\mathbf{p} + \tfrac{1}{2}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi} V, \tag{43}$$

$$\beta V \rightarrow V - \tfrac{1}{2} V\mathbf{p}^2 - \tfrac{1}{2}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi} V, \tag{44}$$

$$\beta\boldsymbol{\alpha}\cdot\mathbf{p} \rightarrow 0, \tag{45}$$

$$\mathbf{p}^2 V \rightarrow V\mathbf{p}^2, \tag{46}$$

$$\boldsymbol{\pi} V\cdot\mathbf{p} \rightarrow -\tfrac{1}{2}\boldsymbol{\pi}^2 V, \tag{47}$$

$$\boldsymbol{\alpha}\cdot\pi V \rightarrow 0, \tag{48}$$

$$i\boldsymbol{\sigma}\cdot\boldsymbol{\pi} V \times \mathbf{p} \rightarrow \beta\alpha\cdot\pi V + \tfrac{1}{2}\pi^2 V, \tag{49}$$

$$V\boldsymbol{\alpha}\cdot\mathbf{p} \rightarrow V\mathbf{p}^2 + \tfrac{1}{2}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi} V, \tag{50}$$

$$\beta V\boldsymbol{\alpha}\cdot\mathbf{p} \rightarrow -\tfrac{1}{2}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi} V, \tag{51}$$

$$\boldsymbol{\alpha}\cdot\mathbf{p}\mathbf{p}^2 \rightarrow \mathbf{p}^4, \tag{52}$$

$$\beta\mathbf{p}^4 \rightarrow \mathbf{p}^4, \tag{53}$$

$$\beta V^2 \rightarrow V^2, \tag{54}$$

$$w = H - 1 \rightarrow \tfrac{1}{2}\boldsymbol{\alpha}\cdot\mathbf{p} + V + \tfrac{1}{8}\mathbf{p}^4 - \tfrac{1}{4}\beta\boldsymbol{\alpha}\cdot\pi V, \tag{55}$$

$$\beta w \rightarrow \tfrac{1}{2}\boldsymbol{\alpha}\cdot\mathbf{p} + V - \tfrac{1}{8}\mathbf{p}^4 - \tfrac{1}{2} V\mathbf{p}^2 - \tfrac{1}{4}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi} V, \tag{56}$$

$$w^2 \rightarrow \tfrac{1}{4}\mathbf{p}^4 + V\mathbf{p}^2 + V^2. \tag{57}$$

From these relations one finds that the total contribution of the static and dynamic terms of the self-energy, apart from the low k contribution of the term involving $D_k{}^+$, is

$$(W_S+W_D)'=(\alpha/\pi)\bigg(a\bigg|\bigg(\frac{3}{2}\int_0^\infty(dk/E_k)+\tfrac{1}{4}\bigg)\beta+\tfrac{1}{6}\boldsymbol{\alpha}\cdot\mathbf{p}+\tfrac{2}{3}\boldsymbol{\alpha}\cdot\mathbf{p}k_i+\tfrac{1}{4}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi}V-(\tfrac{1}{3}\log(1/k_i)-\tfrac{1}{3}\log 2+11/72)\boldsymbol{\pi}^2V\bigg|a\bigg). \quad (58)$$

In order to compute the low k contribution of the term involving $D_k{}^+$, it is convenient to take advantage of the essentially non-relativistic nature of this region and to make use of the previously discussed large and small component reduction Eq. (37). One then readily finds that the resultant expression has, to the order required, just the form of the non-relativistic self-energy, so that Bethe's[1] calculation may be used up to the frequency k_i. The contribution is

$$(\omega_{N.R.})_{k<k_i}=(\alpha/\pi)(a|-\tfrac{2}{3}\mathbf{p}^2k_i-\tfrac{1}{3}(\log k_i/\bar{\epsilon})\boldsymbol{\pi}^2V|a). \quad (59)$$

Adding the two, and observing that $(a|\mathbf{p}^2|a)$ is the same as $(a|\boldsymbol{\alpha}\cdot\mathbf{p}|a)$ to the order required, we find for the total contribution of W_S and W_D

$$W_S+W_D=(\alpha/\pi)\bigg(a\bigg|\bigg(\frac{3}{2}\int_0^\infty(dk/E_k)+\tfrac{1}{4}\bigg)\beta+(\boldsymbol{\alpha}\cdot\mathbf{p}/6)+\tfrac{1}{4}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi}V-\bigg(\tfrac{1}{3}\log\frac{1}{\bar{\epsilon}}-\tfrac{1}{3}\log 2+11/72\bigg)\boldsymbol{\pi}^2V\bigg|a\bigg), \quad (60)$$

and we note that the result is independent of the joining frequency k_i.

As previously mentioned, the direct Coulomb energy term can be expressed in terms of a polarization charge as follows:

$$W_P(a)=e\int d\mathbf{x}|u_a(\mathbf{x})|^2\times\int d\mathbf{x}'\rho(\mathbf{x}')/|\mathbf{x}-\mathbf{x}'|, \quad (61)$$

where

$$\rho(\mathbf{x}')=(e/2)\sum_n\mp|u_n(\mathbf{x}')|^2 \quad (62)$$

is the induced charge density calculated by various authors. To the order required, this is found to be

$$\rho(\mathbf{x})=(e/6\pi^2)\nabla^2V\bigg(\tfrac{1}{6}+\int(k^2dk/E_k{}^3)\bigg)+(e/60\pi^2)\nabla^4V, \quad (63)$$

from which one finds

$$W_P(a)=-(2e^2/3\pi)\bigg(\tfrac{1}{6}+\int(k^2dk/E_k{}^3)\bigg)\times(a|V'|a)-(e^2/15\pi)(a|\nabla^2V|a). \quad (64)$$

The prime appearing on V' is used to indicate that the gauge of V' has been determined by the fact that it arises from an expression of the form

$$-1/4\pi\int d\mathbf{x}'\nabla^2V(\mathbf{x}')/|\mathbf{x}-\mathbf{x}'|. \quad (65)$$

We should like to point out that the expression for $\rho(\mathbf{x}')$ can be readily and neatly calculated by methods very similar to those used above in the case of the static and dynamic terms in the self-energy. To show this we first evaluate

$$\begin{aligned}\rho(\mathbf{x}',\mathbf{x}'')&=-(e/2)\sum_n\pm u_n{}^*(\mathbf{x}')u_n(\mathbf{x}'')\\&=-(e/2)\sum_n u_n{}^*(\mathbf{x}')(H/|H|)u_n(\mathbf{x}'')\\&=-(e/2)\sum_n\sum_{\mu=1}^{4}\sum_{\nu=1}^{4}(H/|H|)_{\mu\nu}\times u_{n\mu}{}^*(\mathbf{x}')u_{n\nu}(\mathbf{x}''),\end{aligned} \quad (66)$$

where the $u_{n\mu}$, $\mu=1, 2, 3, 4$ are the components of u_n, and all operators in $H/|H|$ are to be taken with respect to $\mathbf{x}''$. Making use of the completeness relation

$$\sum_n u_{n\mu}{}^*(\mathbf{x}')u_{n\nu}(\mathbf{x}'')=\delta_{\mu\nu}\delta(\mathbf{x}'-\mathbf{x}''), \quad (67)$$

we obtain

$$\begin{aligned}\rho(\mathbf{x}',\mathbf{x}'')&=-(e/2)\sum_\mu(H/|H|)_{\mu\mu}\delta(\mathbf{x}'-\mathbf{x}'')\\&=-(e/2)(\mathrm{Spur}H/|H|)_{x''}\delta(\mathbf{x}'-\mathbf{x}'').\end{aligned} \quad (68)$$

To evaluate this, we Fourier-analyze the delta-function

$$\delta(\mathbf{x}'-\mathbf{x}'')=(1/8\pi^3)\int d\mathbf{k}\exp(i\mathbf{k}\cdot(\mathbf{x}''-\mathbf{x}')), \quad (69)$$

TABLE I.

Quantity	State $2^2S_{1/2}$	$2^2P_{1/2}$	$2^2P_{3/2}$
$\nabla^2 V$	1	0	0
$i\beta\boldsymbol{\alpha}\cdot\nabla V$	$-1/2$	$1/6$	$-1/12$

and find

$$\rho(\mathbf{x}',\mathbf{x}'')=(1/8\pi^3)\int d\mathbf{k}\exp(-i\mathbf{k}\cdot\mathbf{x}')$$
$$\times(\mathrm{Spur}H/|H|)\exp(i\mathbf{k}\cdot\mathbf{x}''),$$
$$=(1/8\pi^3)\int d\mathbf{k}\exp(i\mathbf{k}\cdot(\mathbf{x}''-\mathbf{x}'))$$
$$\times(\mathrm{Spur}H/|H|)_{\mathbf{k}+\mathbf{p}}\cdot 1(\mathbf{x}''),\quad(70)$$

when $1(\mathbf{x}'')$ is a constant equal to one. Since

$$\rho(\mathbf{x}')=\rho(\mathbf{x}',\mathbf{x}'),\quad(71)$$

we obtain, finally,

$$\rho(\mathbf{x}')=-(e/16\pi^3)$$
$$\times\int d\mathbf{k}(\mathrm{Spur}H/|H|)_{\mathbf{k}+\mathbf{p}}\cdot 1(\mathbf{x}').\quad(72)$$

The expression can now be readily reduced to the form Eq. (63) by expanding

$$(\mathrm{Spur}H/|H|)_{\mathbf{k}+\mathbf{p}}$$

in the manner used for the evaluation of the static and dynamic terms.

IV. INTERPRETATION OF RESULTS

The total expression for the self-energy is

$$W(a)=(\alpha/\pi)\bigg(a\bigg|\bigg(\frac{3}{2}\int(dk/E_k)+\tfrac{1}{4}\bigg)\beta$$
$$-\bigg(\frac{2}{3}\int(k^2dk/E_k{}^3)+\tfrac{1}{9}\bigg)V'$$
$$+(\boldsymbol{\alpha}\cdot\mathbf{p}/6)-(i/4)\beta\boldsymbol{\alpha}\cdot\nabla V$$
$$+\bigg(\tfrac{1}{3}\log(1/\bar{\epsilon})-\tfrac{1}{3}\log 2$$
$$+(11/72)-(1/15)\bigg)\nabla^2V\bigg|a\bigg),\quad(73)$$

where we have made use of the fact that $\boldsymbol{\pi}=-i\nabla$. We observe first of all that the worst divergence is logarithmic, and that the expression is invariant to the gauge of V.

We next see that the difference of the self-energies of the states $2^2S_{\frac{1}{2}}$ and $2^2P_{\frac{1}{2}}$ of the hydrogen atom does converge, since the expectation values of β, V', (and, therefore, $\boldsymbol{\alpha}\cdot\mathbf{p}$) are, respectively, equal for the two states. (These statements follow from the observation that neither a small change of charge nor mass of the electron will remove the degeneracy.) In order to calculate the numerical difference of $W(a)$ for the two states, we need the values of the expectation values of the remaining operators in Eq. (73). These are given in Table I[11] in units of α^2Ry. The energy difference is then

$$\Delta W=(\alpha^3Ry/3\pi)[\log(1/\bar{\epsilon})-\log 2$$
$$+(23/24)-\tfrac{1}{5}],\quad(74)$$

which, using Bethe's revised values[12] for the constants $[(\alpha^3Ry/3\pi)=135.580$ Mc/sec., $\log(1/\bar{\epsilon})=7.7169-0.0293]$, gives $\Delta W=1052$ Mc/sec., and thus differs from the original guess by only a small amount. It should be admitted, however, that one cannot regard this energy difference as uniquely determined, since one is taking the difference of two infinite quantities.

With respect to the determination of the absolute value of the self-energy for a state, it is convenient to attempt a physical interpretation of the terms involved. In this context, it should be observed that even if the coefficients of the V' and β-terms were finite, the effect of these terms would be unobservable. This follows from the fact that they would manifest themselves as a

---

[11] It should be mentioned here that the expected value of $\nabla^2 V$ really diverges for the S states of the Coulomb field, since it then is equal to the square of the absolute value of the wave function at the origin. Since, however, our evaluation is being carried only to order $(v/c)^4$, one should be able to use the spatial dependence of the Schrödinger wave functions for the evaluation of operators which are themselves of fourth order. Thus, where Dirac wave functions are used, the divergent part is of higher order in v/c, and its neglect is consistent with the neglect of such divergent expressions as the expected value of p^6. If one rounds off the Coulomb potential at a radius considerably smaller than the classical electron radius, the contribution of the divergent part of $(S|\nabla^2 V|S)$ is still quite negligible. (If the charge is assumed to be evenly distributed over a sphere of radius a, then the ratio of the expected value of $\nabla^2 V$ for a Dirac S state to that for a Schrödinger S state is of the order $a^{-\alpha^2}\sim 1-\alpha^2\log a$.)

[12] H. A. Bethe, Pocono Conference, 1948.

modification in the real charge and mass of the electron, and thus be included in the observed charge and mass. We shall assume that these terms have been so included in the observed charge and mass and drop them from the self-energy expression. The term in $i\beta\boldsymbol{\alpha}\cdot\nabla V$ is just of the form of the interaction of a Pauli-type intrinsic magnetic moment with a static potential V and can thus be interpreted as implying an additional electronic magnetic moment of $\alpha/2\pi$-Bohr magentons, while the term $\nabla^2 V$ implies a correction to the external potential, or, more specifically, an additional short-range interaction between the electron and a point charge. The term in $\boldsymbol{\alpha}\cdot\mathbf{p}$ is not subject to a direct physical interpretation, and, in fact, must be regarded as having no physical significance. Thus if one applies the self-energy expression (73) (with the β- and V' terms omitted as explained above) to a free electron of momentum $\mathbf{p}$, only the term in $\boldsymbol{\alpha}\cdot\mathbf{p}$ contributes, yielding for the self-energy $(\alpha/\sigma\pi)[\mathbf{p}^2/(1+\mathbf{p}^2)^{\frac{1}{2}}]$. Now if the electron is to be regarded as a particle, the relativistic connection between the momentum and energy of a particle must be retained, so that the self-energy should have the momentum dependence appropriate to a mass correction, that is[13] $\sim 1/(1+\mathbf{p}^2)^{\frac{1}{2}}$ corresponding to the term in β already subtracted. The presence of the non-covariant term $(\alpha/\sigma\pi)[\mathbf{p}^2/(1+\mathbf{p}^2)^{\frac{1}{2}}]$, which is reminiscent of the stress terms in the classical self-energy, can be traced to the fact that the total self-energy is infinite, and can be avoided in the case of the free electron by paying proper attention to the domains of integration in the various $\mathbf{k}$-spaces.[14] That is, in order to keep the total self-energy finite it is necessary to integrate over a finite region of the light quantum space and the electron momentum space. If one integrates over a region which would be spherical for an electron at rest, a covariant result is obtained. One cannot, however, apply this prescription to a bound electron, so that some other means of modifying our self-energy expression must be found to give a covariant expression for the free electron. We proceed by subtracting some free electron operator from the operators contained in our self-energy expression such that the self-energy of a free electron is zero, thereby regarding the total self-energy as contained in the observed mass.

Such a procedure is, of course, not unique: we shall make the simplest subtraction, examine the resultant expression, and then investigate the nature of the lack of uniqueness. Thus if one simply drops the $(\alpha/\sigma\pi)\boldsymbol{\alpha}\cdot\mathbf{p}$ term from the self-energy, one obtains

$$W(a)=(\alpha/\pi)(a|-i\beta\boldsymbol{\alpha}\cdot\nabla V/4+\left(\tfrac{1}{3}\log(1/2\bar{\epsilon})\right.$$
$$\left.+(11/72)-(1/15)\right)\nabla^2 V|a). \quad (75)$$

This expression can be interpreted as arising from an increase in the magnetic moment of the electron of $\alpha/2\pi$-Bohr magnetons and an additional interaction potential given by

$$\delta V_{\text{eff}}=\left(\tfrac{1}{3}\log(1/2\bar{\epsilon})+(11/72)-(1/15)\right)\nabla^2 V. \quad (76)$$

These contribute 68 and 984 Mc/sec., respectively, to the level shift.

In accordance with our subtraction prescription we could, however, add any linear combination of free electron operators of order up to $(v/c)^4$ whose expectation value is zero for the free electron. There are seven such operators,[15] *viz.*, 1, β, $\mathbf{p}^2$, $\beta\mathbf{p}^2$, $\boldsymbol{\alpha}\cdot\mathbf{p}$, $\mathbf{p}^4$, $\beta\mathbf{p}^4$. The condition that a linear combination gives zero to order constitutes three constraints, so that there should be four linearly independent combinations giving zero for the free electron. A possible choice for these is the following:

$$\Omega_a=1-\beta-\tfrac{1}{2}\mathbf{p}^2-\boldsymbol{\alpha}\cdot\mathbf{p}+\beta\mathbf{p}^2+\tfrac{3}{8}\mathbf{p}^4, \quad (76a)$$

$$\Omega_b=\mathbf{p}^2-\beta\mathbf{p}^2-\tfrac{1}{2}\mathbf{p}^4, \quad (76b)$$

$$\Omega_c=\mathbf{p}^4-\beta\mathbf{p}^4, \quad (76c)$$

$$\Omega_d=\boldsymbol{\alpha}\cdot\mathbf{p}-\beta\mathbf{p}^2. \quad (76d)$$

The expectation values of the above combinations are all zero for the free electron. Their effect upon the self-energy of a bound electron depends upon their expectation values for a

---

[13] The energy of a particle of mass m and momentum p is $(m^2+\mathrm{p}^2)^{\frac{1}{2}}$. If m is modified by a quantity δm, then the energy to first order in δm is

$$(m^2+\mathrm{p}^2)^{\frac{1}{2}}+\delta m/(m^2+\mathrm{p}^2)^{\frac{1}{2}},$$

and the correction term with $m=1$, as is appropriate for the electron, is of the form given.

[14] A. Pais, Verh. d. K. Ned. Akad. v. Wet, Section 1, **19**, No. 1 (1947).

[15] Operators of odd order in v/c have been ignored, as these are all zero for the bound electron.

bound electron. Those for Ω_a, Ω_b, and Ω_c are zero, so that their subtraction would have no physical consequences. On the other hand,

$$(a|\Omega_d|a) = -i(a|\beta\boldsymbol{\alpha}\cdot\nabla V|a)/2, \qquad (77)$$

which is precisely the form of interaction of a magnetic moment with a static potential V. Thus, the lack of uniqueness of the subtraction prescription is just such as to make the magnetic moment correction indeterminate, while the correction to the potential is left uniquely determined. Now a purely magnetic measurement of the correction to the magnetic moment of the electron has been made by Kusch and Foley,[16] who obtain a value in good agreement with the value $\alpha/2\pi$-Bohr magnetons theoretically computed by Schwinger.[17] If we adopt this experimental and theoretical result, the $2^2S_{\frac{1}{2}}-2^2P_{\frac{1}{2}}$ separation becomes uniquely determined to be just the value 1052 Mc/sec. obtained above by a direct subtraction (74) of the self-energies for the two states.

---

[16] P. Kusch and H. M. Foley, Phys. Rev. **74**, 250 (1948), also J. E. Nafe and E. B. Nelson, Phys. Rev. **73**, 718 (1948).

[17] J. Schwinger, Phys. Rev. **73**, 416 (1948) and Pocono Conference, 1948.

PHYSICAL REVIEW VOLUME 75, NUMBER 3 FEBRUARY 1, 1949

Study of Phase Transitions by Means of Nuclear Magnetic Resonance Phenomena*

NELSON L. ALPERT**
Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received October 11, 1948)

Although the nuclear magnetic resonance condition generally depends only on the gyromagnetic ratio of the resonating nuclei, the width and amplitude of the resonance depend critically on the substance containing the resonating nuclei. A basic factor affecting the line width is the characteristic flipping time for the substance, i.e., the average time it takes a molecule to change its orientation appreciably. This fact has been applied in a study of a group of molecular solids which exhibit two or more phases in order to investigate the mechanisms of these transitions. Of the two mechanisms proposed, rotational and order-disorder, the former was eliminated in favor of the latter for HCl, HBr, HI, H_2S, and H_2Se, while free molecular rotation is shown to be plausible in CH_4 and CH_3D.

I. INTRODUCTION

THE first successful detection of radiofrequency transitions between Zeeman levels of nuclei in liquids and solids was announced by Purcell, Torrey, and Pound[1] and by Bloch, Hansen, and Packard[2] in 1946. It became apparent early in these investigations that the characteristics of a nuclear magnetic resonance depend directly on the material in which the resonating nuclei reside. This, coupled with the fact that the ratio of resonant frequency to magnetic field is a linear function of the nuclear *g*-factor, indicated three lines of research:

(a) The accurate measurement of nuclear *g*-factors.[3]

(b) An investigation of the interactions which affect the resonance characteristics, i.e., nuclear relaxation processes.[4]

(c) Study of internal properties of solids and liquids by means of nuclear magnetic resonance phenomena.[5–9] It is one phase of the last of these

---

* This research was supported in part by the Signal Corps, the Air Materiel Command, and the Office of Naval Research. The report given here is a condensation of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology, 1948.

** Now at Rutgers University, New Brunswick, New Jersey.

[1] E. M. Purcell, H. C. Torrey, and R. V. Pound, Phys. Rev. 69, 37 (1946).

[2] F. Bloch, W. W. Hansen, and M. Packard, Phys. Rev. 69, 127 (1946). F. Bloch, W. W. Hansen, and M. Packard, Phys. Rev. **70**, 474 (1946).

[3] F. Bitter, N. L. Alpert, D. E. Nagle, and H. L. Poss, Phys. Rev. **72**, 1271 (1947).

[4] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948), hereafter to be referred to as B.P.P.

[5] F. Bitter, N. L. Alpert, H. L. Poss, C. G. Lehr, and S. T. Lin, Phys. Rev. **71**, 738 (1947).

[6] B. V. Rollin, Nature **158**, 669 (1946).

[7] B. V. Rollin and J. Hatton, Nature **159**, 201 (1947).