Electrodynamic Displacement of Atomic Energy Levels. III. The Hyperfine Structure of Positronium

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A functional integro-differential equation for the electron-positron Green's function is derived from a consideration of the effect of sources of the Dirac field. This equation contains an electron-positron interaction operator from which functional derivatives may be eliminated by an iteration procedure. The operator is evaluated so as to include the effects of one and two virtual quanta. It contains an interaction resulting from quantum exchange as well as one resulting from virtual annihilation of the pair. The wave functions of the electron-positron system are the solutions of the homogeneous equation related to the Green's function equation. The eigenvalues of the total energy of the system may be found by a four-dimensional perturbation technique. The system bound by the Coulomb interaction is here treated as the unperturbed situation. Numerical values for the spin-dependent change of the energy from the Coulomb value in the ground state are finally obtained accurate to order α relative to the hyperfine structure α^2 Ry. The result for the singlet-triplet energy difference is

$$\Delta W_{ts}=\tfrac{1}{2}\alpha^2\,\mathrm{Ry}_\infty[7/3-(32/9+2\ln 2)\alpha/\pi]=2.0337\times 10^5\ \mathrm{Mc/sec}.$$

Theory and experiment are in agreement.

I. INTRODUCTION

THE investigation to be described in this paper was suggested by the current theoretical interest in the quantum-mechanical two-body problem[1–3] and the recent accurate measurement of the ground state hyperfine structure of positronium.[4,5] The system composed of one electron and one positron in interaction is the simplest accessible to calculation because it is purely electrodynamic in nature. Moreover, the success of quantum electrodynamics in predicting with great accuracy the properties of a single particle in an external field indicates the absence of fundamental difficulties from the theory in the range of energies that are significant in positronium.

The discussion of the bound states of the electron-positron system is based upon a rigorous functional differential equation for the Green's function of that system, derived in Sec. II by the method described by Schwinger.[1] In order to obtain a useful approximate form of this equation (and of the associated homogeneous equation) we have iterated the implicitly defined interaction operator, in this way automatically generating to any required order the interaction kernel obtained from scattering considerations by Bethe and Salpeter.[3] In the present case we have included all interaction terms involving the emission and absorption of one or two quanta. The latter include self-energy and vacuum polarization corrections to one-photon exchange processes as well as two-photon exchange terms. The particle-antiparticle relationship of electron and positron is represented by terms describing one- and two-photon virtual annihilation of the pair.[6–8] In contrast to the case of scattering, only the irreducible[3] interactions appear explicitly.

Our subsequent concern is with the solution of the associated homogeneous equation. It should be emphasized at the outset that we shall be silent (out of ignorance) on the question of the fundamental interpretation of a wave function which refers to individual times for each of the particles. The possibility, nevertheless, of obtaining a solution to our problem entirely within the framework of the present formalism depends on two conditions. The first of these is that most of the binding is accounted for by the instantaneous Coulomb interaction. Salpeter[9] has shown that when the interaction is instantaneous, the wave equation can be rigorously reduced to one involving only equal times for the two particles. Moreover, the wave function for arbitrary individual time coordinates can be expressed in terms of that for equal times. This last circumstance can also be exploited in the development of a perturbation theory which yields the contribution to the energy levels of a small non-instantaneous interaction.[9] The relevant results of this treatment are given in Sec. III.

The second condition is that the free particle approximation for all intermediate states shall be an adequate one. The essential point here is that whether one derives an explicit interaction operator by the iteration procedure adopted in the present paper (tantamount to an expansion of the intrinsic nonlinearity in terms of free particle properties) or by a partial summation of a scattering kernel, the propagation which naturally enters in intermediate states is that of free particles. In the treatment of fine-structure effects, the contribu-

[1] J. Schwinger, Proc. Nat. Acad. Sci. US **37**, 452, 455 (1951).
[2] M. Gell-Mann and F. Low, Phys. Rev. **84**, 350 (1951).
[3] H. A. Bethe and E. E. Salpeter, Phys. Rev. **84**, 1232 (1951).
[4] M. Deutsch and S. C. Brown, Phys. Rev. **85**, 1047 (1952).
[5] M. Deutsch, latest result reported at the Washington Meeting of the American Physical Society, May, 1952. Phys. Rev. **87**, 212(T) (1952).
[6] J. Pirenne, Arch. sci. phys. et nat. **28**, 233 (1946); **29**, 121, 207, and 265 (1947).
[7] V. B. Berestetski and L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **19**, 673 (1949). See also V. B. Berestetski, J. Exptl. Theoret. Phys. (U.S.S.R.) **19**, 1130 (1949).
[8] R. A. Ferrell, Phys. Rev. **84**, 858 (1951) and Ph.D. thesis (Princeton, 1951). Dr. Ferrell kindly sent us a copy of his thesis.
[9] E. E. Salpeter, Phys. Rev. **87**, 328 (1952). We are indebted to Dr. Salpeter for making available to us a copy of his paper prior to publication. We have found his ideas very helpful in our work.

tion of nonrelativistic intermediate states, where the Coulomb binding cannot be ignored, must then be obtained in a manner reminiscent of the first treatments of the Lamb shift.[9] This will not be necessary in the present paper since we shall be concerned with the hyperfine (spin-spin) type of interaction to which only relativistic intermediate states contribute to the required precision.[10]

The practical goal of this work is to obtain the splitting of the singlet-triplet ground-state doublet of positronium correct to order α^3 Ry. Previous calculations,[6-8] accurate to order α^2 Ry, have included the lowest order contributions of the ordinary spin-spin coupling arising from the Breit[11] interaction (the analog of which in hydrogen is responsible for its hyperfine structure) and of the one-photon virtual annihilation force, characteristic of the system of particle-antiparticle. The expression for the energy shift given in Sec. III, Eq. (3.6) yields these again in lowest approximation and contains as well the matrix elements of all interactions which can contribute to the required accuracy.

Section IV is devoted to the detailed evaluation of all the matrix elements that may be looked upon as generalized Breit interactions because they depend purely on the exchange of photons between the two particles. In Sec. V we consider the annihilation interaction peculiar to the electron-positron system. Finally, the comparison with experiment is given in Sec. VI.

II. THE WAVE EQUATION

A discussion of the one-particle electron and positron Green's function associated with the vacuum state will serve as an introduction to this section. If the notation of reference 1 is extended to include the positron field variables $\psi'(x)$, $\bar{\psi}'(x)$, and their sources that are related to the electron variables $\psi(x)$, $\bar{\psi}(x)$, and their sources by the usual charge conjugating matrix C,

$$\begin{aligned} &C^\dagger C=1, \quad C=-\tilde{C}, \quad C\tilde{\gamma}C^{-1}=-\gamma, \\ &\psi'=C\bar{\psi}, \quad \bar{\psi}'=C^{-1}\psi, \quad \eta'=C\bar{\eta}, \quad \bar{\eta}'=C^{-1}\eta, \end{aligned} \tag{2.1}$$

the Green's functions are defined by the vacuum expectation values

$$\delta_\eta\langle\psi(x)\rangle_0|_{\eta=0}=\int_{\sigma_2}^{\sigma_1} d^4x' G^-(x,x')\delta\eta(x') \tag{2.2a}$$

and

$$\delta_{\eta'}\langle\psi'(x)\rangle_0|_{\eta'=0}=\int_{\sigma_2}^{\sigma_1} d^4x' G^+(x,x')\delta\eta(x'), \tag{2.2b}$$

where $\delta\eta$ and $\delta\eta'$ are arbitrary variations of the electron and positron sources, respectively. The Green's functions can be expressed in terms of expectation values by

$$G^-(x,x')=i\langle(\psi(x)\bar{\psi}(x'))_+\rangle_0\epsilon(x,x') \tag{2.3a}$$

and

$$G^+(x,x')=i\langle(\psi'(x)\bar{\psi}'(x'))_+\rangle_0\epsilon(x,x') \tag{2.3b}$$

and satisfy the differential equations

$$[\gamma_\mu(-i\partial_\mu-eA_{+\mu}(x)+ie\delta/\delta J_\mu(x))+m] \times G^-(x,x')=\delta(x-x') \tag{2.4a}$$

and

$$[\gamma_\mu(-i\partial_\mu+eA_{+\mu}(x)-ie\delta/\delta J_\mu(x))+m] \times G^+(x,x')=\delta(x-x'), \tag{2.4b}$$

with the outgoing wave boundary condition. They are, of course, related by the matrix C:

$$G_{\alpha\beta}{}^+(x,x')=-C_{\alpha\alpha'}C^{-1}{}_{\beta\beta'}G_{\beta'\alpha'}{}^-(x',x). \tag{2.5}$$

We shall now introduce matrix notation for the combined particle coordinates and spinor indices, and the combined photon coordinates and vector indices. Because the formulas will get quite involved, the matrix indices will be expressed as arguments, by numbers for the particles and by ξ, ξ', $\cdots$ for the photons, and the summation convention will be understood. Functions of one coordinate are to be diagonal matrices; quantities affixed with only one matrix index are to be vectors with respect to that index. The arguments of the Dirac matrices will refer only to the vector and spinor indices of these quantities; they will be unit matrices in the coordinates. Similarly, functions of the coordinates alone must be understood as multiples of the Dirac unit matrix.

As an example, Eqs. (2.4) and (2.5) will be transcribed with the symbols $\mathfrak{F}^-$ and $\mathfrak{F}^+$ standing for the functional differential operators in Eq. (2.4):

$$\mathfrak{F}^-(12)G^-(23)=\delta(13); \tag{2.4'a}$$

$$\mathfrak{F}^+(12)G^+(23)=\delta(13); \tag{2.4'b}$$

$$G^+(12)=-C(11')C^{-1}(22')G^-(2'1'). \tag{2.5'}$$

If the mass operator $M(12)$ is defined in the usual way,

$$M^\pm(12)G^\pm(23)=\mathfrak{M}^\pm(12)G^\pm(23), \tag{2.6}$$

where $\mathfrak{M}$ is the functional differential operator

$$\mathfrak{M}^\pm(12)=m\delta(12)\mp ie\gamma(\xi,12)\delta/\delta J(\xi), \tag{2.7}$$

then the Green's function equations (2.4) can be written in terms of integro-differential operators F that are obtained from the $\mathfrak{F}$ by the replacement of $\mathfrak{M}$ by M.

A vertex operator $\Gamma(\xi,12)$ must now be defined for each Green's function,

$$\Gamma^+(\xi,12)=(\delta/\delta eA_+(\xi))(G^+(12))^{-1} =(\delta/\delta eA_+(\xi))F^+(12) \tag{2.8a}$$

and

$$\Gamma^-(\xi,12)=-(\delta/\delta eA_+(\xi))(G^-(12))^{-1} =-(\delta/\delta eA_+(\xi))F^-(12). \tag{2.8b}$$

In the absence of an external field these two quantities become equal because then the charge occurs always

[10] R. Karplus and A. Klein, Phys. Rev. **85**, 972 (1952).
[11] G. Breit, Phys. Rev. **34**, 553 (1929); **36**, 383 (1930); **39**, 616 (1932).

to an even power only, and the two differ just in the sign of the charge.

We now proceed to the two-particle system. The electron-positron Green's function for the vacuum state is defined by the relation

$$\delta_\eta\delta_{\eta'}\langle((\psi(x_1)\psi'(x_2))_+\rangle_0|_{\eta=\eta'=0}\epsilon(x_1,x_2)$$
$$=\int_{\sigma_2}^{\sigma_1}d^4x_1'\int_{\sigma_2}^{\sigma_1}d^4x_2'G^{-+}(x_1x_2,x_1'x_2')\times\delta\eta(x_1')\delta\eta'(x_2'). \quad (2.9)$$

Evaluation of the variations with the help of Eq. (9), reference 1, leads to the explicit expression

$$G^{-+}(x_1x_2,x_1'x_2')$$
$$=\langle(\psi(x_1)\psi'(x_2)\bar\psi(x_1')\bar\psi'(x_2'))_+\rangle_{0\epsilon}$$
$$-\langle(\psi(x_1)\psi'(x_2))_+\rangle_{0\epsilon}(x_1,x_2)\times\langle(\bar\psi(x_1')\bar\psi'(x_2'))_+\rangle_{0\epsilon}(x_1',x_2'). \quad (2.10)$$

As might be expected, this Green's function is related to a charge conjugate of the two-electron Green's function with arguments interchanged properly, by Eqs. (13, 20), reference 1:

$$G_{\alpha\beta\gamma\delta}{}^{-+}(x_1x_2,x_1'x_2')$$
$$=-C_{\beta\beta'}C^{-1}{}_{\delta\delta'}G_{\alpha\delta'\gamma\beta'}{}^{--}(x_1x_2',x_1'x_2)$$
$$-C_{\beta\beta'}C^{-1}{}_{\delta\delta'}G_{\alpha\beta'}{}^{-}(x_1x_2)G_{\delta'\gamma}{}^{-}(x_2'x_1'). \quad (2.11)$$

The antisymmetry of the two-electron Green's function assures that both direct and exchange processes are contained in the electron-positron Green's function; the second term merely corrects for the fact that the uncoupled electron-positron system cannot undergo an exchange process. In this case,

$$G_{\alpha\delta'\gamma\beta'}{}^{--}(x_1x_2',x_1'x_2)\to G_{\alpha\gamma}{}^{-}(x_1x_1')G_{\delta'\beta'}{}^{-}(x_2'x_2)-G_{\alpha\beta'}{}^{-}(x_1x_2)G_{\delta'\gamma}{}^{-}(x_2'x_1'), \quad (2.12)$$

whence

$$G_{\alpha\beta\gamma\delta}{}^{-+}(x_1x_2,x_1'x_2')$$
$$\to-C_{\beta\beta'}C^{-1}{}_{\delta\delta'}G_{\alpha\gamma}{}^{-}(x_1x_1')G_{\delta'\beta'}{}^{-}(x_2'x_2)=G_{\alpha\gamma}{}^{-}(x_1x_1')G_{\beta\delta}{}^{+}(x_2x_2'), \quad (2.13)$$

the proper description for noninteracting particles.

The differential equation for G^{-+} may be obtained with the help of that for G^{--}, Eq. (21), reference 1, and of Eq. (2.4′). They yield

$$\mathfrak{F}^{-}(11')G^{-+}(1'2,34)=\delta(13)G^{+}(24)+ie\gamma(\xi,11')C(1'2')C^{-1}(44')\times G^{+}(22')(\delta/\delta J(\xi))G^{-}(4'3) \quad (2.14)$$

and

$$F^{+}(22')\mathfrak{F}^{-}(11')G^{-+}(1'2',34)=\delta(13)\delta(24)+ie\gamma(\xi,11')C(1'2)C^{-1}(44')(\delta/\delta J(\xi))G^{-}(4'3). \quad (2.15)$$

Finally, the equation may be written in the form

$$[F^{-}(11')F^{+}(22')-I(12,1'2')]G^{-+}(1'2',34)=\delta(13)\delta(24), \quad (2.16)$$

where the interaction operator $I(1234)$ is defined by

$$I(12,1'2')G^{-+}(1'2',34)$$
$$=-F^{+}(22')[\mathfrak{M}^{-}(11')-M^{-}(11')]G^{-+}(1'2',34)+ie\gamma(\xi,13')C(3'2)C^{-1}(44')(\delta/\delta J(\xi))G^{-}(4'3),$$
$$=-F^{-}(11')[\mathfrak{M}^{+}(22')-M^{+}(22')]G^{-+}(1'2',34)-ie\gamma(\xi,22')C(2'1)C^{-1}(33')(\delta/\delta J(\xi))G^{+}(3'4). \quad (2.17)$$

The second expression arises when $\mathfrak{F}^{+}$ and then F^{-} are applied to the Green's function. These expressions must now be rearranged so as to yield the interaction operator explicitly as an integral operator up to the desired order of accuracy. In other words, the functional derivatives may occur only in terms that contribute negligibly to the effect that is being investigated. The subsequent operations will be directed at finding an expression that is suitable for the purposes of this paper. (For other effects, such as the Lamb shift in positronium, a different form of the interaction operator is necessary.)

With the help of the definition of the vertex operator, Eq. (2.8), the lowest order interaction may be separated as follows:

$$I(12,1'2')G^{-+}(1'2',34)$$
$$=ie^2\gamma(\xi,11')\mathcal{G}_{+}(\xi,\xi')\Gamma^{+}(\xi',22')G^{-+}(1'2',34)$$
$$-[\mathfrak{M}^{-}(11')-M^{-}(11')]F^{+}(22')G^{-+}(1'2',34)$$
$$+ie^2\gamma(\xi,13')C(3'2)\mathcal{G}_{+}(\xi,\xi')C^{-1}(2'4')\times\Gamma^{-}(\xi',4'1')G^{-}(1'3)G^{+}(2'4). \quad (2.18)$$

The second term in Eq. (2.18) can be simplified by the use of Eqs. (2.16) and (2.6), whence it becomes

$$-ie^2\gamma(\xi,11')G^{-}(1'1'')[\delta/\delta eJ(\xi)]\times I(1''2,3'4')G^{-+}(3'4',34). \quad (2.19)$$

The last term, finally, is brought into more useful form with the help of the identity

$$\mathcal{G}_{+}(\xi,\xi')C^{-1}(2'4')\Gamma^{-}(\xi',4'1')G^{-}(1'3)G^{+}(2'4)=D_{+}(\xi,\xi')C^{-1}(2'4')\gamma(\xi',4'1')G^{-+}(1'2',34), \quad (2.20)$$

which may be verified by iteration of both sides. The interaction operator therefore is given by

$$I(12,34)=ie^2\gamma(\xi,13)\mathcal{G}_{+}(\xi,\xi')\Gamma^{+}(\xi',24)+ie^2\gamma(\xi,11')C(1'2)D_{+}(\xi,\xi')C^{-1}(44')\gamma(\xi',4'3)-ie^2\gamma(\xi,11')G(1'1'')[(\delta/\delta eJ(\xi))I(1''2,3'4')\times G^{-+}(3'4',3''4'')][G^{-+}(3''4'',34)]^{-1}. \quad (2.21)$$

This, and a corresponding expression obtained from the alternative form of Eq. (2.17) correspond to Eq. (47), reference 1; the only difference lies in the second term above, which represents the interaction due to the virtual annihilation of the electron-positron pair. The last term contains the effects of higher order electrodynamic processes involving more than one virtual photon, such as multiple photon exchanges and the corrections that symmetrize the first term in the interaction so that it depends on the vertex operator of both the electron and the positron.

We are interested in the effects of one and two virtual quanta, terms of order e^4 in the interaction. For this reason, the functional derivative in Eq. (2.21) needs be evaluated only to the lowest order,

$$\begin{aligned}&[(\delta/\delta eJ(\xi))I(1''2,3'4')G^{-+}(3'4',3''4'')]\\&\times[G^{-+}(3''4'',34)]^{-1}\cong -I(1''2,3'4')\\&\times G^{-+}(3'4',3''4'')[\delta/\delta eJ(\xi)]\\&\times[F^{-}(3''3)F^{+}(4''4)]\cong -ie^2[\gamma(\xi,1''3')\\&\times\gamma(\bar\xi',24')+\gamma(\xi,1''2')C(2'2)C^{-1}(4''2'')\\&\times\gamma(\bar\xi',2''3')]D_+(\xi,\bar\xi')G^{-}(3'3'')G^{+}(4'4'')\\&\times D_+(\xi,\xi')[-F^{+}(4''4)\gamma(\xi',3''3)\\&\qquad+F^{-}(3''3)\gamma(\xi',4''4)].\end{aligned}\tag{2.22}$$

When this expression is multiplied out, the first of the four terms is conveniently included in a symmetrical lowest order interaction, and the $(\pm)$ superscripts can be dropped in the limit of vanishing external field. This form of the approximate interaction operator,

$$\begin{aligned}&I(12,34)\cong ie^2\Gamma(\xi,13)\mathcal{G}_+(\xi,\xi')\Gamma(\xi',24)\\&+ie^2\gamma(\xi,11')C(1'2)D_+(\xi,\xi')C^{-1}(44')\gamma(\xi',4'3)\\&+(ie^2)^2\gamma(\xi,11')G(1'1'')\gamma(\bar\xi,1''3)\gamma(\bar\xi',24')\\&\times G(4'4'')\gamma(\xi',4''4)D_+(\xi,\xi')D_+(\bar\xi,\bar\xi')\\&+(ie^2)^2\gamma(\xi,11')G(1'1'')\gamma(\bar\xi,1''2')C(2'2)D_+(\xi\xi')\\&\times D_+(\bar\xi,\bar\xi')[C^{-1}(33')\gamma(\bar\xi',3'4')G(4'4'')\gamma(\xi',4''4)\\&\qquad+C^{-1}(44')\gamma(\bar\xi',4'3')G(3'3'')\gamma(\bar\xi',3''3)],\end{aligned}\tag{2.23}$$

can be easily understood in terms of the equivalent Feynman diagram.

The wave functions $\psi(12)$ of the electron-positron system are solutions of the homogeneous equation,

$$[F^{-}(11')F^{+}(22')-I(12,1'2')]\psi(1'2')=0,\tag{2.24}$$

related to Eq. (2.16). It is important to realize that the operators $F(12)$ also contain electrodynamic corrections. These may be obtained from the corrections to the one-particle Green's function $G(12)$, of which $F(12)$ is the inverse.[12] For the nonrelativistic states in which we are interested, the operator $F(12)$ is a multiple of the Dirac operator $\bar F(12)$ that depends on the experimental mass m of the electron,

$$F^{\pm}(12)=(1-\alpha B/2\pi)^{-1}\bar F^{\pm}(12),\tag{2.25}$$

with

$$\bar F^{\pm}(x,x')=\delta(x-x')[\gamma_\mu(-i\partial_\mu'\pm eA_{+\mu}(x'))+m].\tag{2.26}$$

We may now introduce the interaction

$$\bar I(12,34)=(1-\alpha B/\pi)I(12,34),\tag{2.27}$$

which enters the equation of the usual form for the wave function,

$$[\bar F^{-}(11')\bar F^{+}(22')-\bar I(12,1'2')]\psi(1'2')=0.\tag{2.28}$$

To find the energy levels of the system, we seek solutions of the form

$$\psi(x_1x_2)=e^{iKX}\varphi_K(x);\quad X=\tfrac12(x_1+x_2),\quad x=x_1-x_2,\tag{2.29}$$

that are eigenfunctions of the total momentum operator with eigenvalue K. This eigenvalue is the goal of the calculation. In the absence of an external field, the interaction operator conserves the total momentum, so that it is possible to write an equation for the function $\varphi_K(x)$ of the relative coordinate x,

$$[F_K(xx')-I_K(x,x')]\varphi_K(x')=0,\tag{2.30}$$

where

$$\begin{aligned}&e^{iKX}[F_K(xx')]_{\alpha\beta\gamma\delta}\\&=\int\bar F_{\alpha\gamma}(X+\tfrac12x,X'+\tfrac12x')\bar F_{\beta\delta}(X-\tfrac12x,X'-\tfrac12x')\\&\qquad\times e^{iK'X'}d^4X',\end{aligned}\tag{2.31}$$

and $I_K(x,x')$ is similarly related to $\bar I(1234)$. The Dirac indices in Eq. (2.30) are summed in the same way as those in Eq. (2.24); φ_K still has two sets of Dirac indices even through it has but one four-vector argument. To avoid complications in the notation, this matrix notation will be continued; where necessary, superscripts 1 and 2 will distinguish Dirac matrices that operate, respectively, on the first and second particle index of the wave function $\varphi_K(x)$.

Before we proceed to solve Eq. (2.30), we shall decompose the first two contributions to $\bar I(1234)$, Eqs. (2.23) and (2.27). With the help of the expressions[12]

$$\Gamma_\mu(\xi,13)=\gamma_\mu(\xi,13)(1+\alpha B/2\pi)+\bar\Lambda_\mu^{(2)}(1-\xi,\xi-3)\tag{2.32}$$

and[12,13]

$$\mathcal{G}_{+\mu\nu}(\xi,\xi')=(1+\alpha A/2\pi)D_+(\xi,\xi')\delta_{\mu\nu}+\bar D_+^{(2)}(\xi,\xi')\delta_{\mu\nu},\tag{2.33}$$

[12] R. Karplus and N. M. Kroll, Phys. Rev. **77**, 536 (1950).

[13] Note that

$$g_+=\tfrac12iD_F',\quad D_+=\tfrac12iD_F,\quad \bar D_+^{(2)}=\tfrac12i\bar D_F^{(2)}.$$

they become

$$4\pi i\alpha\gamma_\mu(\xi,13)D_+(\xi,\xi')\gamma_\mu(\xi',24)$$
$$+ie^2\gamma_\mu(\xi,11')C(1'2)D_+(\xi\xi')C^{-1}(43')\gamma_\mu(\xi',3'3)$$
$$\times(1-\alpha B/\pi)+4\pi i\alpha\gamma_\mu(\xi,13)D_+(\xi,\xi')$$
$$\times\bar{\Lambda}_\mu^{(2)}(2-\xi',\xi'-4)+4\pi i\alpha\bar{\Lambda}_\mu^{(2)}(1-\xi,\xi-3)$$
$$\times D_+(\xi,\xi')\gamma_\mu(\xi',24)+4\pi i\alpha\gamma_\mu(\xi,13)$$
$$\bar{D}_+^{(2)}(\xi\xi')\gamma_\mu(\xi',24), \quad (2.34)$$

up to terms involving two virtual photons. The experimental value of the fine structure constant α has been written to absorb the charge renormalization factor in Eq. (2.33),[12]

$$4\pi\alpha=e^2(1+\alpha A/2\pi)=4\pi/137.03\cdots. \quad (2.35)$$

III. PERTURBATION THEORY

Salpeter[9] has discussed a method for finding the eigenvalues of the total energy of a two-particle system described by an equation like Eq. (2.30) if the interaction function does not differ greatly from a local instantaneous interaction of the form

$$\delta(x-x')\delta(t)f(\mathbf{r}) \quad (x_\mu=\mathbf{r},t;\quad i=1,2,3). \quad (3.1)$$

Such a term can indeed be separated from the center-of-mass transform of the first two contributions of Eq. (2.34), which may be written

$$I^C(x,x')+I_{K1}(x,x')=I^C(x,x')$$
$$+I_{K1B}(x,x')+I_{K1A}(x,x'), \quad (3.2)$$

where

$$I^C(x,x')=-i\alpha\delta(x-x')\gamma_0{}^1\gamma_0{}^2\delta(t)/r, \quad (3.3)$$

the Coulomb interaction, and

$$I_{K1B}=2i\alpha(2\pi)^{-3}\delta(x-x')$$
$$\times\int d^4k e^{ikx}\left[\frac{\boldsymbol{\gamma}^1\cdot\boldsymbol{\gamma}^2}{k_\mu{}^2}-\frac{\gamma_0{}^1\gamma_0{}^2k_0{}^2}{k_i{}^2k_\mu{}^2}\right], \quad (3.4)$$

$$I_{K1A}=ie^2(\gamma_\mu C)\delta(x)\delta(x')(C^{-1}\gamma_\mu)(1-\alpha B/\pi)/K_\nu{}^2. \quad (3.5)$$

These include the Breit[11] interaction, retardation effects, and the virtual annihilation exchange interaction. All the contributions derivable from Eqs. (2.23) and (2.34) that are not included in Eqs. (3.2–5) depend on the appearance of two virtual quanta. The two-quantum terms that are included in Eq. (2.34) will be denoted by $I_{K2B}{}^{(1)}$, while those that are explicit in Eq. (2.23) will be denoted by $I_{K2A}(x,x')$ or $I_{K2B}{}^{(2)}(x,x')$ depending on whether they are exchange or direct interactions.

The change in energy levels produced by the perturbations I_{K1} and I_{K2} acting on the electron-positron system bound by the Coulomb interaction Eq. (3.3) is then given to a sufficient approximation by[9]

$$\Delta E=-i\int d^4x d^4x'\,\bar{\varphi}_C(x)$$
$$\times\Big\{I_{K1}(x,x')+I_{K2A}(x,x')+I_{K2B}{}^{(1)}(x,x')$$
$$+I_{K2B}{}^{(2)}(x,x')+\int d^4x''d^4x'''I_{K1}(x,x'')$$
$$\times[F_{KC}(x'',x''')]^{-1}I_{K1}(x''',x')\Big\}\varphi_C(x'), \quad (3.6)$$

measured in the reference frame in which the total spatial momentum vanishes,

$$K_\mu=(\mathbf{0},K_0). \quad (3.7)$$

The function $\varphi_C(x)$ is the relativistic Coulomb wave function that is a good approximation to the actual wave function of the state whose energy level is sought. It is a solution of

$$[F_{KC}(x,x')-I^C(x,x')]\varphi_C(x')=0, \quad (3.8)$$

whence

$$\Delta E=K_0-K_0{}^C. \quad (3.9)$$

The expression Eq. (3.6) is accurate to order α relative to the fine structure contribution I_{K1} and further presupposes that the intermediate states in the second-order perturbation term, the last in Eq. (3.6), can be replaced by free particle states. This is the case for the spin-spin interaction under investigation.

Before closing this section, we must briefly discuss the wave function $\varphi_C(x)$ that enters into Eq. (3.6). As is the case with the electrodynamic corrections to the magnetic interactions in hydrogen, the contributions to ΔE come mostly from the vicinity of the relative coordinate origin. The two-photon contributions, therefore, will be at most of the order $\alpha^2|\varphi_0(0)|^2$, where $\varphi_0(r)$ is the Pauli wave function for the ground state of positronium. Since this is the smallest magnitude that is being considered, contributions to these terms that are proportional to the relative momentum can be neglected. It therefore suffices to approximate $\bar{\varphi}_C(x)[\ ]\varphi_C(x')$ by the product of $|\varphi_0(0)|^2=(\frac{1}{2}\alpha m)^3/\pi$ and the appropriate spin matrix element, which will be denoted by $\langle\ \rangle$. In calculating the effect of I_{K1}, which contains contributions of order $\alpha|\varphi_0(0)|^2$ due to the exchange of one virtual photon, the relative momentum can no longer be neglected. Indeed, corrections of relative order α that arise from the large momentum components of the wave function must not be omitted. As Salpeter[9] has pointed out, an improvement over the Pauli wave functions is obtained when the integral equation,

$$\varphi_C(x)=-i\alpha\int[F_{KC}(x,x')]^{-1}\varphi_C(\mathbf{r}',0)d\mathbf{r}'/r', \quad (3.10)$$

is used for an iteration procedure based on the Pauli wave function,

$$\varphi_C(x)\cong -i\alpha\int[F_K C(x,x')]^{-1}\varphi_0(\mathbf{r}')d\mathbf{r}'/r'. \quad (3.11)$$

IV. THE DIRECT INTERACTION

We turn now to the evaluation of the matrix elements for the energy shift that was obtained in the previous section. We shall consider first the contributions ΔE_B of those terms which arise from direct interaction, namely, those in which an electron-positron pair is present in each intermediate state. According to Eq. (3.6) and the definition preceding this equation,

$$\begin{aligned}\Delta E_B=&-i\int d^4x d^4x'\,\bar\varphi_C(x)I_{K1B}(x,x')\varphi_C(x')\\&-i|\varphi_0(0)|^2\int d^4x d^4x'\Big\langle I_{K2B}{}^{(2)}(x,x')\\&+\int d^4x''d^4x'''I_{K1B}(x,x'')\\&\times[F_K C(x'',x''')]^{-1}I_{K1B}(x''',x')\Big\rangle\\&-i|\varphi_0(0)|^2\int d^4x d^4x'\langle I_{K2B}{}^{(1)}(x,x')\rangle. \quad (4.1)\end{aligned}$$

The one-photon part of the interaction,

$$\begin{aligned}\Delta E_{B1}=&-i\int d^4x d^4x'\,\bar\varphi_C(x)I_{K1B}(x,x')\varphi_C(x')\\=&\frac{2\alpha}{(2\pi)^3}\int d^4x d^4k\,\bar\varphi_C(x)e^{ikx}\\&\times\left[\frac{\boldsymbol{\gamma}^1\cdot\boldsymbol{\gamma}^2}{k_\mu{}^2}-\frac{\gamma_0{}^1\gamma_0{}^2k_0{}^2}{k_i{}^2k_\mu{}^2}\right]\varphi_C(x), \quad (4.2)\end{aligned}$$

presents the greatest complication because it contains the lowest order hyperfine structure as leading term. When the approximate Coulomb wave function evaluated in the appendix is inserted here, one obtains a spin matrix element and multiple momentum integral which is multiplied by the explicit factor $\alpha^3|\varphi_0(0)|^2$:

$$\begin{aligned}\Delta E_{B1}=&\frac{8\alpha^3|\varphi_0(0)|^2}{(2\pi)^4m^2}\int d^4k d\mathbf{k}'d\mathbf{k}''dte^{-ik_0t}\\&\times\frac{m^2}{(k'^2+\frac14\alpha^2m^2)^2}\frac{m^2}{(k''^2+\frac14\alpha^2m^2)^2}\delta(\mathbf{k}-\mathbf{k}'+\mathbf{k}'')\\&\times\left\langle F_{k'}(-t)\left[\frac{\boldsymbol{\gamma}^1\cdot\boldsymbol{\gamma}^2}{k_\mu{}^2}-\frac{\gamma_0{}^1\gamma_0{}^2k_0{}^2}{k_i{}^2k_\mu{}^2}\right]F_{k''}(t)\right\rangle. \quad (4.3)\end{aligned}$$

The following observations can now be made about that part of the energy change which depends on the spin of both particles. Only large contributions of magnitude α^{-2} and α^{-1} will be important in the integral. It can be seen that only small values of the momenta k', $k''\lesssim\alpha m$ make such large contributions. The important region of integration, therefore, extends over small values of either or of both these momenta. When both momenta are large, k' and $k''\gtrsim m$, the integral becomes negligible for the purposes of the present calculation. A term proportional to k'^2 and k''^2 in the spin matrix element, for instance, is negligible because in its evaluation one may neglect $(\alpha m)^2$ compared to k'^2 and k''^2, so that the integral in Eq. (4.3) becomes effectively independent of α.[14] One may now see that the spin-dependent contribution of the retarded Coulomb interaction involves one of the $\boldsymbol{\alpha}^1\cdot\mathbf{k}'\boldsymbol{\alpha}^2\cdot\mathbf{k}'$ terms of both $F(t)$ operators and is therefore a negligible large momentum effect. The Breit interaction, of course, is important and contributes in conjunction with only one factor $\boldsymbol{\alpha}^1\cdot\mathbf{k}'\boldsymbol{\alpha}^2\cdot\mathbf{k}'$. Since corrections that involve an additional factor k''^2 are too small, one may use an approximate expression

$$\begin{aligned}F_k(t)\cong&\tfrac12(1+\boldsymbol{\alpha}^1\cdot\mathbf{k}/2m)(1-\boldsymbol{\alpha}^2\cdot\mathbf{k}/2m)\\&\times[(m/E)(e^{-i(E-m)|t|}+e^{-i(E+m)|t|})\\&+(e^{-i(E-m)|t|}-e^{-i(E+m)|t|})] \quad (4.4)\end{aligned}$$

to evaluate ΔE_{B1}.

The spin matrix element has now become quite simple,

$$\begin{aligned}&\langle(1+\boldsymbol{\alpha}^1\cdot\mathbf{k}'/2m)(1-\boldsymbol{\alpha}^2\cdot\mathbf{k}'/2m)\\&\quad\times\boldsymbol{\alpha}^1\cdot\boldsymbol{\alpha}^2(1+\boldsymbol{\alpha}^1\cdot\mathbf{k}''/2m)(1-\boldsymbol{\alpha}^2\cdot\mathbf{k}''/2\mathrm{m})\rangle\\&\quad\to\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2k^2-\boldsymbol{\sigma}^1\cdot\mathbf{k}\boldsymbol{\sigma}^2\cdot\mathbf{k}\rangle\to\tfrac23\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2\rangle k^2, \quad (4.5)\end{aligned}$$

since the δ-function implies that $\mathbf{k}'-\mathbf{k}''=\mathbf{k}$, and the integrand has the necessary spherical symmetry. The k_0 integration with the usual treatment of the poles yields

$$\int_{-\infty}^{\infty}e^{-ik_0t}dk_0(k^2-k_0{}^2-i\epsilon)^{-1}=\pi ik^{-1}e^{-ik|t|}(\epsilon>0). \quad (4.6)$$

The function of time in Eq. (4.3) is therefore even, so that the time integration may be carried out only over positive values if a factor of two is supplied. The integrals encountered are of the form

$$\begin{aligned}\int_0^{\infty}dte^{-i(E'\pm m)t}e^{-ikt}e^{-i(E''\pm m)t}&\\=-i(k+E'+E''\pm m\pm m)^{-1}&, \quad (4.7)\end{aligned}$$

since the denominator never vanishes. The energy

[14] Detailed examination shows that the integral actually is proportional to $\log\alpha$ in this case. This dependence, however, is still negligible for our purposes.

change has now been reduced to

$$\Delta E_{B1}=\frac{4}{3}\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2\rangle\alpha^3(2\pi)^{-3}|\,\varphi_0(0)\,|^2$$
$$\times\int d\mathbf{k}d\mathbf{k}'d\mathbf{k}''\delta(\mathbf{k}-\mathbf{k}'+\mathbf{k}'')(k'^2+\tfrac{1}{4}\alpha^2m^2)^{-2}$$
$$\times(k''^2+\tfrac{1}{4}\alpha^2m^2)^{-2}\Big\{\frac{(E'+m)(E''+m)}{4E'E''}$$
$$\times\frac{k}{k+E'+E''-2m}+\frac{m^2-E'E''}{2E'E''}\frac{k}{k+E'+E''}$$
$$+\frac{(E'-m)(E''-m)}{4E'E''}\frac{k}{k+E'+E''+2m}\Big\}. \quad (4.8)$$

As it stands, the integral in Eq. (4.8) is quite difficult to carry out. We must remember, however, that at least one of the two variables k', k'' must be small compared to m, a fact which permits replacement of the corresponding kinetic energy by the rest energy. Furthermore, the occurrence of a factor $(E'-m)$ implies that the particular term contributes only for large $k'\sim m$, whence k'' must be small, and *vice versa*. In such a case, the small momentum may also be neglected in the argument of the δ-function. The remaining integration can then be carried out:

$$\Delta E_{B1}=\frac{4}{3}\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2\rangle\alpha^3(2\pi)^{-3}|\,\varphi_0(0)\,|^2$$
$$\times\int d\mathbf{k}d\mathbf{k}'d\mathbf{k}''\{(m^2/E'E'')\delta(\mathbf{k}+\mathbf{k}''-\mathbf{k}')$$
$$\times(k'^2+\tfrac{1}{4}\alpha^2m^2)^{-2}(k''^2+\tfrac{1}{4}\alpha^2m^2)^{-2}$$
$$+((k-E')/2mE'kk'^2)\delta(\mathbf{k}-\mathbf{k}')(k''^2+\tfrac{1}{4}\alpha^2m^2)^{-2}$$
$$+((k-E'')/2mE''kk'^2)\delta(\mathbf{k}+\mathbf{k}'')(k'^2+\tfrac{1}{4}\alpha^2m^2)^{-2}\}$$
$$=\frac{2\pi}{3}\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2\rangle\frac{\alpha}{m^2}|\,\varphi_0(0)\,|^2\Big\{1-\frac{4\alpha}{\pi}-\frac{2\alpha}{\pi}\ln\frac{m}{2k_m}\Big\}. \quad (4.9)$$

In the first term both k' and k'' are of the order αm, in the second $k'\sim m$, and in the third $k''\sim m$. A cutoff k_m has here been introduced as a lower limit on the final momentum integration. Its presence shows that some contributions of order $\alpha^2|\,\varphi_0(0)\,|^2$ to ΔE_{B1} do arise from small values of momentum, contrary to expectation. It will be seen, however, that the direct interaction $I_{K2B}{}^{(2)}$ and the second-order effect of I_{K1B} also contain contributions from small values of the momentum as represented by the appearance of $\ln(m/2k_m)$. Just as here, these are being treated incorrectly because of the assumption of free intermediate states that is implicit in the derivation of the interaction operator. The justification of this treatment lies in the fact that the sum of the direct interactions is independent of the cutoff; that a cutoff need not have been introduced at all if the terms had been grouped properly according to the photon momentum that makes the contribution rather than according to the physical process that is represented.

The evaluation of the remainder of Eq. (4.1) is relatively simple. The second line contributes

$$\Delta E_{B2}{}^{(2)}=-i|\,\varphi_0(0)\,|^2(4\pi i\alpha)^2$$
$$\times\int d^4xd^4x'e^{-iK^C(X-X')}d^4X'$$
$$\times\{\langle(\gamma_\mu{}^1G^1(X+\tfrac{1}{2}x,\,X'+\tfrac{1}{2}x')\gamma_\nu{}^1)$$
$$\times(\gamma_\nu{}^2G^2(X-\tfrac{1}{2}x,\,X'-\tfrac{1}{2}x')\gamma_\mu{}^2)\rangle$$
$$\times D_+(X-X'+\tfrac{1}{2}(x-x'))D_+(X'-X+\tfrac{1}{2}(x+x'))$$
$$+(2\pi)^{-8}\int d^4kd^4k'e^{ikx}e^{ik'x'}/k_\mu{}^2k_\mu{}'^2$$
$$\times\langle(\boldsymbol{\gamma}^1\cdot\boldsymbol{\gamma}^2-\gamma_0{}^1\gamma_0{}^2(k_0{}^2/k_i{}^2))G^1(X+\tfrac{1}{2}x,\,X'+\tfrac{1}{2}x')$$
$$\times G^2(X-\tfrac{1}{2}x,\,X'-\tfrac{1}{2}x')(\boldsymbol{\gamma}^1\cdot\boldsymbol{\gamma}^2-\gamma_0{}^1\gamma_0{}^2(k_0{}^2/k_i{}^2))\rangle, \quad (4.10)$$

an expression derived from Eqs. (2.23), (2.31), and (3.4). When Fourier transforms are introduced for the Green's functions, the energy may be written

$$\Delta E_{B2}{}^{(2)}=\frac{4\alpha^2}{(2\pi)^2}|\,\varphi_0(0)\,|^2\int d^4k(k_\mu{}^2)^{-2}$$
$$\times\Big\langle\Big(\gamma_\mu{}^1\frac{\gamma^1(\frac{1}{2}K^C-k)-m}{E^2-(m-k_0)^2}\gamma_\nu{}^1\Big)$$
$$\times\Big(\gamma_\nu{}^2\frac{\gamma^2(\frac{1}{2}K^C-k)-m}{E^2-(m-k_0)^2}\gamma_\mu{}^2\Big)$$
$$+(\boldsymbol{\gamma}^1\cdot\boldsymbol{\gamma}^2-\gamma_0{}^1\gamma_0{}^2k_0{}^2/k_i{}^2)\frac{\gamma^1(\frac{1}{2}K^C-k)-m}{E^2-(m-k_0)^2}$$
$$\cdot\frac{\gamma^2(\frac{1}{2}K^C+k)-m}{E^2-(m+k_0)^2}(\boldsymbol{\gamma}^1\cdot\boldsymbol{\gamma}^2-\gamma_0{}^1\gamma_0{}^2k_0{}^2/k_i{}^2)\Big\rangle, \quad (4.11)$$

where, as before,

$$E^2=k^2+m^2-i\epsilon\quad(\epsilon>0),\quad \tfrac{1}{2}K_0{}^C\simeq m \quad (4.12a)$$

and

$$k_\mu{}^2=k^2-k_0{}^2-i\epsilon \quad (4.12b)$$

define the treatment of the poles.

Explicit display of the spin matrix element and spherical averaging wisely precede the momentum

integration,

$$\Delta E_{B2}{}^{(2)}=(8\alpha^2/\pi)\,|\,\varphi_0(0)\,|^2\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2\rangle \times\int_0^\infty k^2dk\int_{-\infty}^\infty dk_0(k_\mu{}^2)^{-2} \times\{(k_0{}^2-\tfrac{2}{3}k^2)[E^2-(m-k_0)^2]^{-2} +\tfrac{1}{3}k_0{}^2[E^2-(m-k_0)^2]^{-1}[E^2-(m+k_0)^2]^{-1}\}; \quad (4.13)$$

it depends on the identities

$$\gamma_i\gamma_j=-\delta_{ij}-i\sigma_{ij};\quad \langle\sigma_{ij}{}^1\sigma_{ij}{}^2\rangle=2\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2\rangle. \quad (4.14)$$

The evaluation of the integrals is straightforward, except that the same cutoff k_m for small momentum values must be introduced. The result is

$$\Delta E_{B2}{}^{(2)}=\frac{2\pi}{3}\frac{\alpha}{m^2}\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2\rangle\,|\,\varphi_0(0)\,|^2\left\{\frac{5}{2}\frac{\alpha}{\pi}+\frac{2\alpha}{\pi}\ln\frac{m}{2k_m}\right\}, \quad (4.15)$$

and gives the total effect independent of k_m of processes where all quanta are exchanged between the two particles,

$$\Delta E_{B1}+\Delta E_{B2}{}^{(2)}=\frac{2\pi}{3}\frac{\alpha}{m^2}\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2\rangle\,|\,\varphi_0(0)\,|^2\left\{1-\frac{3}{2}\frac{\alpha}{\pi}\right\}. \quad (4.16)$$

The perturbation $\Delta E_{B2}{}^{(1)}$ includes effects of vacuum fluctuations on the exchange of a single quantum. The spin-dependent corrections to the vertex operator are contained in the anomalous-magnetic moment $(\alpha/2\pi)(e/2m)$ of each particle while the vacuum polarization has no effect on the singlet-triplet separation. The added contribution is therefore

$$\Delta E_{B2}{}^{(1)}=\frac{2\pi}{3}\frac{\alpha}{m^2}\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2\rangle\,|\,\varphi_0(0)\,|^2\{\alpha/\pi\}. \quad (4.17)$$

V. EXCHANGE INTERACTION

In this section we shall evaluate the matrix elements of the exchange energy, embracing all processes in which there is an intermediate state with no pairs present. The energy change, according to Eq. (3.6), is

$$\Delta E_A=-i\int d^4xd^4x'\,\bar\varphi_C(x)I_{K1A}(x,x')\varphi_C(x')(1-\alpha B/\pi) -i\,|\,\varphi_0(0)\,|^2\int d^4xd^4x'\langle I_{K2A}(x,x')\rangle -i\,|\,\varphi_0(0)\,|^2\int d^4xd^4x'd^4x''d^4x''' \times\langle I_{K1A}(x,x'')[F_{KC}(x'',x''')]^{-1}I_{K1A}(x''',x') +I_{K1B}(x,x'')[F_{KC}(x'',x''')]^{-1}I_{K1A}(x''',x') +I_{K1A}(x,x'')[F_{KC}(x'',x''')]^{-1}I_{K1B}(x''',x')\rangle. \quad (5.1)$$

Consideration of the virtual two-quantum annihilation I_{K2A} and of the second-order single-quantum annihilation will be postponed to the end of this section. We only anticipate the result [see Appendix, Eq. (A.3)] that the latter will contribute a term that renormalizes the charge occurring in the first-order virtual annihilation from its uncorrected value e^2 to the measured value $4\pi\alpha$ [see Eq. (2.35)]; to the order considered in this paper, therefore, all quantities depend on α from here on.

The first one and last two terms in Eq. (5.1) present some complications since the quantity B is actually a divergent integral.[12] We expect that other divergent integrals will make the complete result finite, but we must exercise great care to obtain the correct finite result. For purposes of orientation it is instructive to consider briefly the matrix element in Eq. (5.1) for noninteracting, nonrelativistic initial and final states, because the high energy divergences may be expected to be the same in this simpler case as in the positronium atom. The wave function $\varphi_C(x)$ then represents the initial state plus a correction due to one Coulomb scattering, while $\int[F(x,x')]^{-1}I_{K1B}(x',x'')\varphi_0(0)d^4x'd^4x''$ represents the correction to the initial state due to the Breit interaction and retardation effects. The three terms we are now considering, therefore, comprise the matrix element of the virtual annihilation in the initial

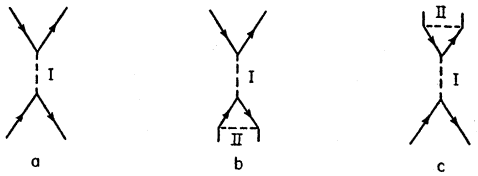

FIG. 1. Feynman diagrams for virtual annihilation electron-positron scattering.

state plus a correction due to the four-dimensional interaction represented by one quantum exchange. The Feynman diagrams for these processes, Fig. 1, show that the electrodynamic corrections, Fig. 1b, 1c, are just the correction to the vertex operator, and therefore contain each a contribution $(\alpha/2\pi)B$ multiplying the basic interaction Fig. 1a.[12,15] To our order of accuracy, the divergent integrals disappear.

With this understanding we can attempt to evaluate the actual matrix element in Eq. (5.1). In order to keep track of the infinite quantities, it is very convenient to regulate the interaction brought about by photon II in Fig. 1 with a heavy photon of mass Λ.[16] The integral B can be evaluated to B_Λ,[12]

$$B_\Lambda=(i\pi^2)^{-1}\int_0^1 udu\int d^4k \times\{(k^2+m^2u^2)^{-2}-(k^2+m^2u^2+\Lambda^2(1-u))^{-2} -4m^2(1-u-\tfrac{1}{4}u^2)(k^2+m^2u^2)^{-3}\} =\ln(\Lambda/m)+\tfrac{1}{4}-\ln(m/2k_m), \quad (5.2)$$

[15] J. C. Ward, Phys. Rev. **78**, 182 (1950).
[16] R. P. Feynman, Phys. Rev. **74**, 1430 (1948); W. Pauli and F. Villars, Revs. Modern Phys. **21**, 434 (1949).

where quantities depending inversely on Λ have been omitted and the low energy cutoff k_m has been introduced [see text following Eq. (4.9)].

The structure of the exchange interaction I_{K1A} implies that the energy change corresponding to Fig. 1 can be written

$$\Delta E_{A1}=-\pi\alpha m^{-2}\bar{\varphi}_\Lambda(0)_{\alpha\beta}(\gamma_j C)_{\alpha\beta}\times(C^{-1}\gamma_j)_{\beta'\alpha'}\varphi_\Lambda(0)_{\alpha'\beta'}, \quad (5.3)$$

where

$$\begin{aligned}(C^{-1}\gamma_j)_{\beta'\alpha'}\varphi_\Lambda(0)_{\alpha'\beta'}&=\mathrm{Tr}[C^{-1}\gamma_j\varphi_\Lambda(0)]\\
&=[1-(\alpha/2\pi)B_\Lambda]2\alpha(2\pi)^{-2}\,\mathrm{Tr}\Big[\int d\mathbf{k}(m^2/E)\\
&\times(k^2+\tfrac{1}{4}\alpha^2m^2)^{-2}\Big\{(1-\tilde{\boldsymbol{\gamma}}\cdot\mathbf{k}/2m)\\
&\times C^{-1}\gamma_j(1+\boldsymbol{\gamma}\cdot\mathbf{k}/2m)+C^{-1}\gamma_j k^2/4m^2\Big\}\varphi_0(0)\\
&+(i/2\pi)\int d^4k\{\tilde{\gamma}_i(m-\tilde{\gamma}(\tfrac{1}{2}K^C+k))\\
&\times C^{-1}\gamma_j(m-\gamma(\tfrac{1}{2}K^C-k))\gamma_i-(k_0^2/k_i^2)\\
&\times\tilde{\gamma}_0(m-\tilde{\gamma}(\tfrac{1}{2}K^C+k))C^{-1}\gamma_j(m-\gamma(\tfrac{1}{2}K^C-k))\gamma_0\}\\
&\times[k_\mu^2]^{-1}[E^2-(m+k_0)^2]^{-1}[E^2-(m-k_0)^2]^{-1}\varphi_0(0)\\
&-(i/2\pi)\int d^4k\{\tilde{\gamma}_\mu(m-\tilde{\gamma}(\tfrac{1}{2}K^C+k))\\
&\times C^{-1}\gamma_j(m-\gamma(\tfrac{1}{2}K^C-k))\gamma_\mu\}[k_\mu^2+\Lambda^2]^{-1}\\
&\times[E^2-(m+k_0)^2]^{-1}[E^2-(m-k_0)^2]^{-1}\varphi_0(0)\Big]. \quad (5.4)\end{aligned}$$

In writing the contribution of the regulating term, the last in Eq. (5.4), we have taken advantage of the fact that a very short range potential has no bound state so that the scattering picture described by Fig. 1 is applicable. The total energy has been approximated by $2m$ everywhere except in the correction to the Coulomb wave function, which comes from Eq. (A.9) evaluated at the origin. Only a space-like pair-producing Dirac matrix need be taken in Eq. (5.3). The trace is evaluated with the help of the facts that the Pauli wave function has only large components and that the charge-conjugating matrix C is an odd Dirac matrix. After integrating over k_0 with the usual treatment of the poles and after spherical averaging of the momentum integral, Eq. (5.4) becomes

$$\begin{aligned}&\mathrm{Tr}[C^{-1}\gamma_j\varphi_\Lambda(0)]\\
&=[1-(\alpha/2\pi)B_\Lambda]\,\mathrm{Tr}[C^{-1}\gamma_j\varphi_0(0)](-\alpha/\pi m^2)\\
&\times\int_0^\infty k^2dk\{-m^2E^{-1}(4k^2/3+2m^2)\\
&\times(k^2+\tfrac{1}{4}\alpha^2m^2)^{-2}+\tfrac{1}{3}(E^{-1}-k^{-1})+m^2k^{-3}\\
&-k^2(k^2+\Lambda^2-\Lambda^4/4m^2)^{-1}[-(m^2-\tfrac{1}{4}\Lambda^2)\\
&\times E^{-1}(4k^2/3+2m^2)k^{-4}+\tfrac{1}{3}(E^{-1}-E'^{-1})\\
&+(m^2-\tfrac{1}{2}\Lambda^2)k^{-2}E'^{-1}]\}. \quad (5.5)\end{aligned}$$

Here

$$E'=(k^2+\Lambda^2)^{\frac{1}{2}}, \quad (5.6)$$

in the second set of terms, which came from the regulating expression. One can observe that these reduce to the first set when $\Lambda=0$ if αm there is neglected with respect to k. The integrations are similar to the ones encountered in connection with Eq. (4.9) but made more complicated by the regulator. If one expands the result in powers of $(m/\Lambda)^2$ and keeps only the leading term, one obtains

$$\begin{aligned}&\mathrm{Tr}[C^{-1}\gamma_j\varphi_\Lambda(0)]\\
&=[1-(\alpha/2\pi)B_\Lambda]\,\mathrm{Tr}[C^{-1}\gamma_j\varphi_0(0)]\\
&\times\{1+(\alpha/2\pi)[\ln(\Lambda/m)]-4+\tfrac{1}{4}-\ln(m/2k_m)\}\\
&=(1-2\alpha/\pi)\,\mathrm{Tr}[C^{-1}\gamma_j\varphi_0(0)], \quad (5.7)\end{aligned}$$

with B_Λ given by Eq. (5.2), whence

$$\Delta E_{A1}=-(\pi\alpha/m^2)(1-4\alpha/\pi)\times\mathrm{Tr}[\bar{\varphi}_0(0)\gamma_jC]\,\mathrm{Tr}[C^{-1}\gamma_j\varphi_0(0)], \quad (5.8)$$

because γ_jC is a symmetrical matrix. When the usual representation of the charge conjugating matrix

$$C=C^{-1}=\gamma_0\gamma_2 \quad (5.9)$$

is inserted, the direct product of the Dirac matrices in Eq. (5.8) can be relabeled so that the operators refer to the spins of the individual particles:[6-8]

$$\begin{aligned}\bar{\varphi}_0(0)_{\alpha\beta}(\gamma_jC)_{\beta\alpha}(C^{-1}\gamma_j)_{\beta'\alpha'}\varphi_0(0)_{\alpha'\beta'}&\rightarrow-\varphi_0{}^*(0)_{\alpha\beta}\\
\times[\tfrac{3}{2}\delta_{\alpha\alpha'}\delta_{\beta\beta'}+\tfrac{1}{2}\boldsymbol{\sigma}_{\alpha\alpha'}\cdot\boldsymbol{\sigma}_{\beta\beta'}]\varphi_0(0)_{\alpha'\beta'}&\\
=-|\varphi_0(0)|^2\langle S^2\rangle, \quad (5.10)&\end{aligned}$$

where S is the total spin of the system,

$$\mathbf{S}=\tfrac{1}{2}(\boldsymbol{\sigma}^1+\boldsymbol{\sigma}^2). \quad (5.11)$$

We then obtain the known effect of the virtual annihilation[6-8] plus a large correction of relative order α,

$$\Delta E_{A1}=(\pi\alpha/m^2)\langle S^2\rangle|\varphi_0(0)|^2\{1-4\alpha/\pi\}. \quad (5.12)$$

We now turn to the contribution of the second-order single quantum annihilation,

$$\Delta E_{A2}^{(1)}=i\pi^2\alpha^2m^{-4}\,\mathrm{Tr}[\varphi_0(0)\gamma_iC](C^{-1}\gamma_i)\times[F_{K^C}(0,0)]^{-1}(\gamma_jC)\,\mathrm{Tr}[C^{-1}\gamma_j\varphi_0(0)],\quad(5.13)$$

with the spin sums as inferred from the derivation of this expression. In the appendix this effect is interpreted in terms of the polarization of the vacuum by the photon produced in the virtual annihilation. The evaluation given there together with Eq. (5.10) shows that the effect on the singlet-triplet splitting is[8]

$$\Delta E_{A2}^{(1)}=(\pi\alpha/m^2)\langle S^2\rangle|\,\varphi_0(0)\,|^2\{-8\alpha/9\pi\},\quad(5.14)$$

since the renormalization constant A, Eq. (A.3) has been incorporated already.

The final item to be discussed in this section is the energy shift associated with two-quantum virtual annihilation given by

$$\begin{aligned}\Delta E_{A2}^{(2)}=&\frac{i\alpha^2}{\pi^2}|\,\varphi_0(0)\,|^2\\&\times[k_\rho{}^2(K^C-k)_\sigma{}^2[(\tfrac{1}{2}K^C-k)_\lambda{}^2+m^2]^2]^{-1}\\&\times\langle(\gamma_\mu[\gamma(\tfrac{1}{2}K^C-k)-m]\gamma_\nu C)\\&\times(-C^{-1}\gamma_\mu[\gamma(\tfrac{1}{2}K^C-k)m]\gamma_\nu\\&\qquad+C^{-1}\gamma_\nu(\gamma(\tfrac{1}{2}K^C-k)-m]\gamma_\mu)\rangle,\end{aligned}\quad(5.15)$$

when Fourier representations are introduced for the Green's functions. The spin matrix elements of the two parentheses is to be taken as trace with the final and initial state wave functions, as in Eqs. (5.3) and (5.4). The momentum integration is simplified by the usual procedure of combining the three distinct denominators according to the formula

$$\begin{aligned}\int d^4k\,&[k_\mu{}^2(K^C-k)_\nu{}^2[(\tfrac{1}{2}K^C-k)_\lambda{}^2+m^2]^2]^{-1}\\&=6\int_0^1x^2dx\int_0^1ydy\int d^4k\\&\times[[k-\tfrac{1}{2}K^C(xy+2(1-x))]^2\\&\qquad+xm^2(xy^2-4(1-x)(1-y))-i\epsilon]^{-4}.\end{aligned}\quad(5.16)$$

The displacement $k_0\to k_0+m(y+2(1-x))$ brings the denominator into the form

$$k^2+xm^2[x(2-y)^2-4(1-y)]\quad(5.17)$$

and leaves the numerator proportional to

$$\tfrac{1}{4}k_\lambda{}^2\langle(\gamma_\mu\gamma_\rho\gamma_\nu C)(-C^{-1}\gamma_\mu\gamma_\rho\gamma_\nu+C^{-1}\gamma_\nu\gamma_\rho\gamma_\mu)\rangle\quad(5.18)$$

after hyperspherical averaging and the discarding of some terms whose dependence on the Dirac matrices prevents them from contributing. Since the wave functions in which the spin matrix elements are evaluated have only large components, Eq. (5.18) can be simplified to

$$-3k_\mu{}^2\langle(\gamma_0\gamma_5C)(C^{-1}\gamma_0\gamma_5)\rangle=3k_\mu{}^2\langle(\gamma_2\gamma_5)(\gamma_2\gamma_5)\rangle,\quad(5.19)$$

where

$$\gamma_5=\gamma_1\gamma_2\gamma_3\gamma_0,\quad\gamma_5{}^2=-1.\quad(5.20)$$

Rearrangement of indices according to Eq. (5.10) finally produces the ordinary spin matrix element of a function of the total spin, Eq. (5.11),

$$3k_\mu{}^2\langle 2-S^2\rangle.\quad(5.21)$$

The momentum integration,

$$\int d^4kk_\mu{}^2[k_\nu{}^2+\Delta^2]^{-4}=i\pi^2/3\Delta^2,\quad(5.22)$$

brings the energy perturbation into the form

$$\begin{aligned}\Delta E_{A2}^{(2)}=&-6\alpha^2m^{-2}\langle 2-S^2\rangle|\,\varphi_0(0)\,|^2\\&\times\int_0^1ydy\int_0^1xdx[x(2-y)^2-4(1-y)-i\epsilon]^{-1}\\&=-(\alpha^2/m^2)\langle 2-S^2\rangle|\,\varphi_0(0)\,|^2(2-2\ln 2+\pi i).\end{aligned}\quad(5.23)$$

The real part of this expression corresponds to the energy change of the level while the imaginary part corresponds to the well-known[17] decay rate of the singlet state by two-photon annihilation,

$$\tau^{-1}=\alpha^3\,\mathrm{Ry}_\infty=0.804\times10^{10}\ \mathrm{sec}^{-1}.\quad(5.24)$$

The total contribution of the virtual annihilation interaction may be collected from Eqs. (5.12), (5.13), and (5.23),

$$\begin{aligned}\Delta E_A=&(\pi\alpha/m^2)|\,\varphi_0(0)\,|^2\{\langle S^2\rangle(1-4\alpha/\pi-8\alpha/9\pi)\\&+2\langle S^2-2\rangle(1-\ln 2)\}.\end{aligned}\quad(5.25)$$

VI. SUMMARY

The dependence of the 1^1S and 1^3S states in positronium on the spin of the system is obtained by the addition of Eqs. (4.16), (4.17), and (5.25):

$$\begin{aligned}\Delta E=&(2\pi\alpha/m^2)|\,\varphi_0(0)\,|^2\{\tfrac{1}{3}\langle\boldsymbol{\sigma}^1\cdot\boldsymbol{\sigma}^2\rangle[1-\tfrac{1}{2}\alpha/\pi]\\&+\tfrac{1}{2}\langle S^2\rangle[1-(26/9+2\ln 2)\alpha/\pi]\}.\end{aligned}$$

By taking the difference of the value of these operators in the singlet and triplet states, one arrives at the hyperfine splitting

$$\begin{aligned}\Delta W_{ts}&=(2\pi\alpha/m^2)|\,\varphi_0(0)\,|^2\{7/3-(32/9+2\ln 2)\alpha/\pi\}\\&=\tfrac{1}{2}\alpha^2\,\mathrm{Ry}_\infty\{7/3-(32/9+2\ln 2)\alpha/\pi\}\\&=2.0337\times10^5\ \mathrm{Mc/sec}.\end{aligned}$$

[17] J. A. Wheller, Ann. N. Y. Acad. Sci. 48, 219 (1946).

The singlet state is the lower one. It can be seen that most of the rather large negative electrodynamic correction comes from the virtual annihilation interaction.

When the experiment of Deutsch and Brown[4] is interpreted on the basis of a Zeeman effect that depends on the total magnetic moment $(e\hbar/2mc)(1+\alpha/2\pi)$ of each particle, the value of the separation obtained by them is[5]

$$\Delta W_{ts}=(2.035\pm0.003)10^5 \text{ Mc/sec.}$$

Theory and experiment are thus in satisfactory agreement.

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APPENDIX

The operator $[F^-(13)F^+(24)]^{-1}=G^-(13)G^+(24)$, the noninteracting two-particle Green's function, and its Fourier transforms appear so frequently that this appendix will be devoted to a discussion of some of its properties.

In connection with the second-order effect of the virtual annihilation, there appears the tensor

$$(C^{-1}\gamma_i)[F_{KC}(0,0)]^{-1}(\gamma_j C)$$
$$=\int d^4X' e^{-iK(X-X')}(C^{-1}\gamma_i)_{\alpha\alpha'}G_{\alpha'\beta'}{}^-(X,X')$$
$$\times G_{\alpha\beta}{}^+(X,X')(\gamma_j C)_{\beta'\beta}=\int d^4X' e^{-iK(X-X')}$$
$$\times\mathrm{Tr}[\gamma_i G^-(X,X')\gamma_j G^-(X',X)], \quad \text{(A.1)}$$

by Eq. (2.5). This is, however, precisely the quantity that appears in the vacuum polarization tensor.[12] It is equal to

$$-\frac{i}{(4\pi)^2}(\delta_{ij}(K^C)^2-K_i{}^C K_j{}^C)$$
$$\times\left[2A+\int_0^1 dV\frac{V^2(1-\frac{1}{3}V^2)(K^C)^2}{m^2+\frac{1}{4}(K^C)^2(1-V^2)}\right]. \quad \text{(A.2)}$$

In the frame where $K_i{}^C=0$, $(K^C)^2\cong-4m^2$, the tensor becomes

$$\frac{im^2}{\pi\alpha}\delta_{ij}\left(\frac{\alpha}{2\pi}A-\frac{8}{9}\frac{\alpha}{\pi}\right). \quad \text{(A.3)}$$

The center-of-mass transform of the noninteracting Green's function appears in the integral equation (3.10). Its Fourier representation is

$$[F_{KC}(x,x')]^{-1}=\frac{1}{(2\pi)^4}\int d^4k e^{ik(x-x')}$$
$$\times\frac{[m-\gamma^1(\frac{1}{2}K^C+k)][m-\gamma^2(\frac{1}{2}K^C-k)]}{[E^2-(\frac{1}{2}K_0{}^C+k_0)^2][E^2-(\frac{1}{2}K_0{}^C-k_0)^2]}, \quad \text{(A.4)}$$

when the center of mass is at rest. The quantity E^2 is defined by

$$E^2=k^2+m^2-i\epsilon, \quad \epsilon>0, \quad \text{(A.5)}$$

since Eq. (A.4) represents the noninteracting two-particle Green's function for outgoing waves. The integration over the fourth component of the momentum can be carried out with the help of the prescription Eq. (A.5). It gives the explicit function of the relative time coordinates,

$$[F_{KC}(x,x')]^{-1}=i(2\pi)^{-3}\int d\mathbf{k}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}$$
$$\times(k^2+\tfrac{1}{4}\alpha^2m^2)F_k(t-t'), \quad \text{(A.6)}$$

where

$$F_k(t)=\frac{m}{2E}[e^{-i(E-m)|t|}+e^{-i(E+m)|t|}]$$
$$\times\left[\left(1+\frac{\boldsymbol{\alpha}^1\cdot\mathbf{k}}{2m}\right)\left(1-\frac{\boldsymbol{\alpha}^2\cdot\mathbf{k}}{2m}\right)+\frac{k^2}{4m^2}\right]$$
$$+\tfrac{1}{2}[e^{-i(E-m)|t|}-e^{-i(E+m)|t|}]$$
$$\times\left[\left(1+\frac{\boldsymbol{\alpha}^1\cdot\mathbf{k}}{2m}\right)\left(1-\frac{\boldsymbol{\alpha}^2\cdot\mathbf{k}}{2m}\right)\right.$$
$$\left.-\frac{k^2}{4m^2}\left(1+\frac{t}{|t|}\frac{\boldsymbol{\alpha}^1\cdot\mathbf{k}-\boldsymbol{\alpha}^2\cdot\mathbf{k}}{E}\right)\right], \quad \text{(A.7)}$$

and the total energy of the $1S$ state has been inserted,

$$K_0{}^C=2m-\tfrac{1}{2}\alpha^2m. \quad \text{(A.8)}$$

The wave function derived from Eq. (3.11) with the help of the operator just obtained is

$$\varphi_C(x)=(2\alpha/(2\pi)^2)\int d\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}}m$$
$$\times(k^2+\tfrac{1}{4}\alpha^2m^2)^{-2}F_k(t)\,\varphi_0(0). \quad \text{(A.9)}$$