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[10]For the integration over r_1 in Eq. (16), we made use of Eq. (18) given in Ref. 9, p. 197. Then to integrate over r_2 we used Eq. (10) given in Ref. 9, p. 215. Finally we used the integral representation of the Appell function [see Ref. 8, p. 231, Eq. (5)]. It may be noted that the same order of integration in the two-photon radial matrix elements has been used in Ref. 3, where one can be referred for the details.
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PHYSICAL REVIEW A VOLUME 8, NUMBER 2 AUGUST 1973

Higher-Order Relativistic Contributions to the Combined Zeeman and Motional Stark Effects in Positronium*

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(Received 30 January 1973)

A calculation of higher-order relativistic contributions to the combined Zeeman and motional Stark effects in positronium is presented. These contributions are necessary for the determination of the fine-structure interval in the ground state from the Zeeman effect and may be important in future experiments on the first excited states of positronium. The contributions to the g_J factors have been calculated to order α^2 for all the S states and for the $2P$ states. The energy levels and the higher-order corrections to the motional Stark effect in the first excited state are also presented. Relativistic contributions are obtained from the matrix elements of a Hamiltonian containing the Breit interaction, a Pauli Hamiltonian, and the virtual annihilation interaction. For all nS states the relativistic contributions to the Zeeman effect may be accounted for by the replacement of g_e by $g_e(1 - 5\alpha^2/24n^2 - T/2mc^2)$, where T is the kinetic energy of the atom and g_e is the gyromagnetic ratio of the free electron.

I. INTRODUCTION

Higher-order contributions to the combined Zeeman and motional Stark effects in positronium are needed for the determination of the fine-structure interval $\Delta\nu$ in the ground state from the Zeeman effect and may be important in future experiments on the first excited state. The measurement of $\Delta\nu$ is an important test of quantum electrodynamics and of the Bethe–Salpeter equation for the bound-state lepton-antilepton system.[1,2] In this paper the contributions to the Zeeman effect are calculated to order $\alpha^2\mu_B H$ for all the S states and for the $2P$ states of positronium. Also the energy levels and the higher-order corrections to the motional Stark effect in the first excited state are computed.[3–6]

The fine-structure interval in the ground state of positronium has been calculated to terms of order $\alpha^4\ln\alpha^{-1}\mathcal{R}$. The $\alpha^2\mathcal{R}$ contributions to $\Delta\nu$ were first determined by Pirenne,[7] Berestetski,[8,9] and Ferrell.[10] Karplus and Klein[11] have computed terms of order $\alpha^3\mathcal{R}$ that contribute to $\Delta\nu$. The $\alpha^4\ln\alpha^{-1}\mathcal{R}$ contributions to $\Delta\nu$ were calculated recently by Fulton, Owen, and Repko.[12] In the first excited state of positronium the fine-structure intervals have been calculated to order $\alpha^3\mathcal{R}$. Fulton and Martin[13] have computed all the contributions of order $\alpha^3\mathcal{R}$ to the energy levels of a bound two-fermion system. These values are to be added to the $\alpha^2\mathcal{R}$ contributions calculated by Ferrell.[10]

The relativistic contributions to the Zeeman and motional Stark effects are obtained from matrix elements of the positronium Hamiltonian $\mathcal{H}$. The three terms in $\mathcal{H}$ are the Breit interaction,[14] a Pauli Hamiltonian[15] introducing the anomalous magnetic moments of the electron and positron, and the virtual annihilation interaction.[11] A transformation of two-body equations[16] is used to decouple the positive and negative energy states. A unitary transformation[17] is used to reduce the dependence of the positronium Hamiltonian on the center-of-mass coordinate.

Margenau,[18] Lamb,[19] and Breit[20] have calculated

corrections to the g factors of hydrogenlike atoms to order α^2. The g factor is modified by a change in the magnetic moment of the electron owing to its motion in a potential[18] and by the modification of the potential itself by the presence of an external magnetic field.[19] Higher-order contributions to the g factor of hydrogen, of order $(Z\alpha^2)m/M$, $\alpha(Z\alpha)^2$, and $\alpha(Z\alpha)^2m/M$, where M is the mass of the hydrogen atom, have been calculated by Grotch and Hegstrom.[21]

Grotch and Kashuba[22] have recently calculated the Zeeman effect in positronium.

In Sec. II we give the transformations to decouple a two-body Hamiltonian into positive and negative energy states, and to reduce the dependence of a Hamiltonian on the center-of-mass coordinate. Section III presents the terms in the positronium Hamiltonian and $\mathcal{H}$ is transformed using the transformations in Sec. II. In Sec. IV a Zeeman-effect Hamiltonian and a motional-Stark-effect Hamiltonian are obtained from the transformed Hamiltonian and the relativistic contributions to these effects are computed. Section V is a brief summary of the results of our paper.

A brief description of our calculation of the g factor in the ground state of positronium has been presented,[6] and brief reports of our other calculations have also been given.[3,5]

II. TRANSFORMATIONS

A. Foldy–Wouthuysen Transformation

In a two-particle system the wave function consists of 16 components and the Hamiltonian mixes these components. For a single-particle equation–the Dirac equation–one has four components in the wave function. In order to reduce these problems into a tractable form one may use a transformation that decouples the large components from the small components. The Foldy-Wouthuysen transormation[23] separates the positive and negative energy states for the Dirac equation and leaves the resultant Hamiltonian in Hermitian form. The two-body case is discussed in Sec. II B.

Dirac matrices which couple large and small components are called odd $\mathcal{O}$, and matrices which do not couple large and small components are called even $\mathcal{E}$. The odd matrices are $\vec{\alpha}$, $\beta\vec{\alpha}$, γ^5, and $\beta\gamma^5$ and the even matrices are 1, β, $\vec{\sigma}$, and $\beta\vec{\sigma}$. The Dirac Hamiltonian for an electron in an external field may be written (with $c = 1$)

$$H = \beta m + \mathcal{O} + \mathcal{E}, \tag{2.1}$$

where

$$\mathcal{O} = \vec{\alpha}\cdot[\vec{p} - e\vec{A}(\vec{r})] \quad \text{and} \quad \mathcal{E} = e\Phi(\vec{r}). \tag{2.2}$$

$\vec{A}(\vec{r})$ and $\Phi(\vec{r})$ are the vector and scalar potentials, respectively. The Dirac equation can be exactly separated into two two-component equations describing positive and negative energy states only in the absence of external fields.

In the presence of an external electromagnetic interaction one must perform a set of transformations to obtain a Hamiltonian which is a series in powers of m^{-1}, where m is the particle mass. (The expansion parameter may also be considered as c^{-1}.) We want to introduce a series of canonical transformations

$$\Psi' = e^{iS}\Psi, \tag{2.3}$$

where S is an Hermitian operator. The effect of S is to eliminate the odd term in Eq. (2.1) to the required order in m^{-1}.

B. Two-Body Reduction Techniques

A two-body wave equation acts on a 16-component wave function. Chraplyvy[24] developed a method analogous to the Foldy-Wouthuysen transformation for a two-particle equation. We may write the two-body wave equation as

$$\mathcal{H} = \beta_1 m_1 + \beta_2 m_2 + (\mathcal{E}\mathcal{E}) + (\mathcal{E}\mathcal{O}) + (\mathcal{O}\mathcal{E}) + (\mathcal{O}\mathcal{O}), \tag{2.4}$$

where $(\mathcal{E}\mathcal{E})$ stands for even-even (even in both particles 1 and 2), $(\mathcal{E}\mathcal{O})$ stands for even-odd (even in particle 1 and odd in particle 2), $(\mathcal{O}\mathcal{E})$ stands for odd-even (odd in particle 1 and even in particle 2), and $(\mathcal{O}\mathcal{O})$ stands for odd-odd (odd in particles 1 and 2). The $(\mathcal{E}\mathcal{E})$ matrices include β_1, β_2, $\vec{\sigma}_1$, and $\vec{\sigma}_2$. The $(\mathcal{E}\mathcal{O})$ matrices include $\vec{\alpha}_2$ and γ_2^5. The $(\mathcal{O}\mathcal{E})$ matrices include $\vec{\alpha}_1$ and γ_1^5. The $(\mathcal{O}\mathcal{O})$ matrices include $\vec{\alpha}_1\cdot\vec{\alpha}_2$ and $\gamma_1^5\vec{\sigma}_2$. Chraplyvy developed a transformation that separates the sixteen components of the wave function into four sets of four components. The 16-component spinor is denoted by Ψ_{kK} with $(k, K = 1, 2, 3, 4)$. k signifies the first particle and K the second particle. Chraplyvy classified the components as upper-upper ψ_{uU}, upper-lower ψ_{uL}, lower-upper ψ_{lU}, and lower-lower ψ_{lL} with u, $U = 1, 2$ and $l, L = 3, 4$. The transformation separates the uU, uL, lU, and lL components into separate equations.

In order to remove from the Hamiltonian Eq. (2.4) an $(\mathcal{O}\mathcal{E})$ term t_{oe} the operator S introduced in Eq. (2.3) must contain

$$S_{oe} = \frac{\beta_1}{2m_1}\, t_{oe}\,. \tag{2.5}$$

To remove an $(\mathcal{E}\mathcal{O})$ term t_{eo} the operator S must contain

$$S_{eo} = \frac{\beta_2}{2m_2}\, t_{eo}\ ; \tag{2.6}$$

and to eliminate an $(\mathcal{O}\mathcal{O})$ term t_{oo} we must include

$$S_{oo}=\frac{\beta_1 m_1-\beta_2 m_2}{2(m_1^2-m_2^2)}\,t_{oo}\,. \tag{2.7}$$

This transformation was used to reduce the Breit equation for hydrogen by Grotch and Hegstrom.[21] Brodsky and Primack[25] have shown that the interaction of a composite bound system with an external electromagnetic field can be approximated by a sum of the relativistic Hamiltonians for each particle.

But this transformation[24] is not valid for positronium, because of the equal mass of its constituent particles: $m_1=m_2$. Chraplyvy concluded that in the case of particles of equal mass there exists no finite transformation that changes the Hamiltonian into an $(\mathcal{E}\mathcal{E})$ operator. However, we do not need to separate the wave function into four sets of four components. One would like to isolate the uU components without necessarily separating the uL, lU, and lL terms.

In another paper Chraplyvy[16] developed a second transformation valid for particles of equal mass. Thus instead of the expressions given in Eqs. (2.5)–(2.7), Chraplyvy found

$$S_{eo}=\frac{\beta_2}{2m_2}\left\{t_{eo}+\frac{1-\beta_1}{2}T_{eo}\right\}\,, \tag{2.8}$$

$$S_{oe}=\frac{\beta_1}{2m_1}\left\{t_{oe}+\frac{1-\beta_2}{2}T_{oe}\right\}\,, \tag{2.9}$$

$$S_{oo}=\frac{1}{4}\left\{\frac{\beta_1+\beta_2}{m_1+m_2}\,t_{oo}+\frac{\beta_1-\beta_2}{m_1-m_2}T_{oo}\right\}$$

$$\text{for } m_1\neq m_2, \tag{2.10}$$

$$S'_{oo}=\frac{1}{8m}\{(\beta_1+\beta_2)t_{oo}+(1-\beta_1\beta_2)T'_{oo}\}$$

$$\text{for } m_1=m_2. \tag{2.11}$$

The "least-change" transformation is obtained with $T_{eo}=-t_{eo}$, $T_{oe}=-t_{oe}$, and $T_{oo}=T'_{oo}=0$. The application of this canonical transformation yields a reduced Hamiltonian $\mathcal{H}_r$ which consists of 19 terms:

$$\mathcal{H}_r=\sum_{i=1}^{19}\mathcal{H}(i)\,, \tag{2.12}$$

$$\mathcal{H}(1)=\beta_1 m_1, \tag{2.13}$$

$$\mathcal{H}(2)=\beta_2 m_2, \tag{2.14}$$

$$\mathcal{H}(3)=(\mathcal{E}\mathcal{E})\,, \tag{2.15}$$

$$\mathcal{H}(4)=\frac{\beta_1(1+\beta_2)}{4m_1}(\mathcal{O}\mathcal{E})^2\,, \tag{2.16}$$

$$\mathcal{H}(5)=\frac{\beta_2(1+\beta_1)}{4m_2}(\mathcal{E}\mathcal{O})^2\,, \tag{2.17}$$

$$\mathcal{H}(6)=\frac{1+\beta_2}{16m_1^2}[[(\mathcal{O}\mathcal{E}),\ (\mathcal{E}\mathcal{E})],\ (\mathcal{O}\mathcal{E})], \tag{2.18}$$

$$\mathcal{H}(7)=\frac{1+\beta_1}{16m_2^2}[[(\mathcal{E}\mathcal{O}),\ (\mathcal{E}\mathcal{E})],\ (\mathcal{E}\mathcal{O})], \tag{2.19}$$

$$\mathcal{H}(8)=-\frac{\beta_1(1+\beta_2)}{16m_1^3}(\mathcal{O}\mathcal{E})^4\,, \tag{2.20}$$

$$\mathcal{H}(9)=-\frac{\beta_2(1+\beta_1)}{16m_2^3}(\mathcal{E}\mathcal{O})^4\,, \tag{2.21}$$

$$\mathcal{H}(10)=\frac{\beta_1\beta_2+\beta_1+2\beta_2}{32m_1m_2}[[(\mathcal{O}\mathcal{E}),\ (\mathcal{O}\mathcal{O})]_+,\ (\mathcal{E}\mathcal{O})]_+\,, \tag{2.22}$$

$$\mathcal{H}(11)=\frac{\beta_1\beta_2+\beta_2+2\beta_1}{32m_1m_2}[[(\mathcal{E}\mathcal{O}),\ (\mathcal{O}\mathcal{O})]_+,\ (\mathcal{O}\mathcal{E})]_+, \tag{2.23}$$

$$\mathcal{H}(12)=\frac{1-\beta_2}{32m_1m_2}[[(\mathcal{O}\mathcal{E}),\ (\mathcal{O}\mathcal{O})],\ (\mathcal{E}\mathcal{O})], \tag{2.24}$$

$$\mathcal{H}(13)=\frac{1-\beta_1}{32m_1m_2}[[(\mathcal{E}\mathcal{O}),\ (\mathcal{O}\mathcal{O})],\ (\mathcal{O}\mathcal{E})], \tag{2.25}$$

$$\mathcal{H}(14)=\frac{\beta_1+\beta_2}{4(m_1+m_2)}(\mathcal{O}\mathcal{O})^2\,, \tag{2.26}$$

$$\mathcal{H}(15)=\frac{\beta_1+\beta_2}{16(m_1+m_2)m_1m_2}[(\mathcal{O}\mathcal{E}),\ (\mathcal{E}\mathcal{O})]^2\,, \tag{2.27}$$

$$\mathcal{H}(16)=\frac{-(1+\beta_1)(1+\beta_2)(\beta_1m_1+\beta_2m_2)}{64m_1^2m_2^2}\times[(\mathcal{O}\mathcal{E})^2,\ (\mathcal{E}\mathcal{O})^2]_+\,, \tag{2.28}$$

$$\mathcal{H}(17)=\frac{(1+\beta_1)(\beta_2+7)m_1+(1-\beta_2)(5\beta_1-3)m_2}{128m_1^2m_2^2}\times(\mathcal{E}\mathcal{O})(\mathcal{O}\mathcal{E})^2(\mathcal{E}\mathcal{O})\,, \tag{2.29}$$

$$\mathcal{H}(18)=\frac{(1+\beta_2)(\beta_1+7)m_2+(1-\beta_1)(5\beta_2-3)m_1}{128m_1^2m_2^2}\times(\mathcal{O}\mathcal{E})(\mathcal{E}\mathcal{O})^2(\mathcal{O}\mathcal{E})\,, \tag{2.30}$$

$$\mathcal{H}(19)=\frac{(1+\beta_1\beta_2)(m_1-m_2)}{16(m_1+m_2)m_1m_2}[[(\mathcal{E}\mathcal{O}),\ (\mathcal{O}\mathcal{E})],\ (\mathcal{O}\mathcal{O})]. \tag{2.31}$$

This transformation can be used for positronium. For positive energy states $\beta_1=\beta_2=1$ and both transformations of Chraplyvy yield the same Hamiltonian for positronium. Before we calculate the results of this new transformation we must discuss the problem of motion of the positronium atom.

C. Motion of the Atom

Positronium atoms are of course not formed at rest.[26,27] A system moving in a magnetic field will experience a motional electric field. This Stark effect couples S and P states. The motional Stark

effect does not appreciably perturb the ground state of positronium but does affect the excited states.

The coordinates $\vec{r}_1$ and $\vec{r}_2$ are written in terms of the relative coordinate $\vec{r}$ and the center-of-mass coordinate $\vec{R}$,

$$\vec{r}_1=\vec{R}+\frac{m_2}{m_1+m_2}\vec{r}\,, \tag{2.32}$$

$$\vec{r}_2=\vec{R}-\frac{m_1}{m_1+m_2}\vec{r}\,. \tag{2.33}$$

The momenta $\vec{p}_1$ and $\vec{p}_2$ are written in terms of the relative momentum $\vec{p}$ and the center-of-mass momentum $\vec{P}$,

$$\vec{p}_1=\vec{p}+\frac{m_1}{m_1+m_2}\vec{P}\,, \tag{2.34}$$

$$\vec{p}_2=-\vec{p}+\frac{m_2}{m_1+m_2}\vec{P}\,. \tag{2.35}$$

Lamb[17] considered the effects of a motional electric field on hydrogen. The relevant terms are

$$H'_{\rm II}=-\frac{e_1}{m_1}\vec{A}_1\cdot\vec{p}_1-\frac{e_2}{m_2}\vec{A}_2\cdot\vec{p}_2. \tag{2.36}$$

After a transformation to relative and center-of-mass coordinates with $e_1=-e_2$,

$$H'_{\rm III}=-\frac{1}{2}\frac{e_1}{m_r}\vec{H}\cdot\vec{R}\times\vec{p}-\frac{1}{2}\frac{e_1}{m_t}\vec{H}\cdot\vec{r}\times\vec{P}+\frac{1}{2}e_1\frac{m_1-m_2}{m_1m_2}\vec{H}\cdot\vec{L}\,, \tag{2.37}$$

in which m_r is the reduced mass, m_t is the total mass and $\vec{L}=\vec{r}\times\vec{p}$. If $\vec{V}=\vec{P}/m_t$ is the velocity of the atom and $\vec{A}(\vec{R})=\frac{1}{2}\vec{H}\times\vec{R}$, then

$$H'_{\rm III}=\frac{-e_1}{m_r}\vec{A}(\vec{R})\cdot\vec{p}-\tfrac{1}{2}e_1(\vec{V}\times\vec{H}\cdot\vec{r})+\tfrac{1}{2}e_1\left(\frac{m_1-m_2}{m_1m_2}\right)\vec{H}\cdot\vec{L}\,. \tag{2.38}$$

The second term in Eq. (2.38) is half the usual Stark effect. The first term in Eq. (2.38) can be considered to be equivalent to a gauge transformation. A unitary transformation of the wave function

$$\Psi_1=\Psi\exp[(e_1i/2\hbar)(\vec{H}\times\vec{R}\cdot\vec{r})] \tag{2.39}$$

when acted on by the operator $\vec{p}^2/2m_r$ gives a term which cancels out the first term in Eq. (2.38), and the operator $\vec{P}^2/2m_t$ gives a term which doubles the second term in Eq. (2.38), and thus yields the expected motional Stark effect.

A method similar to Eq. (2.39) was used by Grotch and Hegstrom.[21] The momentum of the positronium atom may not be set equal to zero at the outset of the calculation. This follows because the center-of-mass coordinate $\vec{R}$ and the center-of-mass momentum $\vec{P}$ do not commute. The Hamiltonian depends on $\vec{R}$ because of the interaction with the external magnetic field.

We may use a general unitary transformation U which eliminates $\vec{R}$ in $\mathcal{H}$ for a neutral system such as positronium and hydrogen and reduces the dependence of $\mathcal{H}$ on $\vec{R}$ for a charged system:

$$U=\exp(i\tfrac{1}{2}e_1\vec{r}_1\cdot\vec{H}\times\vec{R})\exp(i\tfrac{1}{2}Ze_2\vec{r}_2\cdot\vec{H}\times\vec{R}), \tag{2.40}$$

where e_1 is the charge of particle 1 and Ze_2 is the charge of particle 2. From Eqs. (2.32) and (2.33) we obtain

$$U=\exp\left[\frac{i}{2}\left(\frac{e_1m_2-Ze_2m_1}{m_1+m_2}\right)\vec{r}\cdot\vec{H}\times\vec{R}\right]. \tag{2.41}$$

If Ψ is the eigenfunction of a Hamiltonian H under consideration, then $\Psi'=U^{-1}\Psi$ will be an eigenfunction of the transformed Hamiltonian $H'=U^{-1}HU$. The transformation U only affects momentum variables and does not affect position variables:

$$U^{-1}\vec{p}_1U=\vec{p}_1+\frac{e_1m_2-Ze_2m_1}{m_1+m_2}\vec{A}(\vec{r}_2), \tag{2.42}$$

$$U^{-1}\vec{p}_2U=\vec{p}_2-\frac{e_1m_2-Ze_2m_1}{m_1+m_2}\vec{A}(\vec{r}_1)\,. \tag{2.43}$$

Then we obtain

$$U^{-1}[\vec{p}_1-e_1\vec{A}(\vec{r}_1)]\,U=\vec{p}_1-e_1\vec{A}(\vec{r})-\frac{(Ze_2+e_1)m_1}{m_1+m_2}\vec{A}(\vec{r}_2)\,, \tag{2.44}$$

$$U^{-1}[\vec{p}_2-Ze_2\vec{A}(\vec{r}_2)]\,U=\vec{p}_2+Ze_2\vec{A}(\vec{r})-\frac{(Ze_2+e_1)m_2}{m_1+m_2}\vec{A}(\vec{r}_1), \tag{2.45}$$

in which $\vec{A}(\vec{r})=\vec{A}(\vec{r}_1)-\vec{A}(\vec{r}_2)$. Thus if $Ze_2+e_1=0$, the case of a neutral system, the transformed mechanical momenta of Eqs. (2.44) and (2.45) depend only on the relative coordinate $\vec{r}$ and not on $\vec{R}$. Thus if $Ze_2+e_1=0$, the case of a neutral system, the transformed mechanical momenta of Eqs. (2.44) and (2.45) depend only on the relative coordinate $\vec{r}$ and not on $\vec{R}$.

III. POSITRONIUM HAMILTONIAN

Breit developed an approximately relativistic two-particle equation[28–31] which may be written

$$(\mathcal{H}_1+\mathcal{H}_2+e^2/r+B)u=Eu\,, \tag{3.1}$$

where $\mathcal{H}_i$ are the usual Dirac Hamiltonians for a single particle,

$$\mathcal{H}_i = \beta_i m - e\Phi(\vec{r}_i) + \vec{\alpha}_i \cdot [\vec{p}_i + e\vec{A}(\vec{r}_i)]; \quad (3.2)$$

B is the Breit interaction

$$B = -\frac{e^2}{2r}\left(\vec{\alpha}_1 \cdot \vec{\alpha}_2 + \frac{\vec{\alpha}_1 \cdot \vec{r}\,\vec{\alpha}_2 \cdot \vec{r}}{r^2}\right), \quad (3.3)$$

$\vec{r}$ is the interparticle distance, and u is a 16-component spinor.

The Breit interaction includes the classical effects of retardation and the effects of the electron spin in the interaction of two electrons.[14] From a field-theoretic viewpoint the Breit interaction includes the lowest-order effects of a single transverse photon exchanged between the two electrons. Because this equation is only an approximation and neglects Dirac's hole theory, Breit[31] demonstrated that B is to be treated only in first-order perturbation theory to obtain correct energies to the order of $\alpha^2\mathcal{R}$. The terms that appear from the reduction of the Breit Hamiltonian using Eq. (2.26) should not be included in the reduced Hamiltonian.[31]

The two-body quantum electrodynamic bound-state equation was developed with the use of the relativistic S-matrix formalism of Feynman[32] by Bethe and Salpeter,[33,34] Schwinger,[35] and Gell-Mann and Low.[36] The Bethe–Salpeter equation is the starting point for the calculation of the fine structure in the first excited state of positronium. Fulton and Martin[13] computed all the contributions of order $\alpha^3\mathcal{R}$ to the energy levels of a bound two-fermion system. These values are added to the $\alpha^2\mathcal{R}$ terms calculated by Ferrell.[10] These results are presented in Table I and are used as the zero-field spectrum of $n = 2$ positronium.

To calculate the Zeeman and Stark effects in positronium to relative order $\alpha^2\mu_B H$, the Breit equation can be used. It has the advantage of reducing to the Dirac equation in the limit of infinite nuclear mass. This is in contrast to the limit of the Bethe–Salpeter equation in the ladder approximation.[21]

We take the Breit equation, without a scalar potential, for two particles with charge and mass e_1, m_1 and e_2, m_2, respectively:

$$\mathcal{H}_B = \vec{\alpha}_1 \cdot [\vec{p}_1 - e_1\vec{A}(\vec{r}_1)] + \beta_1 m_1 + \vec{\alpha}_2 \cdot [\vec{p}_2 - Ze_2\vec{A}(\vec{r}_2)] + \beta_2 m_2 + \frac{Ze_1e_2}{r}\left(1 - \frac{\vec{\alpha}_1 \cdot \vec{\alpha}_2}{2} - \frac{\vec{\alpha}_1 \cdot \vec{r}\,\vec{\alpha}_2 \cdot \vec{r}}{2r^2}\right). \quad (3.4)$$

The unitary transformation U only affects the momentum operators. Using the results of Eqs. (2.42) and (2.43) we obtain

$$\mathcal{H}'_B = U^{-1}\mathcal{H}_B U, \quad (3.5)$$

$$\mathcal{H}'_B = \vec{\alpha}_1 \cdot \left[\vec{p}_1 - e_1\vec{A}(\vec{r}) - \frac{(Ze_2 + e_1)m_1}{m_1 + m_2}\vec{A}(\vec{r}_2)\right] + \vec{\alpha}_2 \cdot \left[\vec{p}_2 + Ze_2\vec{A}(\vec{r}) - \frac{(Ze_2 + e_1)m_2}{m_1 + m_2}\vec{A}(\vec{r}_1)\right] + \beta_1 m_1 + \beta_2 m_2 + \frac{Ze_1e_2}{r} \times \left(1 - \frac{\vec{\alpha}_1 \cdot \vec{\alpha}_2}{2} - \frac{\vec{\alpha}_1 \cdot \vec{r}\,\vec{\alpha}_2 \cdot \vec{r}}{2r^2}\right). \quad (3.6)$$

Both the electron and positron possess an anomalous magnetic moment. The most recent calculation[37] of the sixth-order anomalous magnetic moment of the electron and positron yields the total anomaly

$$a_e^{\text{th}} = 0.5(\alpha/\pi) - 0.328\,48(\alpha/\pi)^2 + (1.29 \pm 0.06)(\alpha/\pi)^3. \quad (3.7)$$

TABLE I. Additions to $n = 2$ nonrelativistic energy levels in positronium.

	$\alpha^2\mathcal{R}$ (MHz)	$\alpha^2\mathcal{R}$ (MHz)	Total (MHz)	
$2\,^1S_0$	−18 135	357	−17 778	E_1
$2\,^3S_1$	7 413	232	7 645	E_2
$2\,^1P_1$	−3 536	−3	−3 539	E_3
$2\,^3P_2$	−981	1	−980	E_6
$2\,^3P_1$	−5 360	−5	−5 365	E_5
$2\,^3P_0$	−10 835	−16	−10 851	E_4

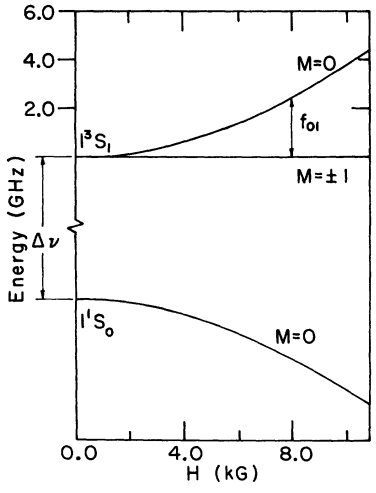

FIG. 1. Fine-structure energy levels in the ground state of positronium as a function of magnetic field.

The corrections due to the lowest-order radiative processes are included by the use of a Pauli Hamiltonian[15,21]:

$$\mathcal{H}_P = -a_1\frac{e_1}{2m_1}(\beta_1\vec{\sigma}_1\cdot\vec{H}_1 - i\beta_1\vec{\alpha}_1\cdot\vec{E}_1) - a_2\frac{Ze_2}{2m_2}(\beta_2\vec{\sigma}_2\cdot\vec{H}_2 - i\beta_2\alpha_2\cdot\vec{E}_2) - \beta_1\beta_2\frac{Ze_1e_2}{4m_1m_2}a_1a_2\left(\frac{\vec{\sigma}_1\cdot\vec{\sigma}_2}{r^3} - 3\frac{\vec{\sigma}_1\cdot\vec{r}\vec{\sigma}_2\cdot\vec{r}}{r^5} - \frac{8\pi}{3}\vec{\sigma}_1\cdot\vec{\sigma}_2\delta(\vec{r})\right), \quad (3.8)$$

where a_1 and a_2 are the anomalous magnetic moments of particles 1 and 2, respectively, and the fields[38] are given by

$$\vec{H}_1 = \vec{H} + Ze_2\frac{\vec{\alpha}_2\times\vec{r}}{r^3}, \qquad \vec{E}_1 = Ze_2\frac{\vec{r}}{r^3},$$
$$\vec{H}_2 = \vec{H} - e_1\frac{\vec{\alpha}_1\times\vec{r}}{r^3}, \qquad \vec{E}_2 = -e_1\frac{\vec{r}}{r^3}. \quad (3.9)$$

Thus $\mathcal{H}_P$ may be written as[39]

$$\mathcal{H}_P = -a_1\frac{e_1}{2m_1}\left(\beta_1\vec{\sigma}_1\cdot\vec{H} + Ze_2\beta_1\vec{\sigma}_1\cdot\frac{\vec{\alpha}_2\times\vec{r}}{r^3} - i\beta_1Ze_2\vec{\alpha}_1\cdot\frac{\vec{r}}{r^3}\right) - a_2\frac{Ze_2}{2m_2}\left(\beta_2\vec{\sigma}_2\cdot\vec{H} - e_1\beta_2\vec{\sigma}_2\cdot\frac{\vec{\alpha}_1\times\vec{r}}{r^3} + i\beta_2e_1\vec{\alpha}_2\cdot\frac{\vec{r}}{r^3}\right) - \beta_1\beta_2\frac{Ze_1e_2}{4m_1m_2}a_1a_2\left[\frac{\vec{\sigma}_1\cdot\vec{\sigma}_2}{r^3} - 3\frac{\vec{\sigma}_1\cdot\vec{r}\vec{\sigma}_2\cdot\vec{r}}{r^5} - \frac{8\pi}{3}\vec{\sigma}_1\cdot\vec{\sigma}_2\delta(\vec{r})\right]. \quad (3.10)$$

Radiative corrections to the Zeeman effect appear in Eq. (3.10). Because no momentum-dependent variables appear in $\mathcal{H}_P$ the unitary transformation, Eq. (2.41), leaves $\mathcal{H}_P$ unchanged:

$$\mathcal{H}_P' = U^{-1}\mathcal{H}_P U = \mathcal{H}_P. \quad (3.11)$$

The last term in the positronium Hamiltonian is the first-order single-quantum virtual-annihila-

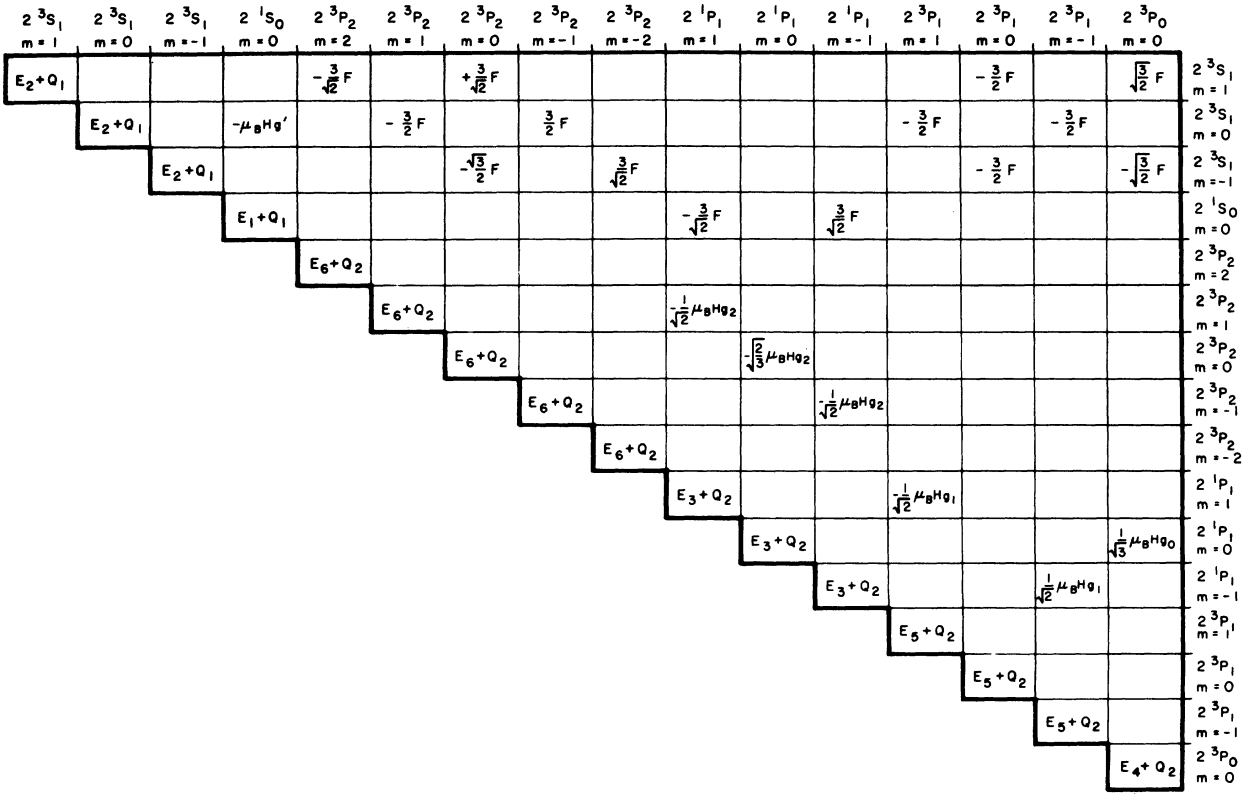

FIG. 2. Secular determinant for the 16 substates of the first excited state of positronium. All empty elements are zero.

tion exchange interaction[11]

$$U_A(\vec{r}_1,\vec{r}_2)=\frac{\pi e_1e_2}{m_1m_2}(\gamma_jC)\delta(\vec{r}_1)\delta(\vec{r}_2)(C^{-1}\gamma_j)\,, \quad (3.12)$$

where the charge-conjugation operator $C=\gamma_0\gamma_2=C^{-1}$ and $\gamma_j=\beta\alpha_j$. The γ_jC are the pair-creation matrices and $C^{-1}\gamma_j$ are the pair-annihilation matrices.

U_A is an even-even operator. The reduced form is[39]

$$U_{A_{\rm red}}=-\frac{\pi e_1e_2}{m_1m_2}\left(\tfrac{3}{2}+\tfrac{1}{2}\vec{\sigma}_1\cdot\vec{\sigma}_2\right)\delta(\vec{r})\,. \quad (3.13)$$

The total transformed positronium Hamiltonian $\mathcal{H}'=U^{-1}\mathcal{H}U$ is formed from Eqs. (3.6), (3.10), and (3.12):

$$\mathcal{H}'=\mathcal{H}_B'+\mathcal{H}_P+U_A\,. \quad (3.14)$$

The Hamiltonian $\mathcal{H}'$ may be written in the form of Eq. (2.4):

$$(\mathcal{E}\mathcal{E})=\frac{Ze_1e_2}{r}-\frac{e_1}{2m_1}a_1\beta_1\vec{\sigma}_1\cdot\vec{H}-\frac{Ze_2}{2m_2}a_2\beta_2\vec{\sigma}_2\cdot\vec{H}-\beta_1\beta_2\frac{Ze_1e_2}{4m_1m_2}a_1a_2\times\left[\frac{\vec{\sigma}_1\cdot\vec{\sigma}_2}{r^3}-3\frac{\vec{\sigma}_1\cdot\vec{r}\vec{\sigma}_2\cdot\vec{r}}{r^5}-\frac{8\pi}{3}\vec{\sigma}_1\cdot\vec{\sigma}_2\delta(\vec{r})\right]+U_A(\vec{r}_1,\vec{r}_2)\,, \quad (3.15)$$

$$(\mathcal{O}\mathcal{E})=\vec{\alpha}_1\cdot\vec{\pi}_1+i\frac{Ze_1e_2}{2m_1}a_1\beta_1\vec{\alpha}_1\cdot\frac{\vec{r}}{r^3}+\frac{Ze_1e_2}{2m_2}a_2\beta_2\vec{\sigma}_2\cdot\vec{\alpha}_1\times\frac{\vec{r}}{r^3}\,, \quad (3.16)$$

$$(\mathcal{E}\mathcal{O})=\vec{\alpha}_2\cdot\vec{\pi}_2-i\frac{Ze_1e_2}{2m_2}a_2\beta_2\vec{\alpha}_2\cdot\frac{\vec{r}}{r^3}-\frac{Ze_1e_2}{2m_1}a_1\beta_1\vec{\sigma}_1\cdot\vec{\alpha}_2\times\frac{\vec{r}}{r^3}\,, \quad (3.17)$$

$$(\mathcal{O}\mathcal{O})=-\frac{Ze_1e_2}{2r}\left[\vec{\alpha}_1\cdot\vec{\alpha}_2+\frac{\vec{\alpha}_1\cdot\vec{r}\vec{\alpha}_2\cdot\vec{r}}{r^2}\right]\,, \quad (3.18)$$

where

$$\vec{\pi}_1=\vec{p}_1-e_1\vec{A}(\vec{r})-\frac{(Ze_2+e_1)m_1}{m_1+m_2}\vec{A}(\vec{r}_2) \quad (3.19)$$

and

$$\vec{\pi}_2=\vec{p}_2+Ze_2\vec{A}(\vec{r})-\frac{(Ze_2+e_1)m_2}{m_1+m_2}\vec{A}(\vec{r}_1)\,. \quad (3.20)$$

The second transformation of Chraplyvy[16] is used to reduce the positronium Hamiltonian $\mathcal{H}'$. We may reorganize the transformed Hamiltonian into

$$\mathcal{H}_r=\sum_{i=0}^{5}H_i\,, \quad (3.21)$$

where

$$H_0=\frac{\vec{\pi}_1^2}{2m_1}+\frac{\vec{\pi}_2^2}{2m_2}+\frac{Ze_1e_2}{r}+U_{A_{\rm red}}+m_1+m_2\,, \quad (3.22)$$

$$H_1=-\frac{\vec{\pi}_1^4}{8m_1^3}-\frac{\vec{\pi}_2^4}{8m_2^3}\,, \quad (3.23)$$

$$H_2=-\frac{Ze_1e_2}{4m_1^2}(1+2a_1)\vec{\sigma}_1\cdot\left(\frac{\vec{r}}{r^3}\times\vec{\pi}_1\right)+\frac{Ze_1e_2}{4m_2^2}(1+2a_2)\vec{\sigma}_2\cdot\left(\frac{\vec{r}}{r^3}\times\vec{\pi}_2\right)\,, \quad (3.24)$$

$$H_3=\frac{Ze_1e_2}{2m_1m_2}(1+a_1)\vec{\sigma}_1\cdot\left(\frac{\vec{r}}{r^3}\times\vec{\pi}_2\right)-\frac{Ze_1e_2}{2m_1m_2}(1+a_2)\vec{\sigma}_2\cdot\left(\frac{\vec{r}}{r^3}\times\vec{\pi}_1\right), \quad (3.25)$$

$$H_4=-\frac{e_1}{2m_1}\left[\vec{\sigma}_1\cdot\vec{H}\left(1-\frac{\vec{\pi}_1^2}{2m_1^2}\right)+a_1\left(\vec{\sigma}_1\cdot\vec{H}-\frac{\vec{\sigma}_1\cdot\vec{\pi}_1\vec{\pi}_1\cdot\vec{H}}{2m_1^2}\right)\right]-\frac{Ze_2}{2m_2}\left[\vec{\sigma}_2\cdot\vec{H}\left(1-\frac{\vec{\pi}_2^2}{2m_2^2}\right)+a_2\left(\vec{\sigma}_2\cdot\vec{H}-\frac{\vec{\sigma}_2\cdot\vec{\pi}_2\vec{\pi}_2\cdot\vec{H}}{2m_2^2}\right)\right]\,, \quad (3.26)$$

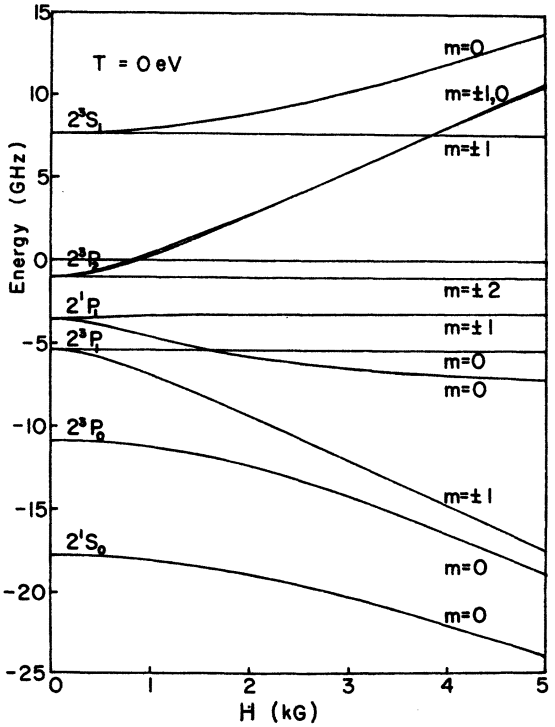

FIG. 3. Fine-structure energy levels in the $n=2$ state of positronium as a function of magnetic field with kinetic energy $T=0$ eV.

$$H_5 = -\frac{Ze_1e_2}{2m_1m_2}\ \frac{1}{r}\,\vec{\pi}_1\cdot\vec{\pi}_2 - \frac{Ze_1e_2}{2m_1m_2}\,\vec{r}\cdot\left(\frac{\vec{r}}{r^3}\cdot\vec{\pi}_1\right)\vec{\pi}_2\ . \tag{3.27}$$

H_0 contains the nonrelativistic Hamiltonian plus the virtual-annihilation interaction. H_1 presents relativistic mass-increase terms. H_2 contains spin-orbit and H_3 contains spin-other-orbit correction terms. H_4 gives the Zeeman effect and higher-order corrections. H_5 includes terms that may be written as relativistic corrections to the motional Stark effect.

The momenta $\vec{\pi}_i$ in Eqs. (3.19) and (3.20) can be transformed into center-of-mass and relative coordinates:

$$\vec{\pi}_1 = \vec{p} + \frac{m_1}{m_1+m_2}\vec{P} - \left[e_1 - (Ze_2+e_1)\left(\frac{m_1}{m_1+m_2}\right)^2\right]\vec{A}(\vec{r}) - (Ze_2+e_1)\frac{m_1}{m_1+m_2}\vec{A}(\vec{R}) \tag{3.28}$$

and

$$\vec{\pi}_2 = -\vec{p} + \frac{m_2}{m_1+m_2}\vec{P} + \left[Ze_2 - (Ze_2+e_1)\left(\frac{m_2}{m_1+m_2}\right)^2\right]\vec{A}(\vec{r}) - (Ze_2+e_1)\frac{m_2}{m_1+m_2}\vec{A}(\vec{R})\ . \tag{3.29}$$

Thus the terms in Eqs. (3.22)–(3.27) may be transformed into relative and center-of-mass coordinates.

IV. POSITRONIUM ZEEMAN AND STARK EFFECTS

A. Hamiltonians

From the transformed Hamiltonians, Eqs. (3.22)–(3.27), terms linear in the external field are combined into a Zeeman Hamiltonian $\mathcal{H}_Z$ and a Stark Hamiltonian $\mathcal{H}_S$. The vector potentials are given by

$$\vec{A}(\vec{r}) = \tfrac{1}{2}\vec{H}\times\vec{r}\ , \tag{4.1}$$

$$\vec{A}(\vec{R}) = \tfrac{1}{2}\vec{H}\times\vec{R}\ . \tag{4.2}$$

For positronium we set $e_1 = -Ze_2 = -e$, $m_1 = m_2 = m$, and $a = a_1 = a_2$; then we find

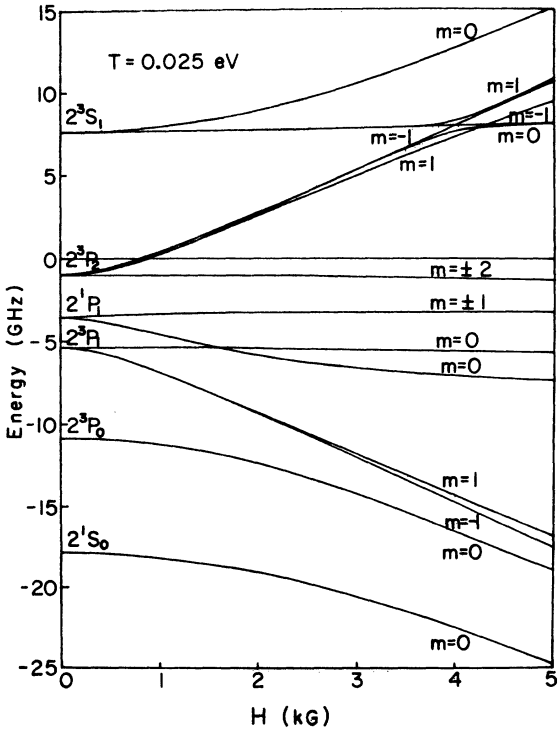

FIG. 4. Fine-structure energy levels of the $n=2$ state of positronium as a function of magnetic field for a kinetic energy $T=0.025$ eV. (The maximum motional Stark effect in the plane perpendicular to the magnetic field is given.)

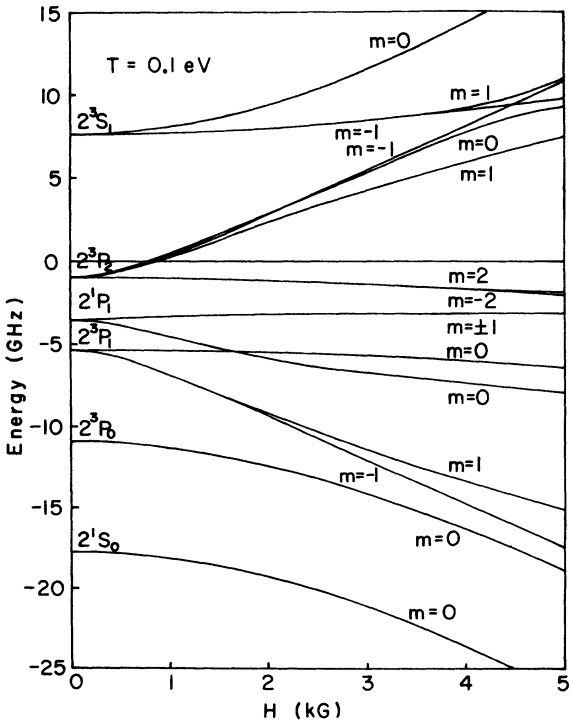

FIG. 5. Fine-structure energy levels as for Fig. 4 with $T=0.1$ eV.

$$\mathcal{H}_Z = \frac{e}{2m}\left\{(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{H}\left(1+a-\frac{\vec{p}^2}{2m^2}-\frac{\vec{P}^2}{8m^2}\right)-(\vec{\sigma}_1+\vec{\sigma}_2)\cdot\vec{H}\,\frac{\vec{P}\cdot\vec{p}}{2m^2}-\frac{a}{2m^2}\right.$$
$$\times[(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{p}\,\vec{p}\cdot\vec{H}+\tfrac{1}{2}(\vec{\sigma}_1+\vec{\sigma}_2)\cdot\vec{p}\,\vec{P}\cdot\vec{H}+\tfrac{1}{2}(\vec{\sigma}_1+\vec{\sigma}_2)\cdot\vec{P}\,\vec{p}\cdot\vec{H}+\tfrac{1}{4}(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{P}\,\vec{P}\cdot\vec{H}]$$
$$\left.-\frac{\alpha}{4mr^3}[(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{H}r^2-(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{r}\,\vec{H}\cdot\vec{r}]\right\} \tag{4.3}$$

and

$$\mathcal{H}_S = \frac{e}{2m}\left[\vec{P}\times\vec{H}\cdot\vec{r}\left(1-\frac{\vec{p}^2}{2m^2}-\frac{\vec{P}^2}{8m^2}+\frac{\alpha}{2m}\frac{1}{r}\right)-\frac{1}{m^2}\vec{H}\times\vec{r}\cdot\vec{p}\,\vec{p}\cdot\vec{P}\right]. \tag{4.4}$$

Matrix elements of these Hamiltonians yield the relativistic contributions to the Zeeman and Stark effects. The Zeeman effect couples ^3S and ^1S states, and ^3P and ^1P states. For any S state with principal quantum number n one can compute a g_J factor g':

$$\langle n\,^3S_1,\ m=0\,|\,\mathcal{H}_Z\,|\,n\,^1S_0,\ m=0\rangle = \frac{e}{2m}\,\frac{g'}{2}$$
$$\times\langle n\,^3S_1,\ m=0\,|\,(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{H}\,|\,n\,^1S_0,\ m=0\rangle\,, \tag{4.5}$$

where

$$g' = g_e\left(1-\frac{5}{24n^2}\,\alpha^2-\frac{T}{2mc^2}\right), \tag{4.6}$$

g_e is the gyromagnetic ratio of the free electron, and T is the total kinetic energy of the atom. Thus for the ground state, $n=1$,

$$g'(n=1) = g_e\left(1-\tfrac{5}{24}\,\alpha^2-\frac{T}{2mc^2}\right) \tag{4.7}$$

and for the first excited state, $n=2$,

$$g'(n=2) = g_e\left(1-\tfrac{5}{96}\,\alpha^2-\frac{T}{2mc^2}\right). \tag{4.8}$$

The Zeeman matrix elements between the $2\,^3P$ and $2\,^1P$ states are given by

TABLE II. Energy levels of the first excited state of positronium: Zeeman and motional Stark effects. $T=0$ eV.

			$2\,^3P_2$				$2\,^3P_1$	
H (kG)	$m=2$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$m=-2$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)
0.0	−0.980	−0.980	−0.980	−0.980	−0.980	−5.365	−5.365	−5.365
0.5	−0.980	−0.618	−0.535	−0.618	−0.980	−5.834	−5.365	−5.834
1.0	−0.980	0.278	0.424	0.278	−0.980	−6.851	−5.365	−6.851
1.5	−0.980	1.429	1.565	1.429	−0.980	−8.062	−5.365	−8.062
2.0	−0.980	2.691	2.788	2.691	−0.980	−9.353	−5.365	−9.353
2.5	−0.980	4.005	4.056	4.005	−0.980	−10.683	−5.365	−10.683
3.0	−0.980	5.347	5.354	5.347	−0.980	−12.035	−5.365	−12.035
3.5	−0.980	6.706	6.673	6.706	−0.980	−13.399	−5.365	−13.399
4.0	−0.980	8.075	8.006	8.075	−0.980	−14.772	−5.365	−14.772
4.5	−0.980	9.452	9.350	9.452	−0.980	−16.152	−5.365	−16.152
5.0	−0.979	10.833	10.703	10.833	−0.979	−17.535	−5.364	−17.535

	$2\,^3P_0$		$2\,^3S_1$			$2\,^1P_1$		$2\,^1S_0$
H (kG)	$m=0$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$m=0$ (GHz)
0.0	−10.851	7.645	7.645	7.645	−3.539	−3.539	−3.539	−17.778
0.5	−10.941	7.645	7.722	7.645	−3.432	−3.894	−3.432	−17.855
1.0	−11.216	7.645	7.950	7.645	−3.311	−4.577	−3.311	−18.083
1.5	−11.687	7.645	8.322	7.645	−3.251	−5.248	−3.251	−18.455
2.0	−12.353	7.645	8.826	7.645	−3.221	−5.805	−3.221	−18.959
2.5	−13.196	7.645	9.448	7.645	−3.205	−6.230	−3.205	−19.581
3.0	−14.182	7.645	10.174	7.645	−3.196	−6.542	−3.196	−20.306
3.5	−15.275	7.645	10.990	7.645	−3.190	−6.767	−3.190	−21.122
4.0	−16.444	7.646	11.882	7.646	−3.186	−6.931	−3.186	−22.014
4.5	−17.668	7.646	12.840	7.646	−3.183	−7.051	−3.183	−22.972
5.0	−18.930	7.646	13.853	7.646	−3.181	−7.141	−3.181	−23.985

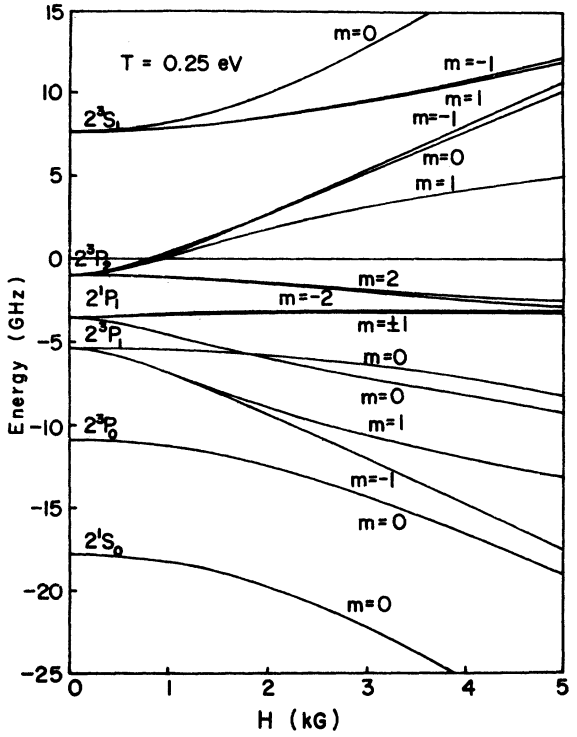

FIG. 6. Fine-structure energy levels as for Fig. 4 with $T=0.25$ eV.

$$\langle 2^3P_2,\ m=\pm 1\,|\,\mathcal{H}_Z\,|\,2^1P_1,\ m=\pm 1\rangle = \frac{e}{2m}\frac{g_2}{2} \times\langle 2^3P_2,\ m=\pm 1\,|\,(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{H}\,|\,2^1P_1,\ m=\pm 1\rangle\,, \tag{4.9}$$

$$\langle 2^3P_2,\ m=0\,|\,\mathcal{H}_Z\,|\,2^1P_1,\ m=0\rangle = \frac{e}{2m}\frac{g_2}{2} \times\langle 2^3P_2,\ m=0\,|\,(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{H}\,|\,2^1P_1,\ m=0\rangle\,, \tag{4.10}$$

$$\langle 2^3P_1,\ m=\pm 1\,|\,\mathcal{H}_Z\,|\,2^1P_1,\ m=\pm 1\rangle = \frac{e}{2m}\frac{g_1}{2} \times\langle 2^3P_1,\ m=\pm 1\,|\,(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{H}\,|\,2^1P_1,\ m=\pm 1\rangle\,, \tag{4.11}$$

$$\langle 2^3P_0,\ m=0\,|\,\mathcal{H}_Z\,|\,2^1P_1,\ m=0\rangle = \frac{e}{2m}\frac{g_0}{2} \times\langle 2^3P_0,\ m=0\,|\,(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{H}\,|\,2^1P_1,\ m=0\rangle\,, \tag{4.12}$$

where

$$g_2 = g_e\left(1-\tfrac{1}{20}\alpha^2-\frac{T}{2mc^2}\right), \tag{4.13}$$

$$g_1 = g_e\left(1-\tfrac{1}{16}\alpha^2-\frac{T}{2mc^2}\right), \tag{4.14}$$

TABLE III. Energy levels of the first excited state of positronium: Zeeman and motional Stark effects. $T=0.025$ eV.

	2^3P_2					2^3P_1		
H (kG)	$m=2$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$m=-2$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)
0.0	−0.980	−0.980	−0.980	−0.980	−0.980	−5.365	−5.365	−5.365
0.5	−0.984	−0.622	−0.536	−0.618	−0.984	−5.835	−5.367	−5.834
1.0	−0.995	0.261	0.420	0.278	−0.995	−6.848	−5.375	−6.851
1.5	−1.014	1.382	1.559	1.429	−1.013	−8.043	−5.387	−8.062
2.0	−1.039	2.587	2.777	2.691	−1.039	−9.302	−5.405	−9.353
2.5	−1.071	3.810	4.040	4.004	−1.072	−10.579	−5.428	−10.683
3.0	−1.111	5.019	5.326	5.347	−1.109	−11.853	−5.456	−12.035
3.5	−1.156	6.199	6.611	6.706	−1.153	−13.116	−5.489	−13.399
4.0	−1.201	7.347	7.707	8.075	−1.206	−14.361	−5.528	−14.722
4.5	−1.255	8.465	8.023	9.452	−1.262	−15.586	−5.572	−16.152
5.0	−1.311	9.559	8.157	10.833	−1.322	−16.792	−5.622	−17.535

	2^3P_0		2^3S_1			2^1P_1		2^1S_0
H (kG)	$m=0$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$m=0$ (GHz)
0.0	−10.851	7.645	7.645	7.645	−3.539	−3.539	−3.539	−17.778
0.5	−10.942	7.651	7.728	7.651	−3.429	−3.894	−3.432	−17.860
1.0	−11.220	7.670	7.977	7.670	−3.305	−4.580	−3.311	−18.102
1.5	−11.694	7.701	8.389	7.701	−3.243	−5.256	−3.251	−18.501
2.0	−12.363	7.745	8.959	7.744	−3.214	−5.824	−3.221	−19.047
2.5	−13.208	7.802	9.680	7.799	−3.198	−6.266	−3.205	−19.729
3.0	−14.194	7.876	10.545	7.865	−3.189	−6.600	−3.196	−20.537
3.5	−15.287	7.981	11.543	7.943	−3.183	−6.853	−3.190	−21.458
4.0	−16.456	8.301	12.660	8.030	−3.180	−7.049	−3.186	−22.481
4.5	−17.679	9.421	13.877	8.128	−3.178	−7.206	−3.183	−23.593
5.0	−18.941	10.742	15.179	8.236	−3.176	−7.338	−3.181	−24.783

$$g_0 = g_e\left(1 - \tfrac{1}{32}\alpha^2 - \frac{T}{2mc^2}\right). \quad (4.15)$$

These g factors given in Eqs. (4.13)–(4.15) differ in part from the corresponding results given by Grotch and Kashuba.[22]

The Stark Hamiltonian $\mathcal{H}_S$ couples $2\,^3S$ and $2\,^3P$, and $2\,^1S$ and $2\,^1P$, states with $\Delta m = \pm 1$. The maximum Stark matrix elements for the $n=2$ state in the plane perpendicular to the magnetic field may be written

$$\langle \mathcal{H}_S \rangle = (e/2m)\langle \vec{P}\times\vec{H}\cdot\vec{r}\rangle\gamma\,, \quad (4.16)$$

where

$$\gamma = 1 + \tfrac{1}{32}\alpha^2 - \frac{T}{2mc^2}\,. \quad (4.17)$$

There is no restriction on the value of Δn in the matrix element of $\mathcal{H}_S$. Calculations of the effect of Stark mixing of the $n=2$ states on the energy levels of the ground state, and of the Stark mixing of the $n=3$ states on the $n=2$ states, both yielded negligible results.

B. Zeeman Effect in the Ground State

The ground state of positronium is split into two states $1\,^3S_1$ and $1\,^1S_0$ by the fine-structure interval $\Delta\nu$. The Zeeman splitting appears in Fig. 1. The theoretical expression[11,12] for $\Delta\nu$, to order $\alpha^4\ln\alpha^{-1}$, is

$$\Delta\nu_{\rm th} = \tfrac{1}{2}\alpha^2 R_\infty\left[\tfrac{7}{3} - (\alpha/\pi)(\tfrac{32}{9} + 2\ln 2) + \tfrac{3}{2}\alpha^2\ln\alpha^{-1}\right]$$
$$= 203.4155 \pm 0.0006\ \text{GHz}\,. \quad (4.18)$$

The Zeeman effect in the ground state of positronium can be used to determine $\Delta\nu$. The splitting f_{01} between the $M=0$ and $M=\pm 1$ magnetic substates of the $1\,^3S_1$ state is related to $\Delta\nu$:

$$f_{01} = \tfrac{1}{2}\Delta\nu\left\{\left[1 + (2\mu_B g' H/\Delta\nu)^2\right]^{1/2} - 1\right\}. \quad (4.19)$$

The relativistic corrections to $g'(n=1)$, about 10 ppm, given in Eq. (4.7) are needed to evaluate $\Delta\nu$ precisely from the observed transitions f_{01}. The latest experimental value[6] is

$$\Delta\nu_{\rm expt} = 203.396 \pm 0.005\ \text{GHz}.$$

The difference between the experimental and theoretical values for $\Delta\nu$ is about four standard deviations of the experimental error. Clearly, a more significant comparison of experiment and theory requires the calculation of the $\alpha^4 R_\infty$ radiative corrections and other $\alpha^4\ln\alpha^{-1}R_\infty$ terms. (See note added in proof.)

TABLE IV. Energy levels of the first excited state of positronium: Zeeman and motional Stark effects. $T = 0.1$ eV.

			$2\,^3P_2$				$2\,^3P_1$	
H (kG)	$m=2$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$m=-2$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)
0.0	−0.980	−0.980	−0.980	−0.980	−0.980	−5.365	−5.365	−5.365
0.5	−0.995	−0.633	−0.539	−0.618	−0.995	−5.838	−5.375	−5.834
1.0	−1.040	0.211	0.411	0.278	−1.039	−6.839	−5.405	−6.851
1.5	−1.112	1.248	1.541	1.429	−1.109	−7.990	−5.456	−8.062
2.0	−1.202	2.305	2.750	2.691	−1.208	−9.158	−5.528	−9.353
2.5	−1.312	3.312	4.000	4.005	−1.324	−10.294	−5.623	−10.683
3.0	−1.434	4.246	5.268	5.347	−1.456	−11.376	−5.741	−12.035
3.5	−1.563	5.115	6.532	6.706	−1.600	−12.399	−5.884	−13.399
4.0	−1.695	5.935	7.739	8.075	−1.751	−13.368	−6.052	−14.772
4.5	−1.824	6.726	8.720	9.452	−1.905	−14.294	−6.247	−16.152
5.0	−1.947	7.501	9.334	10.833	−2.060	−15.187	−6.467	−17.535

	$2\,^3P_0$		$2\,^3S_1$			$2\,^1P_1$		$2\,^1S_0$
H (kG)	$m=0$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$m=0$ (GHz)
0.0	−10.851	7.645	7.645	7.645	−3.539	−3.539	−3.539	−17.778
0.5	−10.946	7.670	7.747	7.670	−3.419	−3.895	−3.432	−17.873
1.0	−11.233	7.743	8.058	7.744	−3.286	−4.587	−3.311	−18.160
1.5	−11.717	7.864	8.583	7.865	−3.221	−5.281	−3.251	−18.637
2.0	−12.395	8.031	9.330	8.030	−3.190	−5.883	−3.221	−19.303
2.5	−13.245	8.242	10.292	8.235	−3.175	−6.377	−3.205	−20.151
3.0	−14.233	8.476	11.452	8.499	−3.167	−6.781	−3.196	−21.171
3.5	−15.326	8.811	12.776	8.748	−3.163	−7.121	−3.190	−22.344
4.0	−16.493	9.223	14.230	9.048	−3.161	−7.421	−3.186	−23.650
4.5	−17.714	9.897	15.780	9.372	−3.160	−7.699	−3.183	−25.066
5.0	−18.974	10.967	17.403	9.717	−3.160	−7.969	−3.181	−26.571

C. Zeeman and Stark Effects in the First Excited State

The first excited state, $n=2$, of positronium consists of 16 substates. The $n=2$ state is 5.1 eV above the ground state. This state has not been experimentally observed.

Figure 2 presents the 16×16 secular matrix for the $n=2$ states of positronium. E_1, E_2, E_3, E_4, E_5, and E_6 represent the zero-field fine structure calculated by Fulton and Martin[13] (see Table I). In Fig. 2,

$$F=\mu_B H\left(\frac{T}{m}\right)^{1/2}\frac{\gamma}{\alpha},$$

$$Q_1=112\frac{\mu_B^2H^2}{m\alpha^2}, \tag{4.20}$$

and

$$Q_2=80\frac{\mu_B^2H^2}{m\alpha^2}.$$

Here we have also included the lowest-order quadratic field-dependent terms that appear in H_0, Eq. (3.22),

$$\mathcal{H}_Q=(e^2/m)\,\vec{A}(\vec{r})^2. \tag{4.21}$$

The energy levels of the 16 substates of $n=2$ positronium are illustrated in Figs. 3–8 for various values of kinetic energy from 0 to 1 eV. The zero of the energy-level diagrams is the nonrelativistic $n=2$ Schrödinger solution for a reduced mass of $0.5m$. The energy levels are also tabulated in Tables II–VII. As the kinetic energy of the atom is increased various degenerate lines are split. In Fig. 9 the motional Stark effect is exhibited at constant magnetic field ($H=1$ kG) with variable kinetic energy.

D. Transitions in the First Excited State

Experiments on the first excited state of positronium might include observing electric dipole transitions between the 16 substates. Transitions between the 2^3S_1 and 2^3P_J states can be induced by a microwave electric field. These transitions can be observed by a change in the ratio of two-photon–to–three-photon annihilations as a function of microwave frequency. Transition probabilities for these $E1$ transitions are given in Table VIII for applied magnetic fields of 0.5 and 1.0 kG. In order to observe a change in the ratio of two-photon–to–three-photon annihilation the transition rate must be comparable to or greater than the annihilation rate. For comparable rates an electric field of from 10 to 20 V/cm is needed depending on the transition.

TABLE V. Energy levels of the first excited state of positronium: Zeeman and motional Stark effects. $T=0.25$ eV.

H (kG)	$m=2$ (GHz)	$m=1$ (GHz)	$2\,^3P_2$ $m=0$ (GHz)	$m=-1$ (GHz)	$m=-2$ (GHz)	$m=1$ (GHz)	$2\,^3P_1$ $m=0$ (GHz)	$m=-1$ (GHz)
0.0	−0.980	−0.980	−0.980	−0.980	−0.980	−5.365	−5.365	−5.365
0.5	−1.018	−0.656	−0.544	−0.618	−1.017	−5.845	−5.390	−5.834
1.0	−1.128	0.116	0.395	0.278	−1.123	−6.826	−5.466	−6.851
1.5	−1.296	1.009	1.513	1.429	−1.282	−7.899	−5.596	−8.062
2.0	−1.476	1.842	2.710	2.691	−1.508	−8.918	−5.785	−9.353
2.5	−1.682	2.560	3.948	4.005	−1.744	−9.833	−6.035	−10.683
3.0	−1.885	3.174	5.209	5.347	−1.989	−10.637	−6.351	−12.035
3.5	−2.072	3.714	6.480	6.706	−2.230	−11.345	−6.731	−13.399
4.0	−2.236	4.207	7.749	8.075	−2.458	−11.979	−7.172	−14.772
4.5	−2.375	4.675	8.999	9.452	−2.667	−12.560	−7.668	−16.152
5.0	−2.492	5.131	10.206	10.833	−2.855	−13.107	−8.212	−17.535

H (kG)	$2\,^3P_0$ $m=0$ (GHz)	$m=1$ (GHz)	$2\,^3S_1$ $m=0$ (GHz)	$m=-1$ (GHz)	$m=1$ (GHz)	$2\,^1P_1$ $m=0$ (GHz)	$m=-1$ (GHz)	$2\,^1S_0$ $m=0$ (GHz)
0.0	−10.851	7.645	7.645	7.645	−3.539	−3.539	−3.539	−17.778
0.5	−10.952	7.707	7.785	7.706	−3.401	−3.897	−3.432	−17.901
1.0	−11.257	7.887	8.215	7.889	−3.249	−4.602	−3.311	−18.273
1.5	−11.764	8.179	8.948	8.175	−3.174	−5.333	−3.251	−18.901
2.0	−12.461	8.561	9.984	8.559	−3.140	−6.004	−3.221	−19.785
2.5	−13.323	9.018	11.294	9.022	−3.124	−6.607	−3.205	−20.913
3.0	−14.318	9.537	12.822	9.554	−3.116	−7.161	−3.196	−22.259
3.5	−15.411	10.104	14.515	10.146	−3.114	−7.689	−3.190	−23.785
4.0	−16.577	10.709	16.324	10.796	−3.113	−8.212	−3.186	−25.454
4.5	−17.795	11.345	18.218	11.507	−3.115	−8.746	−3.183	−27.232
5.0	−19.051	12.006	20.173	12.296	−3.117	−9.298	−3.181	−29.094

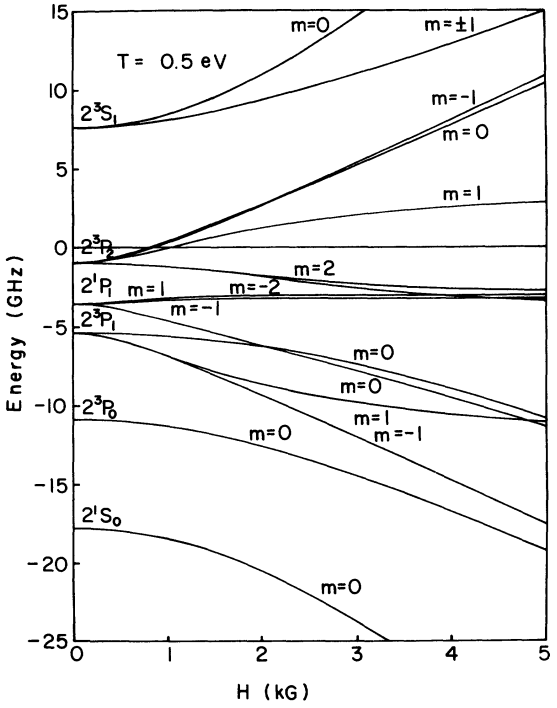

FIG. 7. Fine-structure energy levels as for Fig. 4 with $T=0.5$ eV.

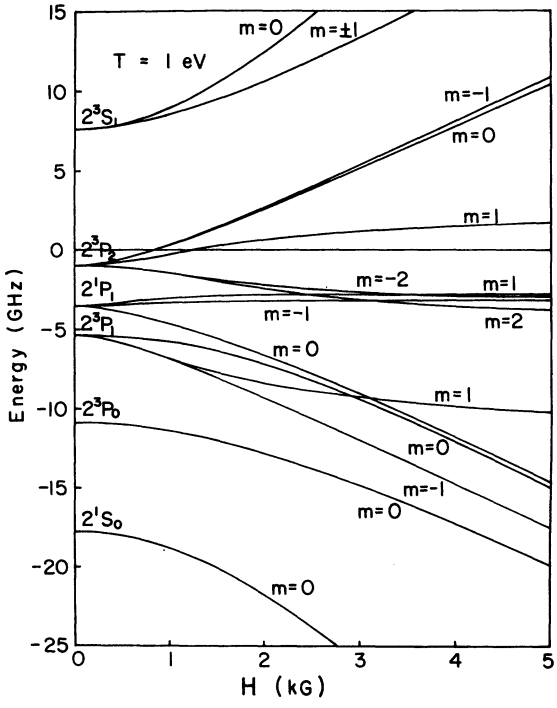

FIG. 8. Fine-structure energy levels as for Fig. 4 with $T=1$ eV.

TABLE VI. Energy levels of the first excited state of positronium: Zeeman and motional Stark effects. $T=0.5$ eV.

H (kG)	$2\,^3P_2$ $m=2$ (GHz)	$m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$m=-2$ (GHz)	$2\,^3P_1$ $m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)
0.0	−0.980	−0.980	−0.980	−0.980	−0.980	−5.365	−5.365	−5.365
0.5	−1.057	−0.692	−0.552	−0.618	−1.053	−5.856	−5.415	−5.834
1.0	−1.269	−0.027	0.373	0.278	−1.252	−6.813	−5.570	−6.851
1.5	−1.525	0.683	1.479	1.429	−1.573	−7.789	−5.840	−8.062
2.0	−1.817	1.272	2.667	2.691	−1.917	−8.635	−6.235	−9.353
2.5	−2.084	1.718	3.901	4.005	−2.260	−9.315	−6.761	−10.683
3.0	−2.307	2.052	5.166	5.347	−2.574	−9.845	−7.407	−12.035
3.5	−2.482	2.311	6.452	6.706	−2.846	−10.260	−8.155	−13.399
4.0	−2.616	2.522	7.752	8.075	−3.074	−10.591	−8.986	−14.772
4.5	−2.718	2.705	9.063	9.452	−3.261	−10.864	−9.878	−16.152
5.0	−2.796	2.870	10.381	10.833	−3.413	−11.099	−10.818	−17.535

H (kG)	$2\,^3P_0$ $m=0$ (GHz)	$2\,^3S_1$ $m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$2\,^1P_1$ $m=1$ (GHz)	$m=0$ (GHz)	$m=-1$ (GHz)	$2\,^1S_0$ $m=0$ (GHz)
0.0	−10.851	7.645	7.645	7.645	−3.539	−3.539	−3.539	−17.778
0.5	−10.964	7.767	7.848	7.768	−3.370	−3.899	−3.432	−17.947
1.0	−11.298	8.117	8.465	8.122	−3.184	−4.627	−3.311	−18.458
1.5	−11.844	8.665	9.499	8.657	−3.090	−5.424	−3.251	−19.318
2.0	−12.578	9.353	10.909	9.342	−3.047	−6.218	−3.221	−20.516
2.5	−13.468	10.145	12.619	10.135	−3.025	−7.012	−3.205	−22.013
3.0	−14.480	11.014	14.546	11.006	−3.013	−7.822	−3.196	−23.755
3.5	−15.582	11.938	16.623	11.936	−3.007	−8.862	−3.190	−25.682
4.0	−16.752	12.902	18.806	12.909	−3.005	−9.539	−3.186	−27.747
4.5	−17.970	13.898	21.062	13.917	−3.005	−10.452	−3.183	−29.912
5.0	−19.224	14.916	23.372	14.953	−3.006	−11.399	−3.181	−32.151

TABLE VII. Energy levels of the first excited state of positronium: Zeeman and motional Stark effects. $T=1.0$ eV.

H (kG)	2^3P_2 $m=2$ (GHz)	2^3P_2 $m=1$ (GHz)	2^3P_2 $m=0$ (GHz)	2^3P_2 $m=-1$ (GHz)	2^3P_2 $m=-2$ (GHz)	2^3P_1 $m=1$ (GHz)	2^3P_1 $m=0$ (GHz)	2^3P_1 $m=-1$ (GHz)
0.0	−0.980	−0.980	−0.980	−0.980	−0.980	−5.365	−5.365	−5.365
0.5	−1.135	−0.762	−0.565	−0.618	−1.123	−5.881	−5.466	−5.834
1.0	−1.532	−0.263	0.342	0.278	−1.476	−6.822	−5.785	−6.851
1.5	−2.025	0.242	1.436	1.429	−1.885	−7.709	−6.351	−8.062
2.0	−2.494	0.637	2.620	2.691	−2.236	−8.416	−7.173	−9.353
2.5	−2.881	0.925	3.858	4.005	−2.493	−8.945	−8.212	−10.683
3.0	−3.179	1.139	5.133	5.347	−2.669	−9.336	−9.412	−12.035
3.5	−3.403	1.307	6.434	6.706	−2.789	−9.632	−10.722	−13.399
4.0	−3.569	1.448	7.754	8.075	−2.873	−9.864	−12.107	−14.772
4.5	−3.695	1.573	9.089	9.452	−2.933	−10.054	−13.543	−16.151
5.0	−3.792	1.689	10.435	10.833	−2.976	−10.218	−15.014	−17.535

H (kG)	2^3P_0 $m=0$ (GHz)	2^3S_1 $m=1$ (GHz)	2^3S_1 $m=0$ (GHz)	2^3S_1 $m=-1$ (GHz)	2^1P_1 $m=1$ (GHz)	2^1P_1 $m=0$ (GHz)	2^1P_1 $m=-1$ (GHz)	2^1S_0 $m=0$ (GHz)
0.0	−10.851	7.645	7.645	7.645	−3.539	−3.539	−3.539	−17.778
0.5	−10.986	7.886	7.971	7.889	−3.308	−3.904	−3.432	−18.037
1.0	−11.383	8.551	8.932	8.561	−3.050	−4.682	−3.311	−18.814
1.5	−12.014	9.517	10.455	9.537	−2.919	−5.618	−3.251	−20.085
2.0	−12.839	10.709	12.412	10.677	−2.858	−6.669	−3.221	−21.791
2.5	−13.814	12.005	14.669	11.962	−2.828	−7.829	−3.205	−23.837
3.0	−14.901	13.382	17.128	13.327	−2.813	−9.083	−3.196	−26.133
3.5	−16.069	14.813	19.721	14.746	−2.807	−10.411	−3.190	−28.605
4.0	−17.297	16.281	22.408	16.203	−2.806	−11.794	−3.186	−31.201
4.5	−18.569	17.777	25.159	17.688	−2.807	−13.215	−3.183	−33.884
5.0	−19.873	19.293	27.959	19.193	−2.812	−14.665	−3.181	−36.632

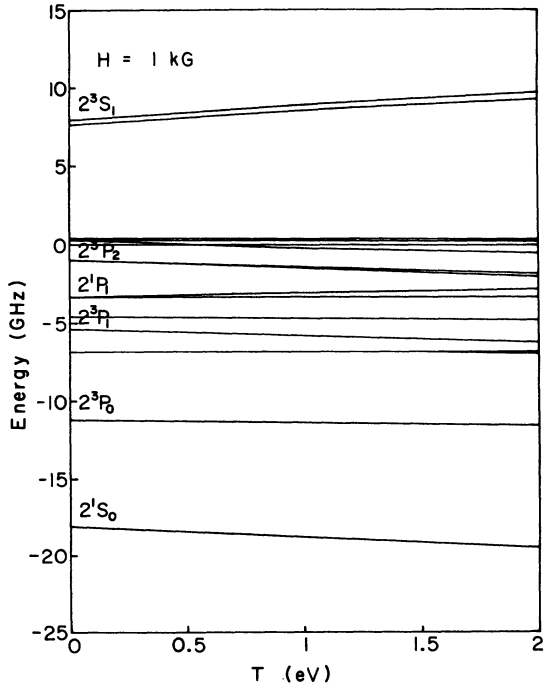

FIG. 9. Fine-structure energy levels of the $n=2$ state of positronium as a function of kinetic energy for a magnetic field $H=1$ kG.

V. SUMMARY

The major results presented here are the calculation of the relativistic contributions to the Zeeman effect in the ground state and the first excited state of positronium. If we write the Zeeman Hamiltonian for positronium as

$$\mathcal{H}_Z=\tfrac{1}{2}\mu_B g'(\vec{\sigma}_1-\vec{\sigma}_2)\cdot\vec{H},$$

then for all S states

TABLE VIII. Transition probabilities W and transition frequencies ν in the $n=2$ state of positronium. W in units of $(10^5\,\mathrm{sec}^{-1})$ $(\mathcal{E})^2/(V/\mathrm{cm})^2$ for $T=0.5$ eV.

Transition	$H=0.5$ kG W	$H=0.5$ kG ν (GHz)	$H=1.0$ kG W	$H=1.0$ kG ν (GHz)
2^3S_1, $m=1\rightarrow 2^3P_2$, $m=2$	0.268	8.823	0.204	9.386
2^3S_1, $m=1\rightarrow 2^3P_2$, $m=0$	0.071	8.319	0.041	8.489
2^3S_1, $m=1\rightarrow 2^3P_0$, $m=0$	0.080	18.730	0.067	19.415
2^3S_1, $m=0\rightarrow 2^3P_2$, $m=1$	0.272	8.540	0.239	8.492
2^3S_1, $m=0\rightarrow 2^3P_1$, $m=1$	0.155	13.703	0.114	15.278
2^3S_1, $m=-1\rightarrow 2^2P_2$, $m=-2$	0.245	8.821	0.183	9.372
2^3S_1, $m=-1\rightarrow 2^3P_1$, $m=0$	0.177	13.183	0.164	13.690
2^1S_0, $m=0\rightarrow 2^1P_1$, $m=1$	0.223	14.576	0.109	15.275

$$g' = g_e\left(1 - \frac{5}{24n^2}\,\alpha^2 - \frac{T}{2mc^2}\right),$$

where g_e is the gyromagnetic ratio of the free electron and T is the total kinetic energy of the atom. For Zeeman matrix elements between $2P$ states we obtain three g_J factors g_2, g_1, and g_0 given in Eqs. (4.13)–(4.15).

The Stark-effect contribution we give is the maximum Stark effect in the plane perpendicular to the magnetic field. The corrections to the Stark effect for $n=2$ may be written

$$\langle \mathcal{H}_S \rangle = (e/2m)\langle \vec{P}\times\vec{H}\cdot\vec{r}\rangle\gamma,$$

where

$$\gamma = 1 + \tfrac{1}{32}\alpha^2 - \frac{T}{2mc^2}.$$

The g factor for the ground state is essential for a determination of the fine-structure interval $\Delta\nu$ from the measurement of the Zeeman effect. The g factors for the first excited state and the corrections to the Stark effect may be of use in future experiments on the $n=2$ state of positronium.

Note added in proof. The fourth-order vacuum polarization correction to the annihilation diagrams has been recently calculated by D. A. Owen [Phys. Rev. Letters 30, 887 (1973)]. The contribution to the positronium ground-state fine structure interval $\Delta\nu$ from Owen's calculation is $-\frac{1}{4}\alpha^4 \ln\alpha^{-1}\mathcal{R}$. The new theoretical expression for $\Delta\nu$ is

$$\Delta\nu_{\text{th}} = \tfrac{1}{2}\alpha^2\mathcal{R}\left[\tfrac{7}{3} - (\alpha/\pi)\left(\tfrac{32}{9} + 2\ln 2\right) + \alpha^2 \ln\alpha^{-1}\right]$$
$$= 203.404 \text{ GHz}.$$

This new theoretical value of $\Delta\nu$ is 1.6 standard deviations of the experimental error above the experimental value.

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*Research supported in part by the Air Force Office of Scientific Research, under AFOSR Contract No. F44620-70-C-0091.

†Paper based in part on a dissertation submitted by M. L. Lewis in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Yale University.

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