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The orbital $\underset{\sim}{\mu}_L \cdot \underset{\sim}{B}$ and diamagnetic A^2 interactions of electrons and positrons with an external magnetic field lead to a small quadratic Zeeman shift in the L=0, $m_S = \pm 1$ states of positronium, which, unlike the $m_S = 0$ states, are not affected by the usual, spin-induced Zeeman shifts. For the n=1 states, this shift would be about 2 kHz in a field of 1000 Gauss. These additional shifts are the same in all spin states for L=0, but do depend on n.

The Zeeman effect in the L=0 states of positronium (Ps) has been studied for many years.[1] It is well-known that the two hyperfine states with $m_S = 0$ both show large quadratic Zeeman shifts in opposite directions. These shifts arise as a second-order effect of the spin magnetic dipole interactions of electron and positron, coupling the hyperfine singlet and triplet states. The Zeeman shifts correspond to magnetic polarizabilities of order a^3, where a is the hydrogen Bohr

radius. The impression is usually given that the L=0, $m_S = \pm 1$ states have no quadratic Zeeman effect. For example, the text by Akhiezer and Berestetski says that these states "do not interact with a magnetic field." The authors of Ref.1 indicate more cautiously only that any Zeeman effect is the same in both the $m_S = +1$ and $m_S = -1$ states, which may be proven using the symmetry under rotation through π about an axis perpendicular to the field, followed by charge conjugation.

However, there actually is a small quadratic Zeeman shift in the L=0, $m_S = \pm 1$ states of positronium, corresponding to a magnetic polarizability of order $\alpha^2 a^3$. This shift arises as a combination of a first-order effect of the diamagnetic A^2 term in the interaction of nonrelativistic charges with electromagnetic fields and a second-order effect of the orbital magnetic moment interactions of the charges with the magnetic field. The latter contributes even in states for which the relative orbital angular momentum, L, is zero, because the difference of the orbital angular momenta of electron and positron, which are what appears in the interaction, involves operators that couple orbital motion with center of mass motion and which are not zero acting on states with L=0. In order to calculate the effect of these operators correctly, it is necessary to treat the center of mass motion carefully.[2]

The combined result of these interactions is to generate a diamagnetic polarizability contribution that is the same in all spin states corresponding to the same n and L values. In particular, they give the same contribution to the quadratic Zeeman shift in all of the four n=1 hyperfine states of Ps. For the $m_S=0$ states, this is a small correction to the spin-induced Zeeman effect. On the other hand, for the $m_S = \pm 1$ states, it is the

only contribution. Because this diamagnetic contribution is the same in all four ground states it does not change the energy <u>differences</u> between these states. However, the diamagnetic quadratic Zeeman shifts are not the same for states with different n values, so that this contribution must be considered when evaluating precision measurements of such quantities as the 2S - 1S splitting.

For the n=1 states, the diamagnetic quadratic Zeeman shifts do not appear to have been discussed previously. For n=2 states, these shifts are correctly contained in the work of Lewis and Hughes,[3] who calculate all relevant contributions to the n=2 Zeeman effect. These authors do not explicitly calculate the spin-independent shifts for states other than n=2.

To determine the quadratic Zeeman shift due to the orbital and diamagnetic interactions we consider the interaction with an external magnetic field of the e^+ and e^- in Ps, given in the nonrelativistic limit by

$$H_{ext.} = H_S + H_L + H_D$$

where

$$H_S = -\underline{\mu}_+ \cdot \underline{B} - \underline{\mu}_- \cdot \underline{B}$$

$$H_L = -\underline{\mu}_L \cdot \underline{B}$$

$$H_D = (e^2/2m) (A_+^2 + A_-^2). \tag{1b}$$

Here $\underline{B}$ is the external field, taken as constant, $\underline{A}_+$ is short for the vector potential evaluated at the position of the positron and $\underline{A}_-$ the same for the electron, so that in a suitable gauge

$$\underline{A}_+ = -\underline{r}_+ \times \underline{B}/2 \; ; \quad \underline{A}_- = -\underline{r}_- \times \underline{B}/2. \tag{2a}$$

The spin magnetic moments of positron and electron are μ_+ and μ_- respectively, and μ_L is the orbital magnetic moment operator,

$$\mu_L = e(L_+ - L_-)/2m .\qquad\qquad (2b)$$

Note that μ_L is proportional to the <u>difference</u> of the orbital moments of electron and positron. The term H_D contains the usual diamagnetic interaction for each particle.

The operator H_S vanishes when acting on a state with $m_S = \pm 1$, so that there is no spin contribution to the Zeeman effect in these states. However, contributions to the Zeeman shift in these states do arise in first order from the term H_D and in second order from the term H_L. These contributions are both independent of spin so they do not affect the energy of hyperfine transitions within the n=1 multiplet. However, they would contribute to transitions in which the principal quantum number changes.

In order to calculate the shifts arising from H_L and H_D it is convenient to express all operators in terms of relative and center of mass coordinates. To do this we note that $r_+ = r/2 + R$, $r_- = -r/2 + R$, where r is the relative coordinate of electron and positron, and R the center of mass coordinate. Similarly, we have $p_+ = p + P/2$, $p_- = -p + P/2$, where p is the relative momentum and P the center of mass momentum.

In terms of these operators the total Hamiltonian can be written as

$$H = H_0 + H_1 + H_{D,cm} + H_{D,rel} \tag{3a}$$

where

$$H_0 = P^2/2M + p^2/2\mu + V$$

$$H_1 = -e/2[\underset{\sim}{R} \times \underset{\sim}{p} \cdot \underset{\sim}{B}/\mu + \underset{\sim}{r} \times \underset{\sim}{P} \cdot B/M]$$

$$H_{D,cm} = e^2(\underset{\sim}{R} \times \underset{\sim}{B})^2/8\mu$$

$$H_{D,rel} = e^2(\underset{\sim}{r} \times \underset{\sim}{B})^2/8M. \tag{3b}$$

Here M=2m is the total mass, μ=m/2 is the reduced mass, and V is the potential.

We note that H_1, which arises from the term previously called H_L, is a sum of terms each of which is a product of one factor involving the relative motion and one factor involving the center of mass motion. Because this is uncommon in atomic problems, the calculation is somewhat more subtle than might be expected. It can be carried out by at least two distinct methods. One involves obtaining the energy shift proportional to B^2 by adding the first order matrix element of H_D to the second order contribution of H_1. In order to do this unambiguously, it is convenient to introduce a binding potential that acts on the center of mass coordinate $\underset{\sim}{R}$. This is done in order to make the center-of-mass wave functions normalizable, so that matrix elements evaluated between such states are finite, and also to give precise meaning to the energy shift.

Alternatively, one can carry out a canonical transformation U = exp(i $\underset{\sim}{R} \times \underset{\sim}{r} \cdot \underset{\sim}{B}$/2) which changes the Hamiltonian into the form

$$H' = H_0 + H_1 + (M/\mu) H_{D,rel} \tag{4}$$

where

$$H_1' = - e(\underline{r} \times \underline{P} \cdot B)/M.$$

In this form, the Hamiltonian is appropriate for calculating the spin-independent quadratic Zeeman shifts in L=0 states for any two bound particles of opposite charge, whatever their masses. (For L≠0 and unequal masses another term must be added to H_1'.)

We note that this transformation has resulted in multiplying $H_{D,rel}$ by the factor M/μ, which is a factor of four in Ps. Its other effects are the elimination of one of the two terms that couples the relative and center of mass motions, and the diamagnetic term $H_{D,cm}$ involving the center of mass coordinate $\underline{R}$. The remaining term H_1', in Eq.(4), which is twice the corresponding term in Eq.(3), represents what is referred to as the 'motional Stark effect' in Ref.2. It contributes zero for a center-of-mass eigenstate of momentum zero. It is worth noting that the same quadratic Zeeman shift is obtained by this canonical transformation as by the direct method of adding the second order contribution of H_1 and the first order contribution of H_D.

The contribution of the operator (M/μ) $H_{D,rel}$ is given by its expectation value in the unperturbed state. Since $H_{D,rel}$ doesn't involve a center of mass operator, we need only calculate its expectation value in the state |n, L, m_L > describing relative motion, provided that the center of mass state is taken to be normalized. For L=0 and arbitrary n we have

$$<(M/\mu) H_D>_{n,L=0} = (e^2/12\mu) B^2 <r^2>_{n,L=0} . \qquad (5)$$

For the remainder of our discussion, we again specialize to

the case of Ps, where $\mu=m/2$. The remaining expectation value in (5)
is, because of the smaller Ps reduced mass, four times greater than
the corresponding value in hydrogen, and is given by

$$<r^2>_{n,L=0} = a^2\, 2n^2(5n^2+1). \tag{6}$$

The total quadratic Zeeman shift in the L=0 state with
$m_S = \pm1$ is therefore given by

$$E_D = \alpha^2\, a^3\, B^2\, n^2\, (5n^2+1)/3 . \tag{7}$$

To get an idea of the magnitude of this shift, we take n=1 and an
external field of 1000 Gauss. Then $E_D/h \approx 2$ kHz. For n=1, this is
approximately 16,000 times smaller than the spin-induced quadratic
Zeeman shift in the $m_S=0$ states.

The shift E_D occurs equally in all spin states of Ps. In the
states with $m_S = \pm1$ it represents the full quadratic Zeeman shift, whereas
in the states with $m_S = 0$ it must be added to the spin induced shifts. It is
not difficult to show that even when relativistic effects are included any
contribution of spin magnetic moments to these Zeeman shifts of the $m_S= \pm1$ states is higher order in α than E_D. On the other hand, relativistic
corrections to the spin induced shifts in the states with $m_S=0$ can be of
the same order in α as E_D.[3] The energy differences among the n=1 states
in a magnetic field are determined by calculating only the effects of the
spin interactions, since the E_D of Eq.(7) applies equally to all four states.
However, the energy differences between, for example, n=1 and n=2 states
now contain an additional contribution from

E_D:

$$\Delta E_D(n=2, L=0; n=1, L=0) = 26 \, \alpha^2 a^3 B^2 \sim 30 \text{ kHz}(B/1000 \text{ Gauss})^2 ,$$

$$\Delta E_D(n=3, L=0; n=1, L=0) = 136 \, \alpha^2 a^3 B^2 \sim 160 \text{ kHz}(B/1000 \text{ Gauss})^2. \quad (8)$$

These terms represent the full quadratic Zeeman shifts to this order for states with $m_S = \pm 1$.

It is possible that a contribution of this magnitude may be observable in future precision measurements, since we understand that measurements of the $n=1$ to $n=2$ transition, eventually at the 10 kHz level of accuracy, are now in preparation.[4]

It is of interest to consider the effect of $H_{D,rel}$ on the annihilation rate of Ps. There are several effects that can be considered. One is the effect on the phase space of the change in energy. Since the latter is of the order of $E_D/mc^2 \sim 10^{-18}$ for a 1000 Gauss field, it is uninteresting. A potentially larger effect would be due to the change in the annihilation matrix element, which is proportional to the square of the relative wave function at $r=0$. This change can be calculated exactly to first-order in $H_{D,rel}$ by the methods of Sternheimer, Dalgarno and Lewis and others.[5] Interestingly, we find that there is no change in the annihilation matrix element because to this order, the change Ψ_1 in the wave function vanishes at $r=0$:

$$\Psi_1 = \text{const} \times (1-\cos^2\theta) \, (r^3/6a^3 + r^2/a^2) \exp(-r/2a). \quad (9)$$

Finally, no additional mixing between the singlet and triplet $m_S=0$ states is induced by $H_{D,rel}$, so that there is no effect on the decay rate for that

reason either.

We conclude with two final points. The first point is that energy shifts in Ps can contain parts arising from annihilation. Some effects of these annihilation terms on measured energy differences have been discussed previously.[6] Their additional effect on the E_D of Eq.(7) is very small, and could easily be incorporated. The second point is that, in astrophysical contexts, Ps could be found in regions of very high magnetic fields (10^6-10^9 Gauss near white dwarfs, 10^{12}-10^{13} Gauss near neutron stars). In such circumstances a nonperturbative analysis of the Ps system including H_D is necessary, such as that carried out by Herold et al.[7]

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