Thermal corrections for positronium

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Temperature-dependent corrections to energy levels, including relativistic effects, for the positronium atom are discussed. The theoretical description of the thermal environment impact on atomic characteristics is carried out within the framework of rigorous relativistic quantum electrodynamics. As a result, the finite temperature corrections to the fine and hyperfine structure of positronium levels are evaluated. In addition, the annihilation rates of a positronium atom placed in an equilibrium thermal environment (blackbody radiation field) are studied. The numerical results are discussed throughout the paper in view of modern experiments.

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I. INTRODUCTION

The continuous development of methods of quantum mechanics (QM) and quantum electrodynamics (QED) for the detailed description of processes occurring in atomic systems and the estimation of the corresponding relativistic QED corrections to bound energies [1–7] play a crucial role in modern physics. Theoretical calculations combined with increasing experimental precision allow one to test our understanding of physics up to 4.2×10^{-15} by measuring the transition frequency in hydrogen [8,9] or, even better, in atomic clocks 2.3×10^{-16} [10,11]. The experiments with such extraordinary precision required theoretical calculations of various QED effects at the α^6m^2/M and α^7m levels (see [12] and references therein), where α is the fine-structure constant, and m and M are the electron and nuclear masses, respectively. However, in a number of cases, theoretical calculations at this level cannot adjust the existing inconsistencies in predicted and measured physical quantities [13–18].

Such a discrepancy has been reported recently for the fine interval $2^3S_1 - 2^3P_0$ in a positronium atom in [19], where the deviation of the experimental value $18\,501.02 \pm 0.61$ MHz and the theoretical value $18\,498.25 \pm 0.08$ MHz exceeds the corresponding uncertainties. The explanation of this discrepancy prompts a theoretical revision of the relevant quantities and provides a basis for searching and testing various physical effects and hypotheses.

The effects caused by blackbody radiation (BBR) can serve this purpose since the appropriate theoretical analysis can hardly be found in the literature. Starting with [20,21], thermal effects consisting of the Stark shift and induced line broadening are well known and have been widely discussed for various atomic systems. Calculations of the Stark shift and line broadening caused by BBR are generally based on the QM approach and are extended to many-electron systems [22]. However, the theory of thermal action on atomic systems can be defined within the framework of the QED at finite temperature; see [23–25] and references therein.

Recently, to study the effects caused by BBR, a rigorous QED approach was used in [26,27], where, in addition to the known effects, a thermal correction to the Coulomb interaction of two charges was introduced. The thermal correction was found to depend cubically on the temperature at the lowest order, while the thermal Stark shift is proportional to the fourth power under laboratory conditions. Being of the same order of magnitude, this temperature behavior shows a fundamental difference in effects, and the atomic energy level shifts caused by this correction turn out to be more significant than the corresponding Stark shift (see [27] for one-electron atoms, and [28] for heliumlike systems). The hypothesis established in [27,28] can be indirectly confirmed by the theoretical prediction in [25] as well as by the experimentally observed thermal effect, scaled as $T^{2.7}$ in [29]. Finally, the relativistic thermal corrections to the Coulomb interaction of bound particles were considered in [30].

In view of the existing discrepancy between the theoretical and experimental value of the transition frequency found in [19], the derivation of leading-order thermal corrections for a positronium atom is of considerable interest. This problem can be solved with the formalism presented in [27,30], which is valid up to temperatures where $r/\beta < 1$ (r is the radius vector of the bound particle, $\beta = 1/(k_BT)$, k_B is the Boltzmann constant, and T is the temperature) in relativistic units. In this work, the thermal corrections resulting from the scalar and transversal parts of the thermal photon propagator are evaluated for the Ps atom. All derivations are carried out in the framework of rigorous quantum electrodynamics at finite temperatures. In addition, the thermal corrections to the two- and three-photon annihilation probabilities of the positronium atom are briefly discussed to provide a detailed description of the lowest-order thermal effects.

II. THERMAL NONRELATIVISTIC AND RELATIVISTIC LOWER-ORDER CORRECTIONS

Starting with the description of the interaction of two charges, one can use the relation from textbooks (see, for example, [2,4,7]) connecting the nuclear current, $j^\nu(x')$, with

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the field, $A_\mu(x)$, it creates:

$$A_\mu(x) = \int d^4x D_{\mu\nu}(x,x')j^\nu(x'), \quad (1)$$

where $x=(t,\vec{r})$ represents the four-dimensional coordinate vector (t represents time and $\vec{r}$ denotes a space vector), $D_{\mu\nu}(x,x')$ is the Green's function of the photon, and μ, ν are the indices running the values 0,1,2,3. Then, the zero component of $A_\mu(x)$ corresponds to the Coulomb interaction, and the components 1,2,3 are the transversal part, which gives the interaction of retardation and advance. According to [23–25], the photon Green's function (also called photon propagator or photon propagation function) is represented by the sum of two contributions, which are the result of the expectation value with the states of zero and heated vacuum, $D_{\mu\nu}(x,x') = D^0_{\mu\nu}(x,x') + D^\beta_{\mu\nu}(x,x')$.

Inclusion of the zero component $D^0_{\mu\nu}(x,x')$ into Eq. (1) yields the Coulomb interaction, while the second part, $D^\beta_{\mu\nu}(x_1,x_2)$, provides thermal interaction. Analytical calculations for the $D^\beta_{00}(x,x')$ component were recently presented in [27], where the thermal interaction corresponding to the one thermal photon exchange diagram was obtained in a closed form. Relativistic corrections arising through the transversal part of Eq. (1), i.e., thermal Breit interaction, were discussed in [30], where the contributions proportional to $1/c^2$ (c is the speed of light) were determined. There are several ways to get these corrections [2,4,6,7]. One of them corresponds to the use of the ladder approximation and the subsequent application of unitary transformations; see pp. 374–379 in [7]. Another one can be attributed to the evaluation of the scattering amplitude in the momentum representation; see Secs. 83 and 84 in [4]. The latter was used in [30] and is more convenient for the thermal case due to the presence of the Planck distribution function, $n_\beta(k) = (e^{\beta k}-1)^{-1}$, which depends on the frequency of the photon responsible for the exchange interaction. In the case of the photon propagation function $D^0_{\mu\nu}(x,x')$, the coordinate representation arises through the Fourier transform, but in the thermal case, it should be doubled; see [30] for details.

Repeating the calculations performed in [30] for particles with the same masses, the total contribution to the binding energy in the lowest order in temperature for the positronium atom can be written as

$$U(\vec{p}_1,\vec{p}_2,\vec{r}_{12}) = -\frac{4\zeta(3)e^2}{3\pi\beta^3}r_{12}^2 + \frac{8\zeta(3)e^2}{5\pi\beta^3m^2c^2}r_{12}^2(\vec{p}_1\cdot\vec{p}_2) + \frac{8\zeta(3)e^2}{15\pi\beta^3m^2c^2}\vec{r}_{12}(\vec{r}_{12}\cdot\vec{p}_2)\vec{p}_1 - \frac{2\zeta(3)e^2}{3\pi\beta^3m^2c^2}[\vec{\sigma}_1\cdot(\vec{r}_{12}\times\vec{p}_1)]$$
$$+ \frac{2\zeta(3)e^2}{3\pi\beta^3m^2c^2}[\vec{\sigma}_2\cdot(\vec{r}_{12}\times\vec{p}_2)] + \frac{4\zeta(3)e^2}{3\pi\beta^3m^2c^2}[\vec{\sigma}_1\cdot(\vec{r}_{12}\times\vec{p}_2)] - \frac{4\zeta(3)e^2}{3\pi\beta^3m^2c^2}[\vec{\sigma}_2\cdot(\vec{r}_{12}\times\vec{p}_1)], \quad (2)$$

where e and m are the charge and mass of the electron, respectively, c is the speed of light (these constants are written out explicitly for clarity), $\vec{\sigma}_i$ with $i=1,2$ is the Pauli matrix, $\vec{r}_i$ represents the radius vector of the corresponding particle, $r_{12}\equiv|\vec{r}_1-\vec{r}_2|$, and $\zeta(s)$ gives the Riemann zeta function [31].

However, the expression (2) corresponds to the "direct" scattering diagram. For positronium, there is also a second independent contribution corresponding to the "exchange" or "annihilation" diagram since the wave function of the electron-positron system need not be antisymmetric [4]. Evaluation of the corresponding operator can be found in Sec. 84 of [4]. Then, applying the Fourier transform as in [30], we find the annihilation amplitude in a coordinate space,

$$U^{(\mathrm{ann})} = \frac{\pi e^2}{m^2c^2}\int\frac{d^3k}{(2\pi)^3}e^{i\vec{k}(\vec{r}_1-\vec{r}_2)}n_\beta(|\vec{k}|)[3+\vec{\sigma}_1\cdot\vec{\sigma}_2]. \quad (3)$$

Performing the remaining integrations, we obtain

$$U^{(\mathrm{ann})} = \frac{ie^2[3+\vec{\sigma}_1\cdot\vec{\sigma}_2]}{4\pi m^2c^2\beta^2 r_{12}}\left[\psi^{(1)}\left(1+\frac{ir}{\beta}\right)-\psi^{(1)}\left(1-\frac{ir}{\beta}\right)\right]$$
$$\approx\left[\frac{e^2\zeta(3)}{\pi\beta^3c^2m^2}-\frac{2e^2\zeta(5)}{\pi\beta^5c^2m^2}r_{12}^2\right](3+\vec{\sigma}_1\cdot\vec{\sigma}_2), \quad (4)$$

where $\psi^{(1)}(x)$ represents the first derivative of the Digamma function. The first term in square brackets is state independent (in the sense of r_{12}) and can simply be omitted or canceled by the coincidence limit; see [27,30] for details. The second contribution is β^2 times smaller [$\beta^{-1}\sim m\alpha^2(k_BT)$ in relativistic units and is about 9.5×10^{-4} in atomic units at 300 K] and therefore insignificant at low temperatures.

In the center-of-mass reference frame, the electron and positron momentum operators in positronium are $\vec{p}_1 = -\vec{p}_2\equiv\vec{p}$, where $\vec{p}=-i\vec{\nabla}$ is the operator of the momentum of relative motion corresponding to relative position vector $\vec{r}\equiv\vec{r}_{12}=\vec{r}_1-\vec{r}_2$. Then the thermal contribution given by Eq. (2) reduces to

$$U = -\frac{4\zeta(3)e^2}{3\pi\beta^3}r^2 - \frac{16\zeta(3)e^2}{15\pi\beta^3m^2c^2}r^2p^2$$
$$-\frac{8\zeta(3)e^2}{15\pi\beta^3m^2c^2}\vec{l}^2 - \frac{4\zeta(3)e^2}{\pi\beta^3m^2c^2}(\vec{S}\cdot\vec{l}), \quad (5)$$

where we have introduced the operators of the total spin $\vec{S}=\frac{1}{2}(\vec{\sigma}_1+\vec{\sigma}_2)$ and the orbital angular momentum $\vec{l}=[\vec{r}\times\vec{p}]$ and used the relation $\vec{l}^2\equiv[\vec{r}\times\vec{p}]^2=r^2p^2-(\vec{r}\cdot\vec{p})^2+i(\vec{r}\cdot\vec{p})$ in combination with the commutator $[r_i,p_j]=i\delta_{ij}$; see [2,4] for details.

Now an estimate of the average values of the operators given by Eq. (5) can be done as follows. Since the reduced mass of a bound electron in a positronium atom is half that in hydrogen, the matrix element $\langle a|r^2|a\rangle = 2n_a^2[5n_a^2+1-3l_a(l_a+1)]$ for an arbitrary a-state. The average value of the third term in Eq. (5) gives $l_a(l_a+1)$ and the fourth can be found as $\langle a|(\vec{S}\cdot\vec{l})|a\rangle = \frac{1}{2}[j_a(j_a+1)-l_a(l_a+1)-S_a(S_a+1)]$.

TABLE I. Numerical values of the energy shift corresponding to thermal corrections given by Eq. (6) at room temperature (300 K) in Hz. The first column indicates the specific state of the positronium atom. The columns show the values obtained for the first, second, and third contributions, respectively.

State	1	2	3
1^1S_0	–84.33	0.0	0.0
1^3S_1	–84.33	0.0	0.0
2^1S_0	–1180.67	-4.491×10^{-4}	0.0
2^3S_1	–1180.67	-4.491×10^{-4}	0.0
2^1P_1	–843.34	-1.048×10^{-3}	0.0
2^3P_0	–843.34	-1.048×10^{-3}	2.246×10^{-3}
2^3P_1	–843.34	-1.048×10^{-3}	1.123×10^{-3}
2^3P_2	–843.34	-1.048×10^{-3}	-1.123×10^{-3}

Finally, to evaluate the second term, we take into account that $p^2\psi_a = (E + 1/r)\psi_a$, which follows from the Schrödinger equation for positronium, where E represents the energy levels of positronium: $E_{n_a} = -1/4n_a^2$. Then, the average value of $(r^2p^2)\psi_a = [-r^2/(4n_a^2) + r]\psi_a$ can be easily calculated using $\langle a|r|a\rangle = 3n_a^2 - l_a(l_a + 1)$ and, therefore, $\langle a|r^2p^2|a\rangle = \frac{1}{2}[n_a^2 - 1 + l_a(l_a + 1)]$. In total, we have

$$\begin{aligned}\langle a|U|a\rangle = &-\frac{8\zeta(3)\alpha^3}{3\pi\beta^3}n_a^2\left[5n_a^2 + 1 - 3l_a(l_a + 1)\right]\\ &-\frac{8\zeta(3)\alpha^5}{15\pi\beta^3}\left[n_a^2 - 1 + 2l_a(l_a + 1)\right]\\ &-\frac{2\zeta(3)\alpha^5}{\pi\beta^3}[j_a(j_a + 1) - l_a(l_a + 1) - S_a(S_a + 1)].\end{aligned} \tag{6}$$

This expression is written in atomic units and $1/\beta = k_BT = 3.16681\times10^{-6}T$.

The numerical results for some low-lying states in the positronium atom are given in Table I. The values listed in Table I demonstrate that the effects described above are two orders of magnitude smaller and thus fall outside the precision of modern laboratory experiments, which is typically around MHz for positronium [19].

III. STARK SHIFT AND BBR-INDUCED WIDTH

In this part of the work, we briefly describe the thermal Stark shift for Ps. The corresponding derivations can be attributed to the earlier work [21], where a quantum mechanical description of the ac-Stark shift and the transition rate induced by blackbody radiation was given. However, here we apply the QED formalism discussed in [26] for the appropriate derivations and further calculations in the positronium atom. According to [26], within the framework of the QED approach at finite temperatures, it is sufficient to evaluate the one-loop self-energy correction (see, also, [27]). Then, replacing the "ordinary" photon line by a thermal one, the real part of this correction gives the ac-Stark effect, while the imaginary part is the level width (the sum of all partial transition to the lower and upper states) induced by the BBR.

After several successive conversions, the thermal photon propagator (see [26,27]) can be found as

$$D^{\beta}_{\mu\nu}(x_1, x_2) = -\frac{g_{\mu\nu}}{\pi r_{12}}\int_{-\infty}^{+\infty} d\omega n_\beta(|\omega|)\sin|\omega|r_{12}e^{-i\omega(t_1-t_2)}. \tag{7}$$

The energy shift determined by the one-loop self-energy correction for an arbitrary state a is

$$\Delta E^{\beta}_a = \frac{e^2}{\pi}\sum_n\left[\frac{1 - \vec{\alpha}_1\cdot\vec{\alpha}_2}{r_{12}}I^{\beta}_{na}(r_{12})\right]_{\text{anna}}, \tag{8}$$

where

$$I^{\beta}_{na}(r_{12}) = \int_{-\infty}^{+\infty} d\omega n_\beta(|\omega|)\frac{\sin|\omega|r_{12}}{E_n(1 - i0) - E_a + \omega}. \tag{9}$$

Here the sum runs over the entire spectrum n, including the continuum, and the matrix element is to be understood as $[\hat{A}(12)]_{abcd} \equiv \langle a(1)b(2)|\hat{A}|c(1)d(2)\rangle$ [6].

Omitting the description of the effect associated with the finite lifetime of states (see [26] for details), the result can be obtained using the Sokhotski-Plemelj theorem:

$$\lim_{\epsilon\to 0}\frac{1}{x \pm i\epsilon} = \text{P.V.}\left(\frac{1}{x}\right) \mp i\pi\delta(x), \tag{10}$$

where P.V. means the principal value. Then, one can find

$$\begin{aligned}I^{\beta}_{na}(r_{12}) = &\sum_{\pm}\text{P.V.}\int_0^{\infty} d\omega\, n_\beta(\omega)\frac{\sin\omega r_{12}}{E_n - E_a \pm \omega}\\ &+ i\pi n_\beta(|E_{an}|)\sin|E_{an}|r_{12},\end{aligned} \tag{11}$$

where $E_{na} = E_n - E_a$ and $\sum_{\pm}$ means the sum of two contributions with $-$ and $+$ before ω in the energy denominator.

Equation (11) already demonstrates the existence of real and imaginary contributions for the energy shift (8). To give them a physical interpretation, it is useful to consider the nonrelativistic limit that arises when using the Taylor series expansion for $\sin\omega r_{12} \approx \omega r_{12} - \frac{1}{6}(\omega r_{12})^3$. Then the imaginary part (see [26,27]) is

$$\Gamma^{\beta}_a \equiv -2\text{Im}\Delta E^{\beta}_a = \frac{4}{3}e^2\sum_n|\langle a|\vec{r}|n\rangle|^2 n_\beta(|\omega_{an}|)\omega^3_{an}. \tag{12}$$

The real part should be considered more carefully. By truncating the sin Taylor series with two terms, the real part is

$$\begin{aligned}\text{Re}\Delta E^{\beta}_a \approx &\frac{e^2}{\pi}\sum_n\text{P.V.}\int_0^{\infty} d\omega n_\beta(\omega)\left(\frac{1}{E_n - E_a - \omega}\right.\\ &\left.+\frac{1}{E_n - E_a + \omega}\right)\left(\omega - \omega\vec{\alpha}_1\vec{\alpha}_2 - \frac{1}{6}\omega^3 r^2_{12}\right)_{\text{anna}}.\end{aligned} \tag{13}$$

Hereafter, we use that the sum in square brackets is $2E_{na}/(E^2_{na} - \omega^2)$. Then the first term is equal to zero due to the orthogonality property of wave functions and the presence of $E_{na} = 0$ in the numerator for $n = a$.

Using the relations $(\vec{\alpha}_1\cdot\vec{\alpha}_2)_{\text{anna}} = E^2_{an}(\vec{r}_1\cdot\vec{r}_2)_{\text{anna}}$, $r^2_{12} = r^2_1 + r^2_2 - 2(\vec{r}_1\cdot\vec{r}_2)$ [6] and substituting $\pm\omega^3$ for the term with

TABLE II. The ac-Stark shift, given by Eq. (15), induced by the blackbody radiation in Hz for the *ns* states in the positronium atom for different temperatures T. The first column contains the considered n values.

a	$T = 5.5$ K	$T = 77$ K	$T = 300$ K	$T = 1000$ K
1s	-1.78×10^{-9}	-8.41×10^{-5}	-0.0194	-2.39
2s	1.09×10^{-6}	-1.93×10^{-3}	-0.495	-63.6
3s	1.83×10^{-6}	-1.85×10^{-2}	-4.47	-736.1
4s	5.76×10^{-7}	-9.28×10^{-2}	-25.2	-1467.5
5s	-8.11×10^{-6}	-0.342	-104.5	856.2

$\vec{\alpha}$ matrices, we find

$$\mathrm{Re}\Delta E_a^{\beta} = \frac{4e^2}{3\pi}\sum_n \mathrm{P.V.}\int_0^{\infty} d\omega \frac{\omega^3 E_{an} n_{\beta}(\omega)}{E_{an}^2-\omega^2}|\langle a|\vec{r}|n\rangle|^2 + \frac{2e^2}{\pi}\sum_n \mathrm{P.V.}\int_0^{\infty} d\omega \frac{E_{na} n_{\beta}(\omega)}{E_{na}^2-\omega^2} \times \left(\omega^3-\omega E_{na}^2\right)|\langle a|\vec{r}|n\rangle|^2. \quad (14)$$

The first contribution represents the well-known ac-Stark shift induced by the blackbody radiation field,

$$\Delta E_a^{\mathrm{Stark}} = \frac{4e^2}{3\pi}\sum_n \mathrm{P.V.}\int_0^{\infty} d\omega \frac{E_{an} n_{\beta}(\omega)\omega^3}{E_{an}^2-\omega^2}|\langle a|\vec{r}|n\rangle|^2. \quad (15)$$

Parametric estimation of Eqs. (12) and (15) is given as $m\alpha^5(k_BT)^4/Z^4$ in relativistic units, where the Boltzmann constant should be taken in atomic units. To get the result in completely atomic units, it is necessary to divide this estimate by $m\alpha^2$.

Then, to evaluate the ac-Stark, $\mathrm{Re}\Delta E_a^{\beta}$, and level width, Γ_a^{β}, for the positronium atom, it is sufficient to take into account the coefficient 1/2, arising from the reduced mass. The calculated values are given in Tables II and III for the Stark shift, given by Eq. (15), and depopulation rates induced by BBR, given by Eq. (12), respectively. The numerical results listed in Tables II and III show that the ac-Stark shift does not exceed a few Hz, while the line broadening remains insignificant at room temperature for low-lying states.

The second term in Eq. (14) (indicated by a cross below) is more delicate. First of all, the energy denominator is canceled by the numerator, which gives

$$\Delta E_a^{\beta,\times} = -\frac{2e^2}{\pi}\sum_n \mathrm{P.V.}\int_0^{\infty} d\omega\, \omega n_{\beta}(\omega) E_{an}|\langle a|\vec{r}|n\rangle|^2. \quad (16)$$

TABLE III. The BBR-induced depopulation rates in s^{-1} for the *ns* states in the positronium atom, given by Eq. (12), for the different temperatures T. The first column contains the considered n values.

a	$T = 5.5$ K	77 K	$T = 300$ K	$T = 1000$ K
$2s$	1.310×10^{-7}	1.826×10^{-6}	7.114×10^{-6}	1.012×10^{-2}
$3s$	8.329×10^{-8}	1.164×10^{-6}	4.018×10^{-5}	2172.99
$4s$	4.130×10^{-8}	5.779×10^{-7}	7.973	3.679×10^{4}
$5s$	2.432×10^{-8}	5.102×10^{-6}	598.2	9.034×10^{4}

Then, using the sum rule for the oscillator strength, one can find that this contribution is constant and independent of states. Thus, it represents an immeasurable contribution to the atomic energy of the bound electron and can be thrown away [32].

The results given by Eqs. (12), (15), and (16) are related to the 'direct' Feynman diagram. Along with this, the annihilation diagram should be considered, when the thermal photon loop connects the electron tail with the positron one. In this case, the energy difference $E_{an} \sim 2mc^2$; see [4]. Then, for the ac-Stark shift, given by Eq. (15), we have

$$\Delta E_a^{\mathrm{Stark\,(ann)}} = -\frac{2e^2\pi^3}{45\beta^4 mc^4}\langle a|r^2|a\rangle \sim \alpha^7(k_BT)^4. \quad (17)$$

The estimate in the expression above is written in atomic units, where we took into account that $\langle r\rangle \sim 1/mc$ for the positronium; see [2]. This contribution is α^4 times less and, therefore, goes beyond the scope of interest. The same conclusion can be made for the imaginary part of Eq. (12), i.e., the broadening of the spectral emission line between bound states due to the annihilation contribution can be neglected since $n_{\beta}(mc^2) \to 0$.

The remaining second term in Eq. (14) turns out to be important for the annihilation contribution. Replacing again E_{an} by the $2mc^2$, we can sum over n and find $\sum_n |\langle a|\vec{r}|n\rangle|^2 = \langle a|r^2|a\rangle$. Then, we arrive at

$$\Delta E_a^{\beta(\mathrm{ann}),\times} = \frac{e^2\pi mc^2}{3\beta^2}\langle a|r^2|a\rangle \sim \alpha^3(k_BT)^2 \text{ in a.u.}, \quad (18)$$

which is opposite in sign to Eq. (16) due to the signs of the charges. The final result for the thermal correction given by Eq. (18) can be written using the analytical relation $\langle a|r^2|a\rangle = 2n_a^2[5n_a^2+1-3l_a(l_a+1)]$ in a positronium:

$$\Delta E_a^{\beta(\mathrm{ann})} = \frac{2\pi\alpha^3}{3}n_a^2\big[5n_a^2+1-3l_a(l_a+1)\big](k_BT)^2. \quad (19)$$

Note that the expression (16) corresponds to a "direct" particle-to-particle loop. Phenomenologically, to get the "annihilation" diagram (particle-to-antiparticle loop) from the direct one, one can change the sign in one of the energies in E_{an}, which will lead to the sum of the energy modules. Then, since we are considering a nonrelativistic atom, this sum is almost equal to the rest mass of the positronium, which is $2mc^2$ up to relativistic corrections.

In particular, from the expression (19) follows that this thermal correction is different for the states with different orbital angular momenta and does not depend on total angular momentum. To approximate the experimental conditions [33–35] and visualize the behavior of the thermal correction with temperature, the numerical results for some transition intervals (or energy difference of atomic states) are collected in Table IV at room $T = 300$ K, $T = 600$ K, and $T = 1000$ K temperatures.

As follows from Table IV, the values obtained using Eq. (19) are at the MHz level at room temperature and have a temperature scaling factor T^2, increasing the correction to several MHz with increasing temperature. It can be seen that the thermal correction (19) becomes essential, reaching a level of experimental uncertainty for the $2s-1s$ transition frequency. Another significant result arises for

TABLE IV. Numerical values of the energy shift of transition intervals corresponding to thermal corrections Eq. (19) at room (300 K), $T = 600$ K and $T = 1000$ K temperatures in MHz (in the fourth, fifth and sixth columns, respectively). The first column indicates the specified energy difference of the positronium atom. The second and third columns show the experimental and theoretical values of the transition frequency with the corresponding uncertainties. Since the thermal correction Eq. (19) does not depend on total angular momentum and spin, we present completely nonrelativistic hydrogen-like values for all transitions, including those between fine structure sublevels.

Transition	Expt. value (MHz)	Theory (MHz)	MHz (300 K)	MHz (600 K)	MHz (1000 K)
$2S - 1S$	$1\,233\,607\,216.4 \pm 3.2$	$1\,233\,607\,221.7 \pm 10$[a]	0.754	3.016	8.378
$2^3S_1 - 2^3P_0$	$18\,501.09 \pm 0.62_{\rm stat} \pm 0.323_{\rm sys}$	$18\,498.25 \pm 0.08$			
$2^3S_1 - 2^3P_1$	$13\,014.13 \pm 0.58_{\rm stat} \pm 0.229_{\rm sys}$	$13\,012.41 \pm 0.08$	0.232	0.928	2.578
$2^3S_1 - 2^3P_2$	$8628.28 \pm 0.35_{\rm stat} \pm 0.157_{\rm sys}$	8626.71 ± 0.08[b]			

[a]The values are borrowed from [36,37].
[b]The values are borrowed from Table VI in [38].

the transition frequencies between fine-structure sublevels in positronium, recently measured in [19,38]. The results of Table IV show that this deviation is eliminated by thermal correction [Eq. (19)], at least partially. For comparison, Table IV also lists theoretical values indicating the existing discrepancies between theory and experiment.

To complete this part of the discussion, we additionally point out that the partial transition rates between hyperfine split bound states are of particular interest. According to Eq. (12), the partial transition rate is determined with a fixed value of n. To obtain the transition rate induced by blackbody radiation, it is sufficient to multiply the spontaneous transition rate by $n_\beta(\omega_0)$, where ω_0 is the resonant frequency. For example, for the transition $1^3S_1 - 1^1S_0$, the coefficient $n_\beta(\omega_{1^3S_1-1^1S_0}) = 4.408$, and for the transition $2^3S_1 - 1^2S_0$, the coefficient $n_\beta(\omega_{2^3S_1-2^1S_0}) = 38.637$ at room temperature, which leads to significant thermal broadening of the corresponding spectral lines.

IV. VACUUM POLARIZATION AND QUADRATIC ZEEMAN SHIFTS: A BRIEF DISCUSSION

To maintain consistency, the effect of vacuum polarization should be taken into account. However, as shown in [27], this effect is proportional to β^{-5} and the additional α due to the factor e^2 in the vacuum polarization operator, so it leads to an insignificant contribution. A similar result can be obtained for the positronium atom. Using the thermal Coulomb gauge, three possibilities arise: (i) the exchange of a thermal photon between the bound particle and the loop, with the "ordinary" photon propagator for the exchange between the loop and the "external" charge; (ii) the reverse case when the thermal and ordinary photon lines replace each other; (iii) both photon lines correspond to the thermal part of the photon propagator. For all these contributions, the estimates turn out to be proportional to $(k_BT)^5$. Finally, the annihilation diagram remains the subject of investigation. Our estimates show that the thermal vacuum polarization is even smaller in this case since the factor $2mc^2$ (representing the energy transfer for an electron and a positron at rest) is included in the Planck's distribution function. It can be concluded that the thermal effect of vacuum polarization is beyond the scope of current interest, at least at room temperature.

Another effect in positronium that occurs in a thermal environment can be easily obtained according to [2]. Since the Ps atom lacks the Zeeman effect linear in the magnetic field, the quadratic shift for S-states was found as

$$\delta E = \pm\frac{\left(\frac{e\hbar}{mc}H\right)^2}{\Delta E}, \tag{20}$$

where H is the magnetic field strength and ΔE is the energy difference between the singlet and triplet levels. The minus sign corresponds to a singlet and the plus sign corresponds to a triplet states (it is assumed that $\Delta E > 0$). Then, following [39], we can estimate field B with the use of relation

$$\begin{aligned} B^2(\omega)d\omega &= \frac{8\alpha^3}{\pi}\frac{\omega^3 d\omega}{e^{\beta\omega}-1}\langle B^2(t)\rangle \\ &= (2.775(\times)10^{-2}G)^2\left[\frac{T(K)}{300}\right]^4, \end{aligned} \tag{21}$$

where B is written in gauss ($1G = 10^{-4}T$) at room temperature. The magnetic field strength H is connected with the B field via the vacuum permeability $\mu_0 = 1.256\,637\,062\,12\times10^{-6}$ H/m. Then, for the ground state with $\Delta E = 203\,389.10(74)$ MHz for the energy splitting, we get 1650 Hz at room temperature and 0.204 MHz at $T = 1000$ K. In turn, for the $2^3S_1 - 2^1S_0$ with the hyperfine structure energy about 25 422 MHz we obtain 13.204 kHz at room temperature and 1.63 MHz at $T = 1000$ K, respectively. These results demonstrate the importance of the Zeeman shift induced by blackbody radiation for the hyperfine energy sublevels in the positronium atom.

From expressions (20) and (21), it is possible to determine the influence of blackbody radiation on the decay probabilities of ortho- and parapositronium. According to the theory in Sec. 39.4 in [2], we can write down the decay rate of positronium as

$$W = |C_0|^2W_0 + |C_1|^2W_1, \tag{22}$$

where W_0 and W_1 are the decay rates of para- and orthopositronium per unit time, respectively. The coefficients C_0 and C_1 can be found with

$$\begin{aligned} &|C_0|^2 + |C_1|^2 = 1, \\ &\left|\frac{C_0}{C_1}\right|^2 = \frac{\left(\frac{e\hbar}{mc}H\right)^2}{\Delta E^2}. \end{aligned} \tag{23}$$

Then the result is $C_0 = 6.37\times10^{-5}$ and $C_1 \approx 1$, which gives the annihilation decay correction expressed in terms of the zero order for the ground state of orthopositronium: $\delta W_1 \approx 4.0574\times10^{-9}[\frac{T(K)}{300K}]^4 W_0$. Considering that the contribution increases with the fourth power of the temperature, one can find the coefficient 5.01×10^{-7} at 1000 K. This contribution can be compared with the multiphoton decay modes (see [40]), where the branching ratio of the 4γ decay to the 2γ annihilation of parapositronium is about 1.48×10^{-6} and $5\gamma/3\gamma$ for orthopositronium is 9.6×10^{-7}. In the same way, one can find a correction for the annihilation decay of the $2s$ triplet state in positronium determined by the coefficients $C_0 = 5.096\times10^{-4}$, $C_1 \approx 1$ at room temperature, leading to $\delta W_1 \approx 2.5969\times10^{-7}[\frac{T(K)}{300K}]^4 W_0$. Using the results $\tau^{\text{ann.}}_{2^1S_0} = 1$ ns and $\tau^{\text{ann.}}_{2^3S_1} = 1\,136$ ns [41], one can easily find the value $\delta W_1 \approx 259.69[\frac{T(K)}{300K}]^4$ s^{-1}.

V. INDUCED ANNIHILATION DECAYS

As the next step of our study, the annihilation decays of positronium induced by blackbody radiation should be considered. Here we restrict ourselves to describing the BBR-induced decays for two- and three-photon processes only as the dominant contributions to the annihilation of para- and orthopositronium, respectively. A large number of theoretical and experimental works are devoted to the study of these processes and the corrections to them (see, for example, works [40,42–47]), although the theory describing the dominant processes can be found in the textbooks [2,4,7].

According to the quantum mechanical approach, stimulated emission is taken into account by inserting the Planck distribution function at the "resonant" frequency of the corresponding process. Then, considering two-photon annihilation in the positronium center-of-mass system, we immediately find that $\omega = \omega'$ [2,4] and the presence of $\delta(\varepsilon_- + \varepsilon_+ - \omega - \omega')$, where ε_-, ε_+ are the rest energies of an electron and a positron, respectively, leads to the fact that $\omega \approx mc^2$. This argument of the Planck distribution function is large and lies in the region of negligible values of $n_\beta(mc^2)$. Thus, a stimulated two-photon process can be excluded from the consideration.

The picture is different for three-photon annihilation decay. According to [2], the total probability of three-photon annihilation is

$$\overline{W}_{3\gamma} = \frac{\alpha^3}{16\pi m^4}\int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \int_0^\pi d\theta\, \sin\theta \times \frac{\omega_1\omega_2}{\omega_3}(1-\cos\theta)^2\delta(\omega_1+\omega_2+\omega_3-2m), \quad (24)$$

where θ is the angle between the photon wave vectors $\vec{k}_1$ and $\vec{k}_2$. The evaluation of these integrals was presented in [48].

To obtain the correction caused by the stimulated emission, we should insert the $[1+n_\beta(\omega_1)][1+n_\beta(\omega_2)][1+n_\beta(\omega_3)]$ into Eq. (24). Numerical calculation of the modified expression (24) leads to the correction $\delta\overline{W}_{3\gamma} \approx 5.28\times10^{-6}\overline{W}_{3\gamma}$ at room temperature, which can be directly compared to five-photon annihilation $\overline{W}_{5\gamma} \approx 0.96\times10^{-6}\overline{W}_{3\gamma}$ [40].

VI. CONCLUSIONS AND DISCUSSION

This work is devoted to the thermal effects of various types on the positronium atom. First, we briefly discussed the effect of thermal one-photon exchange; see Sec. II. In contrast to the results of [27,28] for hydrogen and helium atoms, the lower-order thermal correction and the relativistic corrections resulting from the Bethe-Salpeter equation go beyond the current measurement accuracy for the positronium atom, reaching values around kHz. The results are summarized in Table I. Although the values given in Table I correspond to room temperature (300 K), they can easily be extended to higher temperatures using the scale factor T^3. At the same time, corrections related to the fifth power of temperature (which are not considered in this article) are not interesting for positronium: although they grow faster with temperature, they contain an additional factor α and are much smaller.

The most significant result comes from the description of the thermal one-loop self-energy correction; see Sec. III. As described in [26], the real part of this correction represents the BBR-induced Stark effect, while the imaginary part gives the induced widths of the excited atomic levels corresponding to the transitions between bound states. It is found that the BBR-induced Stark shift for highly excited states cannot exceed a few kHz at room temperature, and the rates of the induced transitions between bound states hardly reach the values of the Doppler broadening [49].

However, the positronium atom is a more specific atomic system with an additional annihilation channel that should be taken into account. In the case of the thermal one-photon exchange between an electron and a positron, this channel does not make a significant contribution, but it is strong in the thermal one-loop self-energy correction. The dominant temperature contribution is expressed by Eq. (18). The numerical values are collected in Table IV at different temperatures for some transition energies. In particular, Table IV shows that this correction is about 1 MHz at room temperature. The values $T = 600$ and 1000 K were chosen to match experimental settings where the target was heated to this temperature range [33–35].

Another remarkable result was obtained by considering the quadratic Zeeman shift; see Sec. IV. A simple quantum mechanical description (see [2]) gives a correction that is quadratic in the magnetic field. The correction, given by Eq. (20), can be fitted to the energy shift caused by blackbody radiation [39]. For the hyperfine splitting of the ground state and the $n = 2$ state in the Ps atom, an additional energy splitting of the order of a few kHz is found at room temperature. The scaling factor T^4 can be used to obtain the corresponding contribution at different temperatures, which increases up to MHz at 1000 K. Moreover, the effect expressed by formula (20) can be taken into account to determine the corrections to the annihilation probabilities; see Eqs. (22) and (23). As mentioned in [2], even a weak magnetic field can significantly increase the annihilation probability of the triplet state due to the admixture of the singlet state. We have found that in the blackbody radiation field at room temperature, the effect is of the order of $\delta W_1/W_1 \sim 4\times10^{-9}$ for the 1^3S_1 state and $\delta W_1/W_1 \sim 2.6\times10^{-7}$ for the 2^3S_1 state.

Finally, in Sec. V, we briefly discussed the stimulated annihilation probabilities induced by blackbody radiation. It was found that in the case of two-photon annihilation, the contribution is completely insignificant. On the contrary, a rough estimate of the probability of stimulated three-photon annihilation at room temperature is comparable to five-photon annihilation.

Summarizing all the results, one can conclude that thermal effects are of particular importance in experiments with positronium. Their contribution can reach a magnitude that can at least partially resolve the disagreement (about 2 MHz) between experiment and theory [19]. The development of positronium experiments at cryogenic temperatures and lower [50] is even more important for the matching between theoretical and experimental results.

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