Some approximate positronium solutions to the Breit-Coulomb equation

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Positronium wave functions that are approximate solutions to the Breit-Coulomb equation are constructed for the $1\,^1S_0$, the $(L+1)\,^3L_J$, and the non-S $n\,^1L_L$ states. The energies of these wave functions are accurate up through $O(\alpha^4)$, giving the correct Coulomb part of the positronium energy levels to this order. Using only first-order perturbation theory, the energy eigenvalues of the Breit-Coulomb equation are calculated to $O(\alpha^6)$ for these quantum states.

I. INTRODUCTION

In many of the calculations that have been done on the energy levels and decay rates of positronium, the starting point has been the Bethe-Salpeter equation, or some variant of it; an approximate solution is found and used as the lowest-order wave function in a perturbation expansion. Examples of approximate solutions are those found by Barbieri and Remiddi[1] and by Lepage.[2] In positronium, the degeneracy of the Schrödinger energy levels is lifted by relativistic corrections to the Coulomb potential, by transverse photon exchange, and by annihilation into one or more photons. Each of these effects contributes a term of $O(\alpha^4)$ to the hyperfine splitting. Even if we consider only the part of the energy that comes from the Coulomb potential, the Barbieri-Remiddi and the Lepage solutions give the correct energy only to $O(\alpha^2)$. We can ask, is it possible to do better than this, and construct approximate wave functions that give the correct $O(\alpha^4)$ energy term (even if only for the Coulomb part of the energy)? Such wave functions would presumably be more accurate than solutions which do not.

The Breit equation, with various expressions for the potential function, has a long history,[3–9] starting with Breit's original paper in 1929. It is perhaps the simplest two-body relativistic wave equation. In a previous paper[10] (paper I), the equal-mass Breit equation, with a Coulomb potential, was reduced to sets of four coupled first-order differential equations for the radial wave functions of the $^{1,3}L_L$ and the $^3P_0$ states, and to a single set of six coupled equations for the $^3L_{L\pm1}$ states. The sets of four coupled equations were then further reduced to an equivalent Schrödinger equation. (See also the earlier paper by Partovi and Jabbarian-Lotfabadi.[7]) In this paper we will show that the coupled radial equations for the $^3L_{L\pm1}$ states can also be reduced to the same Schrödinger equation, once an approximation is made. Then, an additional approximation is made in the equivalent equation which allows us to solve for the ground-state Schrödinger wave functions. From these functions we construct approximate radial functions and energy levels for the Breit-Coulomb equation. These energy levels agree with the Coulomb part of the $O(\alpha^4)$ contribution to the hyperfine splitting, calculated from perturbation theory.

The outline of the paper is as follows: In Sec. II the coupled radial equations for the Breit-Coulomb equation (after an approximation is made for the $L=J\pm1$ functions) are reduced to an equivalent equation for the function $u(r)$. In Sec. III solutions are found to an approximation of this equivalent equation, and in Sec. IV energy eigenvalues of the Breit-Coulomb equation are calculated to $O(\alpha^6)$ using first-order perturbation theory.

II. BREIT-COULOMB RADIAL EQUATIONS

The equal-mass Breit-Coulomb equation is (in units where $\hbar=c=1$)

$$-i\boldsymbol{\alpha}\cdot\nabla\Psi(\mathbf{r})-i\nabla\Psi(\mathbf{r})\cdot\boldsymbol{\alpha}+m[\beta\Psi(\mathbf{r})-\Psi(\mathbf{r})\beta]-\frac{\alpha}{r}\Psi(\mathbf{r})=E\Psi(\mathbf{r})\ , \quad (1)$$

where $\mathbf{r}\equiv\mathbf{r}_- - \mathbf{r}_+$ is the relative separation of the two particles. Due to the invariance of this equation under the parity and charge-conjugation operations, the solutions have either the angular momentum structure,

$$\Psi=N\begin{bmatrix}\dfrac{Q_+(r)}{r}\Omega_{J+11JM}+\dfrac{Q_-(r)}{r}\Omega_{J-11JM} & \dfrac{P(r)}{r}\Omega_{JSJM}\\ \dfrac{R(r)}{r}\Omega_{JSJM} & (-1)^S\left[\dfrac{Q_+(r)}{r}\Omega_{J+11JM}+\dfrac{Q_-(r)}{r}\Omega_{J-11JM}\right]\end{bmatrix} \quad (2a)$$

(with $S=0,1$), or

$$\Psi=N\begin{bmatrix} \frac{Q_0(r)}{r}\Omega_{J0JM}+\frac{Q_1(r)}{r}\Omega_{J1JM} & \frac{P_+(r)}{r}\Omega_{J+11JM}+\frac{P_-(r)}{r}\Omega_{J-11JM} \\ \frac{R_+(r)}{r}\Omega_{J+11JM}+\frac{R_-(r)}{r}\Omega_{J-11JM} & \frac{Q_0(r)}{r}\Omega_{J0JM}-\frac{Q_1(r)}{r}\Omega_{J1JM} \end{bmatrix}, \tag{2b}$$

where the P, Q, and R functions depend only on r, and the $\Omega_{LSJM}(\hat{\mathbf{r}})$ are 2×2 matrices defined in the Appendix which are functions of the angular and spin variables. The inner product of these wave functions is defined as

$$(\Psi|\Phi)\equiv\int \mathrm{Tr}\left[\Psi^\dagger(\mathbf{r})\Phi(\mathbf{r})\right]d\mathbf{r}\ , \tag{3}$$

with normalization[11]

$$(\Psi|\Psi)=2E\ . \tag{4}$$

The wave functions in Eq. (2a) will be labeled by the quantum numbers $L=J$, S, and M; i.e., by the quantum numbers of its "large-large" component. The functions in Eq. (2b) will be labeled by either $L=J+1$, $S=1$, J, and M, if $|P_+|\gg|P_-|$, or by $L=J-1$, $S=1$, J, and M, if $|P_+|\ll|P_-|$.

We define the dimensionless radial variable ρ as $\rho=\alpha Er$. Equation (1) is equivalent, for $S=0$, to the set of coupled equations below for the radial functions:

$$\frac{dP}{d\rho}-\frac{J+1}{\rho}P+\frac{dR}{d\rho}-\frac{J+1}{\rho}R+\frac{i}{\alpha}\left[\frac{2J+1}{J+1}\right]^{1/2}\left[1+\frac{\alpha^2}{\rho}\right]Q_+=0\ , \tag{5a}$$

$$\frac{dP}{d\rho}+\frac{J}{\rho}P+\frac{dR}{d\rho}+\frac{J}{\rho}R-\frac{i}{\alpha}\left[\frac{2J+1}{J}\right]^{1/2}\left[1+\frac{\alpha^2}{\rho}\right]Q_-=0\ , \tag{5b}$$

$$\left[\frac{J+1}{2J+1}\right]^{1/2}\left[\frac{dQ_+}{d\rho}+\frac{J+1}{\rho}Q_+\right]-\left[\frac{J}{2J+1}\right]^{1/2}\left[\frac{dQ_-}{d\rho}-\frac{J}{\rho}Q_-\right]+\frac{i}{2\alpha}\left[1-\frac{2m}{E}+\frac{\alpha^2}{\rho}\right]P=0\ , \tag{5c}$$

$$R=\frac{\rho(E-2m)+\alpha^2E}{\rho(E+2m)+\alpha^2E}P\ , \tag{5d}$$

while for $S=1$, we get

$$\frac{dP}{d\rho}-\frac{J+1}{\rho}P-\frac{dR}{d\rho}+\frac{J+1}{\rho}R-\frac{i}{\alpha}\left[\frac{2J+1}{J}\right]^{1/2}\left[1+\frac{\alpha^2}{\rho}\right]Q_+=0\ , \tag{6a}$$

$$\frac{dP}{d\rho}+\frac{J}{\rho}P-\frac{dR}{d\rho}-\frac{J}{\rho}R-\frac{i}{\alpha}\left[\frac{2J+1}{J+1}\right]^{1/2}\left[1+\frac{\alpha^2}{\rho}\right]Q_-=0\ , \tag{6b}$$

$$\left[\frac{J}{2J+1}\right]^{1/2}\left[\frac{dQ_+}{d\rho}+\frac{J+1}{\rho}Q_+\right]+\left[\frac{J+1}{2J+1}\right]^{1/2}\left[\frac{dQ_-}{d\rho}-\frac{J}{\rho}Q_-\right]-\frac{i}{2\alpha}\left[1-\frac{2m}{E}+\frac{\alpha^2}{\rho}\right]P=0\ , \tag{6c}$$

$$R=-\frac{\rho(E-2m)+\alpha^2E}{\rho(E+2m)+\alpha^2E}P\ . \tag{6d}$$

(To keep the notation from becoming too cumbersome, we will use the same symbols P, R, Q_+, and Q_- for both the $S=0$ and the $S=1$ wave functions. It should be clear from the context which state we are referring to.) As shown in paper I, these two sets of equations are each equivalent to the single equation

$$\frac{d^2u}{d\rho^2}+\left[\frac{1}{2\rho}-\kappa^2-\frac{L(L+1)-\frac{1}{4}\alpha^2}{\rho^2}-\frac{\frac{3}{4}\alpha^4}{\rho^2(\rho+\alpha^2)^2}-\frac{\alpha^2\langle\mathbf{L}\cdot\mathbf{S}\rangle}{\rho^2(\rho+\alpha^2)}\right]u=0\ , \tag{7}$$

$$\langle\mathbf{L}\cdot\mathbf{S}\rangle=\tfrac{1}{2}[J(J+1)-L(L+1)-S(S+1)]\ ,$$

upon the substitution

$$E=\frac{2m}{(1+4\alpha^2\kappa^2)^{1/2}} \tag{8}$$

and

$$P(\rho)=\left[1+\frac{2m}{E}+\frac{\alpha^2}{\rho}\right]\left[\frac{\rho}{\rho+\alpha^2}\right]^{1/2}u(\rho)\ , \tag{9a}$$

where we have used a different normalization for u than in paper I. Then,

$$Q_+=2i\alpha\left[\delta_{S0}\left[\frac{J+1}{2J+1}\right]^{1/2}-\delta_{S1}\left[\frac{J}{2J+1}\right]^{1/2}\right]\times\frac{u}{\sqrt{\rho(\rho+\alpha^2)}}\left[\rho\frac{d\ln u}{d\rho}-J-1-\frac{\frac{1}{2}\alpha^2}{\rho+\alpha^2}\right]\ , \tag{9b}$$

$$Q_-=-2i\alpha\left[\delta_{S0}\left[\frac{J}{2J+1}\right]^{1/2}+\delta_{S1}\left[\frac{J+1}{2J+1}\right]^{1/2}\right]\times\frac{u}{\sqrt{\rho(\rho+\alpha^2)}}\left[\rho\frac{d\ln u}{d\rho}+J-\frac{\frac{1}{2}\alpha^2}{\rho+\alpha^2}\right], \tag{9c}$$

$$R=(-1)^S\left[1-\frac{2m}{E}+\frac{\alpha^2}{\rho}\right]\left[\frac{\rho}{\rho+\alpha^2}\right]^{1/2}u\ . \tag{9d}$$

For the wave function in expression (2b), we define the functions $\tilde{Q}_0$ and $\tilde{Q}_1$ as

$$\tilde{Q}_0=\left[\frac{J+1}{2J+1}\right]^{1/2}Q_0-\left[\frac{J}{2J+1}\right]^{1/2}Q_1\ ,\quad \tilde{Q}_1=\left[\frac{J}{2J+1}\right]^{1/2}Q_0+\left[\frac{J+1}{2J+1}\right]^{1/2}Q_1\ . \tag{10}$$

Then the radial functions in (2b) satisfy the set of coupled equations below:

$$\frac{dP_+}{d\rho}+\frac{J+1}{\rho}P_++\frac{1}{2J+1}\left[\frac{dR_+}{d\rho}+\frac{J+1}{\rho}R_+\right]-\frac{2\sqrt{J(J+1)}}{2J+1}\left[\frac{dR_-}{d\rho}-\frac{J}{\rho}R_-\right]+\frac{i}{\alpha}\left[1+\frac{\alpha^2}{\rho}\right]\tilde{Q}_0=0\ , \tag{11a}$$

$$\frac{dP_-}{d\rho}-\frac{J}{\rho}P_--\frac{1}{2J+1}\left[\frac{dR_-}{d\rho}-\frac{J}{\rho}R_-\right]-\frac{2\sqrt{J(J+1)}}{2J+1}\left[\frac{dR_+}{d\rho}+\frac{J+1}{\rho}R_+\right]-\frac{i}{\alpha}\left[1+\frac{\alpha^2}{\rho}\right]\tilde{Q}_1=0\ , \tag{11b}$$

$$\frac{1}{2J+1}\left[\frac{d\tilde{Q}_0}{d\rho}-\frac{J+1}{\rho}\tilde{Q}_0\right]+\frac{2\sqrt{J(J+1)}}{2J+1}\left[\frac{d\tilde{Q}_1}{d\rho}-\frac{J+1}{\rho}\tilde{Q}_1\right]+\frac{i}{2\alpha}\left[1+\frac{2m}{E}+\frac{\alpha^2}{\rho}\right]R_+=0\ , \tag{11c}$$

$$\frac{1}{2J+1}\left[\frac{d\tilde{Q}_1}{d\rho}+\frac{J}{\rho}\tilde{Q}_1\right]-\frac{2\sqrt{J(J+1)}}{2J+1}\left[\frac{d\tilde{Q}_0}{d\rho}+\frac{J}{\rho}\tilde{Q}_0\right]+\frac{i}{2\alpha}\left[1+\frac{2m}{E}+\frac{\alpha^2}{\rho}\right]R_-=0\ , \tag{11d}$$

$$\frac{d\tilde{Q}_0}{d\rho}-\frac{J+1}{\rho}\tilde{Q}_0+\frac{i}{2\alpha}\left[1-\frac{2m}{E}+\frac{\alpha^2}{\rho}\right]P_+=0, \tag{11e}$$

$$\frac{d\tilde{Q}_1}{d\rho}+\frac{J}{\rho}\tilde{Q}_1-\frac{i}{2\alpha}\left[1-\frac{2m}{E}+\frac{\alpha^2}{\rho}\right]P_-=0\ . \tag{11f}$$

To proceed further, it is necessary to make an approximation. By considering the nonrelativistic (NR) case, we expect that there will be two independent solutions to these equations, corresponding to the NR $L=J-1$ and $L=J+1$ states. The first solution will have $|P_-|\gg|P_+|$, while for the second, $|P_+|\gg|P_-|$. For our approximate solution to the $L=J-1$ state, we will therefore set P_+ to zero. Then from Eq. (11e), $\tilde{Q}_0$ is also zero. We are left with four functions and five equations. Since these are not all compatible (otherwise, $P_+=0$ would be an exact solution) we have to drop one, and we choose to delete Eq. (11c). So our approximate solution for the $L=J-1$ state satisfies Eqs. (11b) and (11f), together with

$$R_-=-\frac{1}{2J+1}\frac{\rho(E-2m)+\alpha^2E}{\rho(E+2m)+\alpha^2E}P_-\ , \tag{12a}$$

$$\frac{d}{d\rho}(\rho^{J+1}R_+)=2\sqrt{J(J+1)}\rho^{2J+1}\frac{d}{d\rho}\left[\frac{R_-}{\rho^J}\right]\ . \tag{12b}$$

This approximation amounts to neglecting the mixing of the different-L, same-J states in the large-large component of Ψ.

Similarly, for the $L=J+1$ state, we set P_- to zero, which by Eq. (11f) requires that $\tilde{Q}_1$ also be zero. We drop the requirement that our functions satisfy Eq. (11d); the remaining four functions then satisfy Eqs. (11a) and (11e) along with

$$R_+=\frac{1}{2J+1}\frac{\rho(E-2m)+\alpha^2E}{\rho(E+2m)+\alpha^2E}P_+\ , \tag{13a}$$

$$\frac{d}{d\rho}\left[\frac{R_-}{\rho^J}\right]=-\frac{2\sqrt{J(J+1)}}{\rho^{2J+1}}\frac{d}{d\rho}(\rho^{J+1}R_+)\ . \tag{13b}$$

[Note that Eqs. (12b) and (13b) do not hold simultaneously, since in the first case $P_+=0$ and in the second, $P_-=0$.] Now employing the substitution (9a) for P_- and P_+, respectively, it is easy to show that both of these sets of equations are also equivalent to Eq. (7). [For the $^3P_0$ state, Eqs. (11a)–(11f) are equivalent to (7) with no approximations, since P_- and $\tilde{Q}_1$ are already zero in this case.]

The justification for these approximations is that, after one further approximation in Sec. III, they allow us to solve for a set of approximate solutions which, when put into the left-hand sides of Eqs. (11c) and (11d), respectively, results in a function which is "small" (of order α^6) for $\rho\gg\alpha^2$.

III. WAVE FUNCTIONS

A. Approximate Schrödinger equation

In this section we make the replacements $\frac{3}{4}\rightarrow\lambda$ and $\langle \mathbf{L}\cdot\mathbf{S}\rangle\rightarrow\mu$ in Eq. (7), and consider instead the operator

$$A(\lambda,\mu)=p^2-\left[\frac{1}{2\rho}-\frac{L(L+1)-\frac{1}{4}\alpha^2}{\rho^2}-\frac{\alpha^4\lambda}{\rho^2(\rho+\alpha^2)^2}-\frac{\alpha^2\mu}{\rho^2(\rho+\alpha^2)}\right], \tag{14}$$

where

$$p=-i\frac{d}{d\rho} \tag{15}$$

and λ and μ are assumed to be adjustable parameters. We are interested in the values of λ and μ for which it is possible to solve for the eigenfunctions of $A(\lambda,\mu)$. In order for these eigenfunctions to be good approximations to the solutions of Eq. (7), we require that

$$\mu\approx\langle \mathbf{L}\cdot\mathbf{S}\rangle \ . \tag{16}$$

To find the eigenvalues and eigenfunctions of A, we use a technique that is described in the elegant little book by Green;[12] we try to write A in the form

$$A=\theta_1^*\theta_1+a^{(1)} , \tag{17}$$

where $a^{(1)}$ is a real number and θ_1^* is the Hermitian conjugate of the operator θ_1. (If this can be done in more than one way, we pick θ_1 to give the largest value of $a^{(1)}$.) We then define the operator A_2 as

$$A_2\equiv\theta_1\theta_1^*+a^{(1)} \tag{18}$$

and attempt to express A_2 as

$$A_2=\theta_2^*\theta_2+a^{(2)} , \tag{19}$$

where θ_2 and $a^{(2)}$ are some other operator and real number, respectively. This process, if continued, will generate a series of operators $A_1=A, A_2, \ldots,$ and real numbers $a^{(1)}, a^{(2)}, \ldots,$ which are the eigenvalues of A. The corresponding eigenfunctions are

$$\psi^{(j)}=\theta_1^*\theta_2^*\cdots\theta_{j-1}^*\phi^{(j-1)} , \tag{20}$$

where $\phi^{(j-1)}$ is defined by

$$\theta_j\phi^{(j-1)}=0 \ . \tag{21}$$

If A is given by expression (14), θ_1 must have the form

$$\theta_1=p+i\left[\frac{a}{\rho}+\frac{b}{\rho+\alpha^2}-\kappa_0\right] , \tag{22}$$

where a, b, and κ_0 are real numbers. The unnormalized ground state is then

$$\psi^{(1)}\equiv u_0=\rho^a(\rho+\alpha^2)^b e^{-\kappa_0\rho} \ . \tag{23}$$

We can see from this that, if the wave function is to be finite at $\rho=0$ and go to zero at $\rho=\infty$, a and κ_0 must both be positive and, in addition, $a+b\approx L+1$. We define δ by

$$a+b=L+1-\delta \tag{24}$$

(δ is analogous to the quantum defect in atomic physics). Equating $\theta_1^*\theta_1+a^{(1)}$ to the right-hand side of Eq. (14), we get (after some algebra)

$$ab+\alpha^2\kappa_0 b=-\lambda-\tfrac{1}{2}\mu , \tag{25}$$

where a, b, and κ_0 are

$$a=\tfrac{1}{2}+[(L+\tfrac{1}{2})^2-\tfrac{1}{4}\alpha^2+\lambda+\mu]^{1/2} ,$$
$$b=\tfrac{1}{2}\pm\tfrac{1}{2}\sqrt{1+4\lambda} , \tag{26}$$
$$\kappa_0=\frac{1}{4(a+b)} ,$$

and $a^{(1)}=-\kappa_0^2$. The energy corresponding to this solution is then

$$E_0=\frac{2m}{[1+\frac{1}{4}\alpha^2/(L+1-\delta)^2]^{1/2}} \ . \tag{27}$$

The solutions to Eqs. (25) and (26) for λ and μ are not unique, although the requirement that μ is equal to $\langle \mathbf{L}\cdot\mathbf{S}\rangle$ to lowest order determines λ to lowest order as well.

$A(\lambda,\mu)$ factorizes in the manner shown in Eq. (17) then for values of λ and μ which satisfy Eqs. (25) and (26). This procedure, however, breaks down at the next step, when we try to write A_2 in the form (19). We again get four equations, but, once λ and μ have been determined in step 1, we are left with only three adjustable parameters in θ_2 and the equations cannot be satisfied. For this reason we will restrict our attention for the most part to the nodeless, ($n_r=0$) wave functions.

B. Radial functions

One solution to these equations is $\lambda=\mu=0$. This corresponds to the Klein-Gordon equation for a spinless particle of mass $2m$ in the field of a nucleus with charge $Z=\frac{1}{2}$. This can, of course, be solved for all values of the radial quantum number. We have in this case

$$a=\tfrac{1}{2}+[(L+\tfrac{1}{2})^2-\tfrac{1}{4}\alpha^2]^{1/2},\quad b=0,\quad \kappa_0=\frac{1}{4(n_r+a)} , \tag{28}$$

and

$$u_0=\rho^a e^{-\kappa_0\rho}{}_1F_1(-n_r,2a;2\kappa_0\rho) , \tag{29}$$

where ${}_1F_1(\alpha,\gamma;x)$ is a confluent hypergeometric function. Since $\mu=0$, we have $S=0$; that is, Eq. (29) represents the singlet states. This solution does not take into account the δ-function-like potential term

$$-\frac{\frac{3}{4}\alpha^4}{\rho^2(\rho+\alpha^2)^2} \tag{30}$$

in Eq. (7), and it is not a good approximation to the singlet $L=0$ states.

We now consider only the $n_r=0$ states. When λ and μ are not zero, the solutions to Eqs. (25) and (26) can be found by first setting α^2 to zero and solving for a_0, b_0, λ_0, and μ_0 (the values of a, b, λ, and μ at $\alpha^2=0$). We then use the freedom we have in the correction terms to set $b=b_0$ and $\lambda=\lambda_0$, and put all of the α^2 dependence into a and μ. Then from Eqs. (26) we get

$$b=\begin{cases}-\frac{1}{2} & (L=0)\\ -\dfrac{\langle \mathbf{L}\cdot\mathbf{S}\rangle}{2L} & (L>0)\end{cases} \tag{31}$$

and

$$\mu=\langle\mathbf{L}\cdot\mathbf{S}\rangle+\frac{\alpha^2}{4}-\left[2L+1+\frac{\langle\mathbf{L}\cdot\mathbf{S}\rangle}{L}\right]\delta+\delta^2 . \quad (32)$$

Equation (25) can be rewritten as

$$\delta=0,\quad \mu=\tfrac{1}{4}\alpha^2 \quad (\text{for } L=0)$$
$$\delta^3-(3L+2)\delta^2+\left[(L+1)(2L+1)+\frac{\alpha^2}{4}\right]\delta-\frac{\alpha^2}{4}\left[L+1-\frac{\langle\mathbf{L}\cdot\mathbf{S}\rangle}{L}\right]=0 \quad (L>0) . \quad (33)$$

Of the three solutions to this cubic equation, we take the one that is of order α^2. Although it is possible to solve the equation for $L>0$ exactly, for the purposes of this paper we only require δ to order α^4, and μ to order α^2. To this order, δ is

$$\delta=\frac{\alpha^2}{4}\frac{L(L+1)-\langle\mathbf{L}\cdot\mathbf{S}\rangle}{L(L+1)(2L+1)}+\frac{\alpha^4}{16}\frac{L(L+1)-\langle\mathbf{L}\cdot\mathbf{S}\rangle}{L(L+1)^2(2L+1)^2}\times\left[\frac{L(L+1)-\langle\mathbf{L}\cdot\mathbf{S}\rangle}{L(2L+1)}-\frac{\langle\mathbf{L}\cdot\mathbf{S}\rangle}{L(L+1)}\right]+O(\alpha^6) . \quad (34)$$

We list below expressions for δ and for the radial functions for the various angular momentum states. The corresponding wave functions Ψ_0 are all mutually orthogonal, as shown in Appendix C.

For the non-S $n\,{}^1L_L$ wave functions,

$$\delta=L+\tfrac{1}{2}-[(L+\tfrac{1}{2})^2-\tfrac{1}{4}\alpha^2]^{1/2} . \quad (35)$$

The radial functions are

$$P(\rho)=\left[1+\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\frac{\rho^{a+1/2}}{\sqrt{\rho+\alpha^2}}e^{-\kappa_0\rho}{}_1F_1(-n_r,2a;2\kappa_0\rho) ,$$
$$Q_+(\rho)=2i\alpha\left[\frac{J+1}{2J+1}\right]^{1/2}\frac{\rho^{a-1/2}}{\sqrt{\rho+\alpha^2}}e^{-\kappa_0\rho}\left[\left[a-\kappa_0\rho-L-1-\frac{1}{2}\frac{\alpha^2}{\rho+\alpha^2}\right]{}_1F_1(-n_r,2a;2\kappa_0\rho)-\frac{n_r\kappa_0\rho}{a}{}_1F_1(1-n_r,2a+1;2\kappa_0\rho)\right] ,$$
$$Q_-(\rho)=-2i\alpha\left[\frac{J}{2J+1}\right]^{1/2}\frac{\rho^{a-1/2}}{\sqrt{\rho+\alpha^2}}e^{-\kappa_0\rho}\left[\left[a-\kappa_0\rho+L-\frac{1}{2}\frac{\alpha^2}{\rho+\alpha^2}\right]{}_1F_1(-n_r,2a;2\kappa_0\rho)-\frac{n_r\kappa_0\rho}{a}{}_1F_1(1-n_r,2a+1;2\kappa_0\rho)\right] ,$$
$$R(\rho)=\left[1-\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\frac{\rho^{a+1/2}}{\sqrt{\rho+\alpha^2}}e^{-\kappa_0\rho}{}_1F_1(-n_r,2a;2\kappa_0\rho) . \quad (36)$$

For the $(L+1)\,{}^3L_L$ states,

$$b=\frac{1}{2L},\quad \lambda=-\frac{2L-1}{4L^2} ,$$
$$\mu=-1-\frac{\alpha^2}{4}\frac{L-1}{L^2(2L+1)}+O(\alpha^4) ,$$
$$\delta=\frac{\alpha^2}{4}\frac{L^2+L+1}{L(L+1)(2L+1)}+\frac{\alpha^4}{16}\frac{L^2+L+1}{L^2(L+1)^2(2L+1)^2}\times\left[\frac{1}{L+1}+\frac{L^2+L+1}{2L+1}\right]+O(\alpha^6) . \quad (37)$$

In particular, $\mu=-1$ for the $2\,{}^3P_1$ level, with

$$\delta=1-(1-\tfrac{1}{4}\alpha^2)^{1/2} . \quad (38)$$

The radial wave functions are then

$$P(\rho)=\left[1+\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\left[1+\frac{\alpha^2}{\rho}\right]^{1/(2L)-1/2}\rho^{L+1-\delta}e^{-\kappa_0\rho} ,$$
$$Q_+(\rho)=2i\alpha\left[\frac{J}{2J+1}\right]^{1/2}\left[\kappa_0\rho+\delta+\frac{L+1}{2L}\frac{\alpha^2}{\rho+\alpha^2}\right]\times\left[1+\frac{\alpha^2}{\rho}\right]^{1/(2L)-1/2}\rho^{L-\delta}e^{-\kappa_0\rho} ,$$
$$Q_-(\rho)=2i\alpha\left[\frac{J+1}{2J+1}\right]^{1/2}\times\left[\kappa_0\rho+\delta+\frac{L+1}{2L}\frac{\alpha^2}{\rho+\alpha^2}-2L-1\right]\times\left[1+\frac{\alpha^2}{\rho}\right]^{1/(2L)-1/2}\rho^{L-\delta}e^{-\kappa_0\rho} , \quad (39)$$

$$R(\rho)=-\left[1-\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\left[1+\frac{\alpha^2}{\rho}\right]^{1/(2L)-1/2}\rho^{L+1-\delta}e^{-\kappa_0\rho}.$$

For the $1\,^1S_0$ and the $(L+1)\,^3L_{L+1}$ states,

$$b=-\tfrac{1}{2},\quad \lambda=\tfrac{3}{4},\quad \mu=L+\frac{\alpha^2}{4}\frac{1}{2L+1}+O(\alpha^4)\,,$$
$$\delta=\frac{\alpha^2}{4}\frac{L}{(L+1)(2L+1)}+\frac{\alpha^4}{16}\frac{L(L^2-L-1)}{(L+1)^3(2L+1)^3}+O(\alpha^6),$$
$$\delta=0 \text{ for } L=0\,. \tag{40}$$

The radial functions for $1\,^1S_0$ are

$$P(\rho)=\left[1+\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\frac{\rho^2}{\rho+\alpha^2}e^{-\rho/4}\,,$$
$$Q_+(\rho)=-\frac{i\alpha}{2}\frac{\rho^2}{\rho+\alpha^2}e^{-\rho/4}\,,$$
$$Q_-(\rho)=0\,, \tag{41}$$
$$R(\rho)=\left[1-\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\frac{\rho^2}{\rho+\alpha^2}e^{-\rho/4}\,,$$

while the $^3L_{L+1}$ functions are

$$P_-(\rho)=\left[1+\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\frac{\rho^{L+2-\delta}}{\rho+\alpha^2}e^{-\kappa_0\rho}\,,$$
$$Q_0(\rho)=2i\alpha\left[\frac{J}{2J+1}\right]^{1/2}(\kappa_0\rho+\delta)\frac{\rho^{L+1-\delta}}{\rho+\alpha^2}e^{-\kappa_0\rho}\,, \tag{42}$$
$$Q_1(\rho)=\left[\frac{J+1}{J}\right]^{1/2}Q_0(\rho)\,,$$
$$R_-(\rho)=-\frac{1}{2J+1}\left[1-\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\frac{\rho^{L+2-\delta}}{\rho+\alpha^2}e^{-\kappa_0\rho}\,.$$

The function R_+ is determined by the differential equation (12b) together with the boundary conditions $R_+(0)=R_+(\infty)=0$. For R_- given above, R_+ is

$$R_+(\rho)=2\sqrt{J(J+1)}\left[R_-(\rho)+\left[1-\frac{2m}{E_0}\right]\rho^{L+1-\delta}e^{-\kappa_0\rho}\frac{{}_1F_1(1,2L+4-\delta;\kappa_0\rho)}{2L+3-\delta}+\frac{2m\alpha^2}{E_0}X(\rho)\right]\,, \tag{43}$$

where $X(\rho)$ is defined as

$$X(\rho)=\begin{cases}\dfrac{\rho^{L+1-\delta}}{\alpha^2}e^{-\kappa_0\rho}\displaystyle\sum_{k=0}^{\infty}\left[-\frac{\rho}{\alpha^2}\right]^k\frac{{}_1F_1(1,2L+4-\delta+k;\kappa_0\rho)}{2L+3-\delta+k} & (\rho<\alpha^2)\\[2ex] \dfrac{(\alpha^2)^{2L+2-\delta}}{\rho^{L+2}}e^{\alpha^2\kappa_0}\dfrac{\pi}{\sin(\pi\delta)}+\rho^{L-\delta}e^{-\kappa_0\rho}\displaystyle\sum_{k=0}^{\infty}\left[-\frac{\alpha^2}{\rho}\right]^k\frac{{}_1F_1(1,2L+3-\delta-k;\kappa_0\rho)}{2L+2-\delta-k} & (\rho>\alpha^2).\end{cases} \tag{44}$$

[As noted above, $\delta=0$ for the $^3S_1$ state. In this case, we interpret the expression for $X(\rho)$ for $\rho>\alpha^2$ as the limit as δ goes to zero. The divergence of the first term in this limit is canceled by a divergence in the sum over the confluent hypergeometric functions in the second term. See Appendix B for alternate expressions for $X(\rho)$.] For $\rho\gg\alpha^2$, R_+ is approximately

$$R_+(\rho)=\frac{4\alpha^2\sqrt{J(J+1)}}{2J+1}\rho^{L-\delta}e^{-\kappa_0\rho}\kappa_0(1+\kappa_0\rho)+O\left[\alpha^4,\frac{\alpha^4}{\rho}\right]\,. \tag{45}$$

For the $^3L_{L-1}$ states, the solutions to Eqs. (24) and (25) are

$$b=\frac{1}{2}+\frac{1}{2L},\quad \lambda=\frac{1}{4L^2}-\frac{1}{4}\,,$$
$$\mu=-L-1-\frac{\alpha^2}{4}\frac{L^2-L-1}{L^2(2L+1)}+O(\alpha^4)\,, \tag{46}$$
$$\delta=\frac{\alpha^2}{4}\frac{L+1}{L(2L+1)}+\frac{\alpha^4}{16}\frac{L^2+4L+2}{L^2(2L+1)^3}+O(\alpha^6)\,.$$

Then the radial functions are

$$P_+(\rho)=\left[1+\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\left[1+\frac{\alpha^2}{\rho}\right]^{1/(2L)}\rho^{L+1-\delta}e^{-\kappa_0\rho},$$
$$Q_0(\rho)=-2i\alpha\left[\frac{J+1}{2J+1}\right]^{1/2}\times\left[\kappa_0\rho-2L-1+\delta+\frac{2L+1}{2L}\frac{\alpha^2}{\rho+\alpha^2}\right]\times\left[1+\frac{\alpha^2}{\rho}\right]^{1/(2L)}\rho^{L-\delta}e^{-\kappa_0\rho}\,, \tag{47}$$
$$Q_1(\rho)=-\left[\frac{J}{J+1}\right]^{1/2}Q_0(\rho)\,,$$
$$R_+(\rho)=\frac{1}{2J+1}\left[1-\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\times\left[1+\frac{\alpha^2}{\rho}\right]^{1/(2L)}\rho^{L+1-\delta}e^{-\kappa_0\rho}\,.$$

R_- is zero for $L=1$ ($J=0$). For $L>1$, with R_+ given as above, the solution to Eq. (13b) which is zero at $\rho=0$ and ∞ is

$$R_-(\rho)=-2\sqrt{J(J+1)}\left[R_+(\rho)+\left[1-\frac{2m}{E_0}\right]Y(\rho)+\frac{2m\alpha^2}{E_0}Z(\rho)\right], \tag{48}$$

where $Y(\rho)$ and $Z(\rho)$ are

$$\begin{aligned}Y(\rho)=&\frac{\rho^{L+1-\delta}e^{-\kappa_0\rho}}{2-\delta}\left[1+\frac{\alpha^2}{\rho}\right]^{1+1/(2L)}\sum_{k=0}^{\infty}\left[\frac{\alpha^2}{\rho+\alpha^2}\right]^k\left[-\frac{2L+1}{2L},k\right]\frac{{}_1F_1(k+1,3-\delta;\kappa_0\rho)}{(-1+\delta,k)}\\&-\frac{\rho^{L-1}}{\kappa_0^{2-\delta}}\Gamma(2-\delta)\,{}_1F_1\left[-\frac{2L+1}{2L},-1+\delta;\alpha^2\kappa_0\right],\\Z(\rho)=&\frac{\rho^{L-\delta}e^{-\kappa_0\rho}}{1-\delta}\left[1+\frac{\alpha^2}{\rho}\right]^{1/(2L)}\sum_{k=0}^{\infty}\left[\frac{\alpha^2}{\rho+\alpha^2}\right]^k\left[-\frac{1}{2L},k\right]\frac{{}_1F_1(k+1,2-\delta;\kappa_0\rho)}{(\delta,k)}\\&-\frac{\rho^{L-1}}{\kappa_0^{1-\delta}}\Gamma(1-\delta)\,{}_1F_1\left[-\frac{1}{2L},\delta;\alpha^2\kappa_0\right].\end{aligned}\tag{49}$$

In these expressions, the symbol (a,k) denotes the Pochhammer polynomial, defined as

$$(a,k)=\frac{\Gamma(a+k)}{\Gamma(a)}=\begin{cases}1 & \text{if } k=0\\ a(a+1)\cdots(a+k-1) & \text{if } k>0,\end{cases}\tag{50}$$

For $\rho \gg a^2$, R_- is approximately

$$R_-(\rho)=\frac{4\alpha^2\sqrt{J(J+1)}}{2J+1}\rho^{L-1-\delta}e^{-\kappa_0\rho}\{4L^2-1-[(2L-1)\kappa_0+\tfrac{1}{2}]\rho+\kappa_0^2\rho^2\}+O\left[\alpha^4,\frac{\alpha^4}{\rho}\right]. \tag{51}$$

At this point, it is useful to go back to the original radial equations (5a)–(5d), (6a)–(6d), and (11a)–(11f), and ask which of these equations are still satisfied by our approximate solutions. Of the $S=0$ equations, Eqs. (5a), (5b), and (5d) are satisfied, since they serve merely to define Q_+, Q_-, and R in terms of P. Equation (5c) is not satisfied since it gives directly Eq. (7), which we have approximated by Eq. (14). Similarly, Eqs. (6a), (6b), and (6d) are satisfied while Eq. (6c) is not. Of the $L=J-1$ solutions, Eqs. (11a), (11b), and (11e) (trivially, since $P_+=\tilde{Q}_0=0$) are all satisfied, while Eqs. (11c), (11d), and (11f) are not [but Eqs. (12a) and (12b) are]. And for $L=J+1$, Eqs. (11c), (11d), and (11e) are not satisfied, while Eqs. (11a), (11b), and (11f), and (13a) and (13b), are.

C. Discussion of $n_r>0$ functions

We conclude with some (rather inconclusive) remarks on the solutions for $n_r>0$, $b\neq 0$. We will try the substitution

$$u_0(\rho)=\rho^a(\rho+\alpha^2)^b e^{-\kappa_0\rho}v(\rho) \tag{52}$$

in the equation $Au_0=-\kappa_0^2u_0$, where (for a given L, S, and J) a and b are the same as in the $n_r=0$ case, but κ_0 is as yet undetermined. Once $v(\rho)$ is known, it is fairly straightforward to construct the radial functions for the $n_r>0$ states from the $n_r=0$ functions.

(1) All of the P functions above, as well as the R functions in Eqs. (39) and (41), the R_-, $L=J-1$ function in Eq. (42), and the R_+, $L=J+1$ function in Eq. (47), are multiplied by $v(\rho)$.

(2) In the case of the R_+, $L=J-1$ function [Eq. (43)], the first term is multiplied by $v(\rho)$, while for the second term we use the integral expression

$$e^{-\kappa_0\rho}\frac{{}_1F_1(1,2L+4-\delta;\kappa_0\rho)}{2L+3-\delta}=\int_0^1 e^{-\kappa_0\rho t}t^{2L+2-\delta}dt \tag{53}$$

and then, to get the corresponding $n_r>0$ term, we multiply the integrand by $v(\rho t)$,

$$\int_0^1 e^{-\kappa_0\rho t}t^{2L+2-\delta}dt\to\int_0^1 e^{-\kappa_0\rho t}t^{2L+2-\delta}v(\rho t)dt\ . \tag{54}$$

Likewise, for the X, Y, and Z functions, we use the integral expressions for these functions in Appendix B, Eqs. (B9) and (B10) and multiply the integrands by $v(\rho t)$ to get the $n_r>0$ functions, while the first term in Eq. (48) is multiplied by $v(\rho)$.

(3) The Q_+ and Q_- functions are determined by Eqs. (9b) and (9c) with the replacement $u\to u_0$ [u_0 given in Eq. (52)], while for the Q_0 functions in Eqs. (42) and (47), we multiply the right-hand side by $v(\rho)$ and, in addition, add a $-\rho d(\ln v)/d\rho$ term inside the square brackets. The Q_1 functions are then given by the same equations, with suitably modified Q_0 functions.

With the change of variable, $x=2\kappa_0\rho$, we get as the equation for v,

$$x(x+2\alpha^2\kappa_0)\frac{d^2v}{dx^2}+[\gamma x-x(x+2\alpha^2\kappa_0)+4\alpha^2\kappa_0 a]\frac{dv}{dx}-\beta\left[x+\frac{2\alpha^2\kappa_0 a}{a+b}\right]v=0\ , \tag{55}$$

$$\beta\equiv a+b-\frac{1}{4\kappa_0},\quad \gamma\equiv 2(a+b)\ .$$

This has the *approximate* solution,

$$v(x)\approx v_0(x)={}_1F_1(\beta,\gamma;x)-4\kappa_0 a^2 b\frac{\gamma-\beta}{\gamma^2}\,{}_1F_1(\beta,\gamma+1;x)\ . \tag{56}$$

If we denote the differential operator on the left-hand side of Eq. (55) by $\mathbf{L}$, then $\mathbf{L}v_0\sim\alpha^4$;

$$\mathbf{L}v_0=8\alpha^4\kappa_0^2 b\frac{\beta(\gamma-\beta)}{\gamma}\left[\frac{2b+1}{\gamma+1}\,{}_1F_1(\beta+1,\gamma+2;x)-\frac{2b}{\gamma}\,{}_1F_1(\beta,\gamma+1;x)\right]\ . \tag{57}$$

To ensure that v_0 does not increase as e^x as $x\to\infty$, we set β equal to a nonpositive integer; $\beta=-n_r$. Then the quantization condition becomes

$$\kappa_0=\frac{1}{4(n_r+a+b)}=\frac{1}{4(n-\delta)}\ ,\qquad n=n_r+L+1\ , \tag{58}$$

in which case the confluent hypergeometric functions are both polynomials of order n_r. The generalization of Eq. (27) is then

$$E_0=\frac{2m}{[1+\frac{1}{4}\alpha^2/(n-\delta)^2]^{1/2}}\ , \tag{59}$$

where δ is determined by Eq. (33).

If we attempt to solve for $v(x)$ as a double power series in the variables α^2 and $x+2\alpha^2\kappa_0$ (to allow the possibility of a summation over negative exponents while keeping v finite at $x=0$),

$$v(x)=\sum_{p=0}^{\infty}\sum_{q=-\infty}^{\infty}c_{pq}(\alpha^2)^p(x+2\alpha^2\kappa_0)^q\ , \tag{60}$$

we get a four-term recursion relation for the c_{pq} coefficients. It is easy to show that, for all values of p, the quantization condition (58) is sufficient to terminate each of the sums over q at $q=n_r$. For $p=0,1$ we can set $c_{0q}=c_{1q}=0$ for $q<0$. However, for $\rho>1$ the recursion relation demands that $c_{pq}\neq 0$ for negative q, and in fact these coefficients behave as $|q|!$ for $|q|\gg 1$. As a result, the series above does not converge for any x.

While Eq. (27) is an exact solution to $A(\lambda,\mu)u_0=-\kappa_0^2 u_0$, Eq. (59) is (apparently) only approximate. Nevertheless, as we will show in Sec. IV, Eq. (59) does agree, up through $O(\alpha^4)$, with the Coulomb energy calculated from perturbation theory.

IV. ENERGY LEVELS

If it were possible to switch off both the transverse-photon interaction and the annihilation interaction in a positronium atom, the energy of the $n\ {}^{2S+1}L_J$ state due to the Coulomb interaction alone would be[10]

$$E_C=2m-\frac{m\alpha^2}{4n^2}+\frac{m\alpha^4}{8n^3}\left[\frac{3}{8n}+\frac{\delta_{L0}-1}{2L+1}+\frac{\langle\mathbf{L}\cdot\mathbf{S}\rangle}{L(L+1)(2L+1)}\right]+O(\alpha^6)\ , \tag{61}$$

where the $O(\alpha^4)$ term has been calculated from perturbation theory using Schrödinger wave functions. (It is understood that the third term in the brackets is zero for $L=0$.) The fourth-order term in the expansion of the energy E_0 derived in Sec. III,

$$E_0=\frac{2m}{[1+\frac{1}{4}\alpha^2/(n-\delta)^2]^{1/2}}=2m-\frac{m\alpha^2}{4n^2}+\frac{m\alpha^2}{8n^3}\left[\frac{3\alpha^2}{8n}-4\delta\right]-\frac{m\alpha^2}{16n^4}\left[\frac{5\alpha^4}{32n^2}-\frac{3\alpha^2\delta}{n}+12\delta^2\right]+O(\alpha^8)\ , \tag{62}$$

agrees with the perturbation calculation, Eq. (61).

The Breit-Coulomb energy for the $n_r=0$ states, as well as for the non-S $n\ {}^1L_L$ states, can be calculated to $O(\alpha^6)$ from first-order perturbation theory using the wave functions found in Sec. III as the unperturbed functions. We define the perturbation operator δU by

$$\delta U\Psi_0\equiv -i\boldsymbol{\alpha}\cdot\nabla\Psi_0-i\nabla\Psi_0\cdot\boldsymbol{\alpha}+m(\beta\Psi_0-\Psi_0\beta)-\left[E_0+\frac{\alpha}{r}\right]\Psi_0\ . \tag{63}$$

Then the sixth-order contribution to the Coulomb energy is

$$\Delta E=\Delta E_0+\Delta E_1\ , \tag{64}$$

where

$$\Delta E_0=-\frac{m\alpha^6}{32n^3}\left[\frac{5}{16n^3}-\frac{3\delta_0}{2n^2}+\frac{3\delta_0^2}{2n}+\delta_1\right]\ ,\qquad \delta=\frac{\alpha^2}{4}\delta_0+\frac{\alpha^4}{16}\delta_1+\cdots\ , \tag{65}$$

and

$$\Delta E_1=\frac{(\Psi_0|\delta U\Psi_0)}{(\Psi_0|\Psi_0)}=\frac{(\Psi_0|\delta U\Psi_0)}{2E_0} \tag{66}$$

is the first-order (in δU) correction to E_0. As noted previously, Eqs. (5a) and (5b), (6a) and (6b), and (11a) and (11b) are satisfied by our approximate solutions. As a consequence, the A and D components of $\delta U\Psi_0$ are zero:

$$\delta U\Psi_0=\begin{bmatrix} 0 & (\delta U\Psi_0)_B \\ (\delta U\Psi_0)_C & 0 \end{bmatrix} . \tag{67}$$

The B and C components of $\delta U\Psi_0$, along with the details of the calculation of ΔE_1, are given in Appendix D, and we will just give the results:

$$\Delta E(1\,{}^1S_0)=\frac{m\alpha^6}{16}[\tfrac{27}{32}+\gamma_E+\ln(\tfrac{1}{2}\alpha^2)] ,$$

$$\Delta E(1\,{}^3S_1)=\frac{m\alpha^6}{12}\left[\tfrac{25}{128}+\gamma_E+\ln(\tfrac{1}{2}\alpha^2)+\frac{\pi^2}{12}\right] ,$$

$$\Delta E(2\,{}^3P_0)=-\frac{1079}{884\,736}m\alpha^6 ,$$

$$\Delta E(n\,{}^1L_L)_{L>0}=-\frac{m\alpha^6}{64n^3}\left[\frac{5}{8n^3}-\frac{3}{n^2(2L+1)}+\frac{3}{n(2L+1)^2}+\frac{2}{(2L+1)^3}-\frac{9n^2-3L(L+1)}{n^2L(2L+3)(L+1)(2L+1)(2L-1)}\right] , \tag{68}$$

$$\Delta E((L+1)\,{}^3L_{L+1})=-\frac{m\alpha^6}{64(L+1)^5}\left[\frac{5}{8}\frac{1}{L+1}+\frac{2L(L^2-L-1)}{(L+1)(2L+1)^3}-\frac{3L}{(2L+1)^2}+\frac{L+1}{L(2L+1)^2}+\frac{1}{L(2L+1)^2(2L+3)}\right] ,$$

$$\Delta E((L+1)\,{}^3L_{L})=-\frac{m\alpha^6}{64(L+1)^6}\left[\frac{5}{8}-\frac{3(L+1)}{L(2L+1)(2L-1)}-\frac{L-1}{L^3(2L+1)}-\frac{3(L^2+L+1)}{L(2L+1)}+\frac{(8L+5)(L^2+L+1)^2}{L^2(2L+1)^3}\right] ,$$

$$\Delta E((L+1)\,{}^3L_{L-1})=-\frac{m\alpha^6}{64(L+1)^4}\left[\frac{5}{8}\frac{1}{(L+1)^2}-\frac{3(L^2-L-1)}{L^2(2L+1)^2}+\frac{2(L+1)(L^2+4L+2)}{L^2(2L+1)^3}-\frac{1}{L^2(4L^2-1)}\left[L-3+\frac{1}{L(2L+1)}-\frac{4L}{(L+1)(2L-1)}\right]\right] \quad (L>1) ,$$

where γ_E is the Euler constant. Note that these results disagree with those in a recent paper by Papp, where he calculates the energy to $O(\alpha^6)$ for the $n\,{}^1L_L$, the $n\,{}^3L_L$, and the $n\,{}^3P_0$ states. In particular, there is no $\ln(\alpha)$ term in Papp's results, and his expression for the energy of the $n\,{}^1L_L$ state has a different dependence on n.[13]

V. CONCLUSION

We have constructed a set of approximate, orthogonal solutions to the Breit-Coulomb equation in coordinate space, which may be useful in perturbative positronium calculations, as well as in giving insight into the structure and behavior of the exact solutions. We have also found an expression for the energy eigenvalue of this equation which is accurate up through $O(\alpha^4)$ for all quantum states.

We summarize our approximations.

(1) For the $1\,{}^1S_0$ state, the $2\,{}^3P_0$ state, the singlet $n_r\geq 0$, $L>0$ states, and the triplet $n_r=0$, $L=J$ states, we made one approximation, that of replacing the coefficients $\frac{3}{4}$ and $\langle \mathbf{L}\cdot\mathbf{S}\rangle$ in Eq. (7) by λ and μ (although $\lambda=\frac{3}{4}$ for both the ${}^1S_0$ and the ${}^3L_{L+1}$ states).

(2) For the triplet $n_r=0$, $L=J\pm1$ states, we made two approximations: the one above, and that of neglecting the mixing of the $L=J-1$ and the $L=J+1$ states in the large-large component of Ψ.

(3) Finally, with one more approximation, that of replacing $v(\rho)$ by $v_0(\rho)$ in Eq. (56), we obtain approximate wave functions for all $n\,{}^{1,3}L_J$ states.

The Breit equation is an "equal-time" equation, in that it does not depend on the relative time separation $t=t_- - t_+$ of the two particles. The full wave function $\psi(r,t)$ (i.e., the solution to the Bethe-Salpeter equation) does depend upon t. As pointed out by Salpeter,[14] in Dirac hole theory, the Bethe-Salpeter (BS) equation reduces to the Salpeter equation when the interaction kernel is instantaneous, while in single electron theory the BS equation reduces to the Breit equation. In order to use the approximate functions above in actual calculations, where there are usually noninstantaneous interaction kernels, it is necessary to continue $\Psi_0(\mathbf{r})$ off of the $t=0$ hyperplane, and to incorporate the difference between the Breit and the Salpeter equations in an additional perturbation kernel. We will not discuss the second point here, but the first point was addressed in Ref. 11, where an equation relating $\psi(\mathbf{r},t)$ to the Fourier transform

$$\Phi(\mathbf{p})=\int \Psi(\mathbf{r})e^{-i\mathbf{p}\cdot\mathbf{r}}d\mathbf{r} \tag{69}$$

of $\Psi(\mathbf{r})$ was found. In momentum space, Eq. (18) in Ref. 11 is

$$\phi(p)=\left[\frac{i\Lambda^{(+)}(\mathbf{p})}{p_0+\frac{1}{2}E_0-E_p+i\varepsilon}+\frac{i\Lambda^{(-)}(\mathbf{p})}{p_0+\frac{1}{2}E_0+E_p+i\varepsilon}\right]\Phi(\mathbf{p}) -\Phi(\mathbf{p})\left[\frac{i\Lambda^{(+)}(-\mathbf{p})}{p_0-\frac{1}{2}E_0-E_p-i\varepsilon}+\frac{i\Lambda^{(-)}(-\mathbf{p})}{p_0-\frac{1}{2}E_0+E_p-i\varepsilon}\right] \tag{70}$$

or

$$\phi(p)=[iS_F(p+\tfrac{1}{2}P)\beta+2\pi\delta(p_0+\tfrac{1}{2}E_0+E_p)\Lambda^{(-)}(\mathbf{p})]\Phi(\mathbf{p}) -\Phi(\mathbf{p})[i\beta S_F(p-\tfrac{1}{2}P) -2\pi\delta(p_0-\tfrac{1}{2}E_0-E_p)\Lambda^{(+)}(-\mathbf{p})] , \quad (71)$$

with

$$S_F(p)=\frac{1}{\not p-m+i\varepsilon}, \quad \Lambda^{(\pm)}(\mathbf{p})=\frac{E_p\pm(\boldsymbol{\alpha}\cdot\mathbf{p}+m\beta)}{2E_p} . \quad (72)$$

and $P=(E_0,\mathbf{0})$.

For a typical radial wave function $F(r)$, we can do the integration over the angular variables in the Fourier transform integral in Eq. (69), with the result,

$$\int \frac{F(r)}{r}\Omega_{LSJM}(\hat{\mathbf{r}})e^{-i\mathbf{p}\cdot\mathbf{r}}d\mathbf{r} =4\pi(-i)^L\Omega_{LSJM}(\hat{\mathbf{p}})\int_0^\infty rF(r)j_L(pr)dr , \quad (73)$$

where $j_L(x)$ is a spherical Bessel function,

$$j_L(x)=(-x)^L\left[\frac{1}{x}\frac{d}{dx}\right]^L\frac{\sin(x)}{x} . \quad (74)$$

As we saw in Sec. III, the R_+, $L=J-1$ approximate function, Eq. (43), is quite complicated. With $F=R_+$, we can use the recurrence formulas for j_L[15]

$$\frac{d}{dx}[x^{L+1}j_L(x)]=x^{L+1}j_{L-1}(x) ,$$
$$\frac{d}{dx}\left[\frac{j_L}{x^L}\right]=-\frac{j_{L+1}(x)}{x^L} , \quad (75)$$

together with Eq. (12b) to express this integral, after integrating by parts, in terms of the much simpler R_- function, Eq. (42),

$$\int \frac{R_+(r)}{r}\Omega_{J+11JM}(\hat{\mathbf{r}})e^{-i\mathbf{p}\cdot\mathbf{r}}d\mathbf{r} =-8\pi(-i)^{J+1}\sqrt{J(J+1)}\Omega_{J+11JM}(\hat{\mathbf{p}}) \times\int_0^\infty rR_-(r)j_{J-1}(pr)dr . \quad (76)$$

Similarly, for $L=J+1$, $F=R_-$ [Eq. (48)], we get

$$\int \frac{R_-(r)}{r}\Omega_{J-11JM}(\hat{\mathbf{r}})e^{-i\mathbf{p}\cdot\mathbf{r}}d\mathbf{r} =8\pi(-i)^{J-1}\sqrt{J(J+1)}\Omega_{J-11JM}(\hat{\mathbf{p}}) \times\int_0^\infty rR_+(r)j_{J+1}(pr)dr . \quad (77)$$

Therefore, the momentum-space wave function may be more convenient to use in a perturbation calculation; it allows the perturbation kernels to be expressed in terms of Feynman diagrams, and it results in a considerable simplification in the "small-small" component. It has the disadvantage, however, that the integral on the right-hand side of Eq. (73) does not appear to be expressible in elementary form.

APPENDIX A: ORBITAL-SPIN MATRICES

The 2×2 matrices in Eqs. (2a) and (2b) are defined as

$$\Omega_{L0LM}(\hat{\mathbf{r}})=\frac{1}{\sqrt{2}}\begin{bmatrix}1&0\\0&1\end{bmatrix}Y_L^M(\hat{\mathbf{r}}) ,$$
$$\Omega_{L1JM}(\hat{\mathbf{r}})=\sum_{m=-1}^{+1}\langle LM-m\,1m|L1JM\rangle\frac{\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\epsilon}}_m}{\sqrt{2}}Y_L^{M-m}(\hat{\mathbf{r}}) , \quad (A1)$$

with

$$\hat{\boldsymbol{\epsilon}}_+=-\frac{\hat{\mathbf{x}}+i\hat{\mathbf{y}}}{\sqrt{2}},\quad \hat{\boldsymbol{\epsilon}}_0=\hat{\mathbf{z}},\quad \hat{\boldsymbol{\epsilon}}_-=\frac{\hat{\mathbf{x}}-i\hat{\mathbf{y}}}{\sqrt{2}} . \quad (A2)$$

We use the phase convention of Condon and Shortley for the Clebsch-Gordan coefficients and the spherical harmonic functions.[16] These matrices are eigenstates of the operators L^2, S^2, J^2, and J_z, and are normalized according to

$$\int \mathrm{Tr}(\Omega^\dagger_{L'S'J'M'}\Omega_{LSJM})\sin\theta\,d\theta\,d\phi=\delta_{L'L}\delta_{S'S}\delta_{J'J}\delta_{M'M} . \quad (A3)$$

Further properties of these matrices are given in Ref. 10.

APPENDIX B: ALTERNATE EXPRESSIONS FOR THE FUNCTIONS X, Y, AND Z

Expression (44) for $X(\rho)$ in the region $\rho<\alpha^2$ was analytically continued into $\rho>\alpha^2$ by first absorbing the exponential factor into the confluent hypergeometric functions using the identity[17]

$$e^{-z}{}_1F_1(\alpha,\gamma;z)={}_1F_1(\gamma-\alpha,\gamma;-z) \quad (B1)$$

and then using the series expansions

$${}_1F_1(\alpha,\gamma;z)=\sum_{n=0}^\infty\frac{(\alpha,n)}{(\gamma,n)}\frac{z^n}{n!} ,$$
$${}_2F_1(\alpha,\beta,\gamma;z)=\sum_{k=0}^\infty\frac{(\alpha,k)(\beta,k)}{(\gamma,k)}\frac{z^k}{k!} . \quad (B2)$$

Summing over the index k, we get

$$X(\rho)=\frac{\rho^{x-L-2}}{\alpha^2}e^{-\kappa_0\rho}\sum_{k=0}^\infty\left[-\frac{\rho}{\alpha^2}\right]^k\frac{{}_1F_1(1,k+x+1;\kappa_0\rho)}{k+x} =\frac{\rho^{x-L-2}}{\alpha^2}\sum_{n=0}^\infty\frac{(-\kappa_0\rho)^n}{n!(n+x)} \times{}_2F_1\left[1,n+x,n+x+1;-\frac{\rho}{\alpha^2}\right] , \quad (B3)$$

with $x=2L+3-\delta$. The hypergeometric functions were then continued into the region $\rho/\alpha^2>1$ by using the identity

$${}_2F_1(\alpha,\beta,\gamma;z) =\frac{\Gamma(\gamma)\Gamma(\beta-\alpha)}{\Gamma(\beta)\Gamma(\gamma-\alpha)}(-z)^{-\alpha} \times{}_2F_1\left[\alpha,\alpha+1-\gamma,\alpha+1-\beta;\frac{1}{z}\right]+(\alpha\leftrightarrow\beta) , \quad (B4)$$

expressing the hypergeometric functions as power series, and then summing over n. The result is the expression for $X(\rho)$ in Eq. (44). If, however, we use the identity

$$ {}_2F_1(\alpha,\beta,\gamma;z)=(1-z)^{-a}{}_2F_1\left[\alpha,\gamma-\beta,\gamma;\frac{z}{z-1}\right] \quad \text{(B5)} $$

in Eq. (B3), we get

$$ X(\rho)=\frac{\rho^{x-L-2}}{\rho+\alpha^2}\sum_{n=0}^{\infty}\frac{(-\kappa_0\rho)^n}{n!(n+x)} \times {}_2F_1\left[1,1,n+1+x;\frac{\rho}{\rho+\alpha^2}\right] . \quad \text{(B6)} $$

Thus sum converges for all ρ in the range $0\leq\rho<\infty$. Equation (44) is more useful for expanding $X(\rho)$ in powers of α^2/ρ, but the expression above has the advantage of being a single power-series expansion for X, as well as all terms remaining finite as $\delta\to 0$.

Similarly, we get the alternative series expansions for Y and Z, which converge in the region $\rho>\alpha^2$,

$$ Y(\rho)=\rho^{L+1-\delta}e^{-\kappa_0\rho}\sum_{k=0}^{\infty}\left[-\frac{\alpha^2}{\rho}\right]^k\frac{1}{k!}\left[-\frac{2L+1}{2L},k\right] \times\frac{{}_1F_1(1,3-\delta-k;\kappa_0\rho)}{2-\delta-k} -\frac{\rho^{L-1}}{\kappa_0^{2-\delta}}\Gamma(2-\delta){}_1F_1\left[-\frac{2L+1}{2L},-1+\delta;\alpha^2\kappa_0\right] , \quad \text{(B7)} $$

$$ Z(\rho)=\rho^{L-\delta}e^{-\kappa_0\rho}\sum_{k=0}^{\infty}\left[-\frac{\alpha^2}{\rho}\right]^k\frac{1}{k!}\left[-\frac{1}{2L,}k\right] \times\frac{{}_1F_1(1,2-\delta-k;\kappa_0\rho)}{1-\delta-k} -\frac{\rho^{L-1}}{\kappa_0^{1-\delta}}\Gamma(1-\delta){}_1F_1\left[-\frac{1}{2L},\delta;\alpha^2\kappa_0\right] . $$

These three functions can be expressed more compactly in integral form. We will use the integral expression for the confluent hypergeometric function

$$ {}_1F_1(\alpha,\gamma;z)=-\frac{1}{2\pi i}\frac{\Gamma(\gamma)\Gamma(1-\alpha)}{\Gamma(\gamma-\alpha)} \times\oint_C e^{zt}(-t)^{\alpha-1}(1-t)^{\gamma-\alpha-1}dt , \quad \text{(B8)} $$

where C is a contour that starts at $1+i\varepsilon$ above the real axis, passes around the origin counterclockwise, and ends at $1-i\varepsilon$ below the real axis. Substituting this into Eq. (B3), we get

$$ X(\rho)=\rho^{L+1-\delta}\int_0^1\frac{e^{-\kappa_0\rho t}t^{2(L+1)-\delta}}{\rho t+\alpha^2}dt , \quad \text{(B9)} $$

while from Eqs. (B7) for Y and Z we have

$$ Y(\rho)=-\rho^{L+1-\delta}\int_1^{\infty}e^{-\kappa_0\rho t}t^{l-\delta}\left[1+\frac{\alpha^2}{\rho t}\right]^{(2L+1)/(2L)}dt , $$

$$ Z(\rho)=-\rho^{L-\delta}\int_1^{\infty}e^{-\kappa_0\rho t}t^{-\delta}\left[1+\frac{\alpha^2}{\rho t}\right]^{1/(2L)}dt . \quad \text{(B10)} $$

APPENDIX C: ORTHOGONALITY OF Ψ_0

The set of wave functions $\Psi_0(^{1,3}L_{J=L,L\pm1})$ are all mutually orthogonal under the inner product (3). That $\Psi_0(^1L_L)$ and $\Psi_0(^3L_L)$ are orthogonal to each other and to $\Psi_0(^3L_{L\pm1})$ is apparent from the orthogonality of the Ω_{LSJM} matrices. It is not so apparent that $\Psi_0(^3L_{L+1})$ is orthogonal to $\Psi_0(^3L_{L-1})$, since these are eigenfunctions of different Hamiltonians. In this section we will distinguish the radial $J=L+1$ functions from the $J=L-1$ functions by a superscript. We have for their inner product

$$ (\Psi_0(^3L_{L+1})|\Psi_0(^3L_{L-1})) =\frac{N^{(+)}N^{(-)}}{\alpha E_0}\int_0^{\infty}[2(Q_0^{(+)}Q_0^{(-)}+Q_1^{(+)}Q_1^{(-)}) +R_+^{(+)}R_+^{(-)}+R_-^{(+)}R_-^{(-)}]d\rho. \quad \text{(C1)} $$

But

$$ Q_0^{(+)}Q_0^{(-)}+Q_1^{(+)}Q_1^{(-)}=\tilde{Q}_0^{(+)}\tilde{Q}_0^{(-)}+\tilde{Q}_1^{(+)}\tilde{Q}_1^{(-)}=0 , \quad \text{(C2)} $$

which leaves only the terms containing the R functions. We can write the term with the R_+ functions as

$$ \int_0^{\infty}R_+^{(+)}R_+^{(-)}d\rho=-\frac{1}{2J+1}\int_0^{\infty}(\rho^{J+1}R_+^{(+)})(\rho^{J+1}R_+^{(-)}) \times\frac{d}{d\rho}\left[\frac{1}{\rho^{2J+1}}\right]d\rho . \quad \text{(C3)} $$

By integrating by parts a couple of times and using the relations (12b) and (13b) to eliminate the R_+ functions in favor of the R_- ones, we get

$$ \int_0^{\infty}R_+^{(+)}R_+^{(-)}d\rho=-\int_0^{\infty}R_-^{(+)}R_-^{(-)}d\rho , \quad \text{(C4)} $$

which proves the orthogonality of two wave functions.

APPENDIX D: EVALUATION OF FIRST-ORDER ENERGY PERTURBATIONS

We wish to evaluate $(\Psi_0|\delta U\Psi_0)$ to leading order. To this order we can, after factoring out of the integral an α^6, set α to zero in the integrand as long as the resulting integral does not diverge at $\rho=0$. We have

$$ (\Psi_0|\delta U\Psi_0)=\int\mathrm{Tr}[(\Psi_0)_B^{\dagger}(\delta U\Psi_0)_B+(\Psi_0)_C^{\dagger}(\delta U\Psi_0)_C]d\mathbf{r} =\frac{1}{(\alpha E_0)^3}\int\mathrm{Tr}[(\Psi_0)_B^{\dagger}(\delta U\Psi_0)_B +(\Psi_0)_C^{\dagger}(\delta U\Psi_0)_C]d\rho . \quad \text{(D1)} $$

Consider, for example, the $S=0$, $L=J$ states. The B component of $\delta U\Psi_0$ is equal to the left-hand side of Eq. (5c) multiplied by $(2iN/r)\Omega_{J0JM}$. This would equal zero if we had not made the approximation in Sec. III. We define $\delta A(\lambda,\mu)$ as

$$\delta A(\lambda,\mu)=\alpha^4\frac{\frac{3}{4}-\lambda}{\rho^2(\rho+\alpha^2)^2}+\alpha^2\frac{\langle\mathbf{L}\cdot\mathbf{S}\rangle-\mu}{\rho^2(\rho+\alpha^2)} . \tag{D2}$$

Then, in general, the B component of $\delta U\Psi_0$ is

$$(\delta U\Psi_0)_B=4N\alpha^3E_0^2\delta A(\lambda,\mu)\frac{u_0(\rho)}{\sqrt{\rho(\rho+\alpha^2)}}\Omega_{LSJM} . \tag{D3}$$

The normalization constant N^2 is, to leading order,

$$N^2=\frac{2m^2\alpha}{(2n)^{2L+4}}\frac{(n+L)!}{(n-L-1)![(2L+1)!]^2}+O(\alpha^3) . \tag{D4}$$

The evaluation of the integrals for the $L=J$ states is straightforward, because, for these wave functions,

$$(\delta U\Psi_0)_C=(-1)^S(\delta U\Psi_0)_B . \tag{D5}$$

Then,

$$\Delta E_1(1\,{}^1S_0)=\frac{m\alpha^6}{16}[1+\gamma_E+\ln(\tfrac{1}{2}\alpha^2)] ,$$

$$\Delta E_1(n\,{}^1L_L)=\frac{m\alpha^6}{64n^5}\frac{9n^2-3L(L+1)}{L(2L+3)(L+1)(2L+1)(2L-1)} , \tag{D6}$$

$$\Delta E_1((L+1)\,{}^3L_L)=\frac{m\alpha^6}{64L(L+1)^5(2L+1)}\left[\frac{3}{2L-1}-\frac{1}{L^2}+\frac{2(L+2)}{L(2L+1)}\right] .$$

Adding these expressions to ΔE_0, we get the results in Eqs. (68).

The integrals for the $L=J-1$, $(L=J+1)$ states are more complicated due to the R_+, (R_-) functions. For $L=J-1$, the C component of $\delta U\Psi_0$ is

$$(\delta U\Psi_0)_C=-\frac{(\delta U\Psi_0)_B}{2J+1}-\frac{\alpha E_0^2N}{\rho}\left[\left[1+\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]R_+-\frac{4i\alpha\sqrt{J(J+1)}}{2J+1}\left[\frac{d\tilde{Q}_1}{d\rho}-\frac{J+1}{\rho}\tilde{Q}_1\right]\right]\Omega_{J+11JM} . \tag{D7}$$

Then,

$$(\Psi_0|\delta U\Psi_0)=\frac{N^2}{\alpha}\int_0^\infty\left[\left[P_--\frac{R_-}{2J+1}\right]\left[4\alpha^2\delta A(\tfrac{3}{4},\mu)\frac{\rho^{L+2-\delta}}{\rho+\alpha^2}e^{-\kappa_0\rho}\right]\right.$$
$$\left.-\left[1+\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]R_+^2+\frac{4i\alpha\sqrt{J(J+1)}}{2J+1}R_+\left[\frac{d\tilde{Q}_1}{d\rho}-\frac{J+1}{\rho}\tilde{Q}_1\right]\right]d\rho . \tag{D8}$$

This integral can be simplified considerably by using the same trick as in Appendix C to eliminate all but one of the R_+ terms. Integrating by parts and using Eq. (12b), we have

$$\int_0^\infty R_+^2d\rho=4J(J+1)\int_0^\infty R_-^2d\rho , \tag{D9}$$

$$\int_0^\infty R_+\left[\frac{d\tilde{Q}_1}{d\rho}-\frac{J+1}{\rho}\tilde{Q}_1\right]d\rho=2\sqrt{J(J+1)}\int_0^\infty R_-\left[\frac{d\tilde{Q}_1}{d\rho}+\frac{J}{\rho}\tilde{Q}_1\right]d\rho , \tag{D10}$$

and

$$\int_0^\infty\frac{R_+^2}{\rho}d\rho=4J^2\int_0^\infty\frac{R_-^2}{\rho}d\rho+2\left[\frac{J}{J+1}\right]^{1/2}\int_0^\infty\frac{R_-R_+}{\rho}d\rho . \tag{D11}$$

Then,

$$(\Psi_0|\delta U\Psi_0)=4\alpha N^2\int_0^\infty\left[2a^2(\langle\mathbf{L}\cdot\mathbf{S}\rangle-\mu)\frac{\rho^{2L+1-2\delta}}{(\rho+\alpha^2)^2}e^{-2\kappa_0\rho}+\frac{J}{\rho}R_-\left[R_--\frac{R_+}{2\sqrt{J(J+1)}}\right]\right]d\rho . \tag{D12}$$

So far, no approximations have been made in the integrand. To leading order (for non-S states), we can use the approximation (45) for R_+, as well as approximating the $(\rho+a^2)^{-2}$ factors in the integrand by ρ^{-2}. Then we get

$$\Delta E_1((L+1)\,{}^3L_{L+1})=-\frac{m\alpha^6}{64}\frac{1}{L(L+1)^4(2L+1)^2}\left[1+\frac{1}{(L+1)(2L+3)}\right](L>0) . \tag{D13}$$

For the $1\,{}^3S_1$ state, we have to be more careful about making approximations in Eq. (D12); otherwise, the integral will diverge logarithmically at $\rho=0$, which indicates an $\alpha^6\ln\alpha$ term in ΔE_1. Since this integration is more involved than the ones above, we will give some of the details of the calculation. We have

$$\Delta E_1(1\,^3S_1)$$
$$=-\frac{\alpha N^2}{E_0}\int_0^\infty \frac{\rho}{\rho+\alpha^2}\left\{\alpha^4\frac{e^{-\rho/2}}{\rho+\alpha^2}+\frac{2e^{-\rho/4}}{3}\left[1-\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]\left[\left[1-\frac{2m}{E_0}\right]\frac{\rho e^{-\rho/4}}{3}{}_1F_1(1,4;\rho/4)+\frac{2m\alpha^2}{E_0}X(\rho)\right]\right\}d\rho\ . \tag{D14}$$

We can write this as

$$\Delta E_1(1\,^3S_1)=I_1+I_2+I_3\ , \tag{D15}$$

where

$$I_1\equiv-\frac{\alpha^5N^2}{E_0}\int_0^\infty\frac{\rho e^{-\rho/2}}{(\rho+\alpha^2)^2}d\rho$$
$$=\frac{m\alpha^6}{16}[1+\gamma_E+\ln(\tfrac{1}{2}\alpha^2)]+O(m\alpha^8\ln\alpha)\ , \tag{D16}$$

$$I_2\equiv-\frac{2\alpha N^2}{9E_0}\left[1-\frac{2m}{E_0}\right]\int_0^\infty\frac{\rho^2e^{-\rho/2}}{\rho+\alpha^2}\left[1-\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]{}_1F_1(1,4;\rho/4)d\rho$$
$$=\frac{m\alpha^6}{96}[4\ln(2)-\tfrac{5}{2}]+O(m\alpha^8\ln\alpha)\ , \tag{D17}$$

and

$$I_3\equiv-\frac{4m\alpha^3N^2}{3E_0^2}\int_0^\infty e^{-\rho/4}\left[\left[1-\frac{2m}{E_0}\right]\frac{\rho X(\rho)}{\rho+\alpha^2}+\alpha^2\frac{X(\rho)}{\rho+\alpha^2}\right]d\rho\ . \tag{D18}$$

For the $1\,^3S_1$ wave function it is more convenient to use expression (B6) for $X(\rho)$,

$$X(\rho)=\frac{\rho}{\rho+\alpha^2}\sum_{n=0}^\infty\frac{(-\frac{1}{4}\rho)^n}{n!(n+3)}{}_2F_1\left[1,1,n+4;\frac{\rho}{\rho+\alpha^2}\right]\approx\tfrac{1}{2}e^{-\rho/4}{}_1F_1(1,3;\rho/4)\quad(\text{for }\rho\gg\alpha^2)\ . \tag{D19}$$

In the first term in (D18) we can set α^2 in the denominator to zero and use the approximation above for $X(\rho)$:

$$\int_0^\infty e^{-\rho/4}\frac{\rho X(\rho)}{\rho+\alpha^2}d\rho\approx\tfrac{1}{2}\int_0^\infty e^{-\rho/2}{}_1F_1(1,3;\rho/4)d\rho=4[1-\ln(2)]\ . \tag{D20}$$

For the second integral we have

$$\int_0^\infty e^{-\rho/4}\frac{X(\rho)}{\rho+\alpha^2}d\rho=\sum_{n=0}^\infty\frac{(-\frac{1}{4})^n}{n!(n+3)}\int_0^\infty\frac{\rho^{n+1}e^{-\rho/4}}{(\rho+\alpha^2)^2}{}_2F_1\left[1,1,n+4;\frac{\rho}{\rho+\alpha^2}\right]d\rho$$
$$\approx\tfrac{1}{3}\int_0^\infty\frac{\rho e^{-\rho/4}}{(\rho+\alpha^2)^2}{}_2F_1\left[1,1,4;\frac{\rho}{\rho+\alpha^2}\right]d\rho+\sum_{n=1}^\infty\frac{(-\frac{1}{4})^n}{n!(n+3)}{}_2F_1(1,1,n+4;1)\int_0^\infty\rho^{n-1}e^{-\rho/4}d\rho$$
$$=2\sum_{k=0}^\infty\frac{k!}{(k+3)!}\int_0^\infty\frac{\rho^{k+1}e^{-\rho/4}}{(\rho+\alpha^2)^{k+2}}d\rho+\sum_{n=1}^\infty\frac{(-1)^n}{n(n+2)}\ . \tag{D21}$$

We have for the second summation

$$\sum_{n=1}^\infty\frac{(-1)^n}{n(n+2)}=-\tfrac{1}{4}\ . \tag{D22}$$

By integrating by parts $k+1$ times,

$$\int_0^\infty \frac{\rho^{k+1}e^{-\rho/4}}{(\rho+\alpha^2)^{k+2}}d\rho=\frac{1}{(k+1)!}\int_0^\infty \frac{1}{\rho+\alpha^2}\frac{d^{k+1}}{d\rho^{k+1}}(\rho^{k+1}e^{-\rho/4})d\rho$$
$$=\sum_{m=0}^{k+1}\frac{(-\frac{1}{4})^m(k+1)!}{(m!)^2(k+1-m)!}\int_0^\infty \frac{e^{-\rho/4}\rho^m}{\rho+\alpha^2}d\rho$$
$$\approx\int_0^\infty \frac{e^{-\rho/4}}{\rho+\alpha^2}d\rho+\sum_{m=1}^{k+1}\frac{(-\frac{1}{4})^m(k+1)!}{(m!)^2(k+1-m)!}\int_0^\infty e^{-\rho/4}\rho^{m-1}d\rho$$
$$\approx -[\gamma_E+\ln(\tfrac{1}{4}\alpha^2)]-\sum_{m=1}^{k+1}\frac{1}{m}\ , \tag{D23}$$

where we have used the identity[18]

$$\sum_{m=1}^{N}\frac{(-1)^{m+1}N!}{m(N-m)!m!}=\sum_{m=1}^{N}\frac{1}{m} \tag{D24}$$

in the second term. Then,

$$\sum_{k=0}^{\infty}\frac{k!}{(k+3)!}\int_0^\infty \frac{\rho^{k+1}e^{-\rho/4}}{(\rho+\alpha^2)^{k+2}}d\rho\approx -[\gamma_E+\ln(\tfrac{1}{4}\alpha^2)]\sum_{k=0}^{\infty}\frac{k!}{(k+3)!}-\sum_{k=0}^{\infty}\frac{k!}{(k+3)!}\sum_{m=1}^{k+1}\frac{1}{m}$$
$$=-\tfrac{1}{4}[\gamma_E+\ln(\tfrac{1}{4}\alpha^2)]-\frac{\pi^2}{12}+\tfrac{1}{2}\ . \tag{D25}$$

I_3 is therefore

$$I_3=-\frac{m\alpha^6}{12}\left[\tfrac{1}{8}+\tfrac{1}{2}\ln(2)-\tfrac{1}{4}\gamma_E-\tfrac{1}{4}\ln(\tfrac{1}{2}\alpha^2)-\frac{\pi^2}{12}\right]+O(m\alpha^8\ln\alpha) \tag{D26}$$

and ΔE_1 is

$$\Delta E_1(1\,^3S_1)=\frac{m\alpha^6}{12}\left[\tfrac{5}{16}+\gamma_E+\ln(\tfrac{1}{2}\alpha^2)+\frac{\pi^2}{12}\right]\ . \tag{D27}$$

For $L=J+1$, we have

$$(\delta U\Psi_0)_C=\frac{(\delta U\Psi_0)_B}{2J+1}-\frac{\alpha E_0^2 N}{\rho}\left[\left[1+\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]R_-+\frac{4i\alpha\sqrt{J(J+1)}}{2J+1}\left[\frac{d\tilde{Q}_0}{d\rho}+\frac{J}{\rho}\tilde{Q}_0\right]\right]\Omega_{J-1 1JM}\ . \tag{D28}$$

Again we can simplify the resulting integral for $(\Psi_0|\delta U\Psi_0)$, this time by using Eq. (13b) to eliminate the function R_- as much as possible. The result is

$$(\Psi_0|\delta U\Psi_0)=-\frac{N^2}{\alpha}\int_0^\infty\left\{[P_++(2J+1)R_+]\left[\left[1-\frac{2m}{E_0}+\frac{\alpha^2}{\rho}\right]P_+-2i\alpha\left[\frac{d\tilde{Q}_0}{d\rho}-\frac{J+1}{\rho}\tilde{Q}_0\right]\right]\right.$$
$$\left.+4\alpha^2(1-\delta_{0J})\frac{J+1}{\rho}R_+\left[R_++\frac{R_-}{2\sqrt{J(J+1)}}\right]\right\}d\rho$$
$$=4\alpha N^2\int_0^\infty\left[2\left[1+\frac{\alpha^2}{\rho}\right]^{(L+1)/L}\rho^{2L+2-2\delta}e^{-2\kappa_0\rho}\delta A(\lambda,\mu)+(1-\delta_{0J})\frac{J+1}{\rho}R_+\left[R_++\frac{R_-}{2\sqrt{J(J+1)}}\right]\right]d\rho\ . \tag{D29}$$

Approximating R_- by expression (51) and making other approximations in the integrand, the energy perturbation is

$$\Delta E_1((L+1)\,^3L_{L-1})=\frac{m\alpha^6}{64L^2(L+1)^4(4L^2-1)}\left[L-3+\frac{1}{L(2L+1)}-\frac{4L}{(L+1)(2L-1)}\right]\quad(L>1)$$
$$\Delta E_1(2\,^3P_0)=\frac{5m\alpha^6}{18\,432}\ . \tag{D30}$$

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