Quantum-electrodynamic corrections to the 1*s*3*d* states of the helium atom

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We perform quantum-electrodynamic calculations of the ionization energy of the 1*s*3*d* states of the ^{4}He atom, including a complete evaluation of the $m\alpha^6$ correction. We find a large contribution from the nonradiative part of this correction, which has not been accounted for in previous investigations. The additional contribution shifts theoretical predictions for ionization energies by about 10σ. Despite this shift, we confirm the previously reported systematic deviations between measured experimental results and theoretical predictions for transitions involving 3*D* states. The reason for these deviations remains unknown.

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A steadily increasing accuracy of spectroscopic experiments on the helium atom opens new possibilities for improved determinations of fundamental physical constants, tests of the standard model of fundamental interactions, and a search for the new physics. The recent measurement of the $2\,^3P_1$–$2\,^3P_2$ helium transition frequency with an accuracy of 25 Hz [1] demonstrated a potential for determining the fine-structure constant α with a sub-parts-per-billion accuracy. The main obstacle in achieving this goal is that the present theory of the helium fine structure [2] is not yet developed enough. Another prominent example is the recent measurement of the $2\,^3P$–$2\,^3S$ transition frequency with an accuracy of 1.4 kHz [3]. This accuracy is sufficient for the determination of the nuclear charge radius with a precision below 0.1%, which is better than what is expected from the muonic helium Lamb shift. This determination also requires further developments of the helium theory, the corresponding project being under way [4].

It has been previously pointed out [5] that experimental results for helium transitions involving 3*D* states do not agree well with theoretical predictions. The theoretical values of energy levels of the *D* states were obtained by Drake and co-workers [6–9] and have not been verified by independent calculations. Moreover, their calculations did not fully account for the $m\alpha^6$ QED effects, in contrast to more complete calculations available for the $n = 1$ and $n = 2$ states [5,10]. Motivated by the reported disagreements, in this work we perform calculations of the ionization energies of the 1*s*3*d* states of ^{4}He. We extend the previous works [6–9] by completing the leading QED effects of order $m\alpha^5$ and performing calculations of the next-order corrections of orders $m\alpha^6$ and $m\alpha^5\, m/M$.

I. NONRELATIVISTIC QED EXPANSION

Within the QED theory, the bound-state energies are defined as the positions of the poles of the Fourier transform of the equal-time n-particle propagator as a function of the complex energy argument. To calculate the position of these poles for light atoms, it is convenient to use the nonrelativistic QED (NRQED), which is an effective quantum field theory that gives the same predictions as the full QED in the region of small momenta, i.e., those of the order of the characteristic electron momentum in an atom.

The basic assumption of the NRQED is that the bound-state energy E can be expanded in powers of the fine-structure constant α,

$$E\left(\alpha, \frac{m}{M}\right) = \alpha^2\, E^{(2)}\left(\frac{m}{M}\right) + \alpha^4\, E^{(4)}\left(\frac{m}{M}\right) + \alpha^5\, E^{(5)}\left(\frac{m}{M}\right) + \alpha^6\, E^{(6)}\left(\frac{m}{M}\right) + \alpha^7\, E^{(7)}\left(\frac{m}{M}\right) + \cdots, \quad (1)$$

where m/M is the electron-to-nucleus mass ratio and the expansion coefficients $E^{(n)}$ may contain finite powers of $\ln\alpha$. The coefficients $E^{(i)}(m/M)$ are further expanded in powers of m/M:

$$E^{(i)}\left(\frac{m}{M}\right) = E^{(i,0)} + \frac{m}{M}\, E^{(i,1)} + \left(\frac{m}{M}\right)^2 E^{(i,2)} + \cdots. \quad (2)$$

According to NRQED, the expansion coefficients in Eqs. (1) and (2) can be expressed as expectation values of some effective Hamiltonians with the nonrelativistic wave function. The derivation of these effective Hamiltonians is the central problem of the NRQED approach. While the leading-order expansion terms are simple, formulas become increasingly complicated for higher powers of α.

II. NONRELATIVISTIC ENERGY

The first term of the NRQED expansion of the bound-state energy, $E^{(2,0)} \equiv E$, is the eigenvalue of the Schrödinger-Coulomb Hamiltonian in the infinite nuclear mass limit,

$$H_0 \equiv H = \frac{p_1^2}{2} + \frac{p_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r}, \quad (3)$$

where $r_i = |\vec{r}_i\,|$ and $\vec{r} = \vec{r}_1 - \vec{r}_2$. The finite-nuclear-mass corrections are induced by the nuclear kinetic energy operator

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$(m/M)\,\delta_M H$,

$$\delta_M H = \frac{\vec{P}^2}{2}, \tag{4}$$

where $-\vec{P}$ is the nuclear momentum, and in the center-of-mass frame $\vec{P} = \vec{p}_1 + \vec{p}_2$. In the literature, $\delta_M H$ is often separated into two parts:

$$\delta_M H = \frac{p_1^2 + p_2^2}{2} + \vec{p}_1 \cdot \vec{p}_2. \tag{5}$$

The first part can be absorbed in the nonrelativistic Hamiltonian by introducing the reduced mass, whereas the second part is called the mass polarization operator. In the present work, we prefer to express the recoil corrections in terms of $\delta_M H$, since it makes the resulting formulas simpler and more transparent.

The first- and second-order recoil corrections to the nonrelativistic energy are given by

$$E^{(2,1)} = \langle \delta_M H \rangle, \tag{6}$$

$$E^{(2,2)} = \left\langle \delta_M H \, \frac{1}{(E-H)'} \, \delta_M H \right\rangle. \tag{7}$$

It is also possible to account for the nonrelativistic recoil effect nonperturbatively, by including $(m/M)\,\delta_M H$ into the nonrelativistic Hamiltonian. In the present work, we use the nonperturbative approach. For the convenience of the presentation, we express the complete nonrelativistic energy as $E^{(2)} = E^{(2,0)} + E^{(2,1)} + E^{(2,2+)}$, where $E^{(2,2+)}$ contains corrections of second and higher orders in m/M.

The spatial part of the nonrelativistic wave function of a D state is represented in Cartesian coordinates as a second-rank traceless and symmetric tensor ϕ^{ij},

$$\phi^{ij}(\,^{1,3}D) = \left(r_1^i\, r_1^j\right)^{(2)} F + \left(r_1^i\, r_2^j\right)^{(2)} G \pm (1 \leftrightarrow 2), \tag{8}$$

where $(r_a^i\, r_b^j)^{(2)} = \frac{1}{2}(r_a^i r_b^j + r_a^j r_b^i - \frac{2}{3}\,\delta^{ij} r_a^k r_b^k)$ and the upper (lower) sign corresponds to the singlet (triplet) state, respectively. The functions F and G are scalar functions of r_1, r_2, and r. In our case they are chosen to be linear combinations of exponentials of the form $e^{-\alpha\, r_1 - \beta\, r_2 - \gamma\, r}$ with different nonlinear parameters α, β, and γ. The normalization is taken to be

$$\langle \phi^{ij} | \phi^{ij} \rangle = 1. \tag{9}$$

Here and in what follows, we assume the implicit summation over the repeated Cartesian indices. The matrix element of the nonrelativistic Hamiltonian (or any other spin-independent operator) between the states a and b is of the form

$$\langle a | H | b \rangle = \left\langle \phi_a^{ij} \middle| H \middle| \phi_b^{ij} \right\rangle. \tag{10}$$

The Hamiltonian is represented as a large square matrix, whose eigenvalues are upper bounds of the exact nonrelativistic energies. By increasing the size of the basis, one determines the nonrelativistic energy with a well-controlled uncertainty. The obtained nonrelativistic wave functions are used for calculating relativistic and QED corrections discussed in the next sections.

III. LEADING-ORDER RELATIVISTIC CORRECTION

The leading relativistic correction to the nonrelativistic energy is of order $m\alpha^4$ and is given by the expectation value of the Breit Hamiltonian, which is of the form

$$\begin{aligned} H^{(4+)} = {} & Q_A\left(\frac{m}{M}, a_e\right) + \vec{Q}_B\left(\frac{m}{M}, a_e\right) \cdot \frac{(\vec{\sigma}_1 + \vec{\sigma}_2)}{2} \\ & + \vec{Q}_C\left(\frac{m}{M}, a_e\right) \cdot \frac{(\vec{\sigma}_1 - \vec{\sigma}_2)}{2} + Q_D^{ij}\left(\frac{m}{M}, a_e\right) \sigma_1^i\, \sigma_2^j. \end{aligned} \tag{11}$$

The operators Q_i include the dependence on the nuclear mass M and the electron anomalous magnetic moment (amm) $a_e = \alpha/(2\pi) + \cdots$. They are given by

$$\begin{aligned} Q_A\left(\frac{m}{M}, a_e\right) = {} & -\frac{1}{8}\left(p_1^4 + p_2^4\right) + \frac{Z\pi}{2}\,[\delta^3(r_1) + \delta^3(r_2)] \\ & + \pi\,\delta^3(r) - \frac{1}{2}\, p_1^i \left(\frac{\delta^{ij}}{r} + \frac{r^i\, r^j}{r^3}\right) p_2^j \\ & - \frac{Z\,m}{2\,M}\left[p_1^i \left(\frac{\delta^{ij}}{r_1} + \frac{r_1^i\, r_1^j}{r_1^3}\right)\right. \\ & \left. + p_2^i \left(\frac{\delta^{ij}}{r_2} + \frac{r_2^i\, r_2^j}{r_2^3}\right)\right] P^j, \end{aligned} \tag{12}$$

$$\begin{aligned} \vec{Q}_B\left(\frac{m}{M}, a_e\right) = {} & \frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3} \times \vec{p}_1 + \frac{\vec{r}_2}{r_2^3} \times \vec{p}_2\right)(1 + 2\,a_e) \\ & - \frac{3}{4}\frac{\vec{r}}{r^3} \times (\vec{p}_1 - \vec{p}_2)\left(1 + \frac{4}{3}\,a_e\right) \\ & + \frac{m}{M}\frac{Z}{2}\left(\frac{\vec{r}_1}{r_1^3} + \frac{\vec{r}_2}{r_2^3}\right) \times \vec{P}(1 + a_e), \end{aligned} \tag{13}$$

$$\begin{aligned} \vec{Q}_C\left(\frac{m}{M}, a_e\right) = {} & \frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3} \times \vec{p}_1 - \frac{\vec{r}_2}{r_2^3} \times \vec{p}_2\right)(1 + 2\,a_e) \\ & + \frac{1}{4}\,\frac{\vec{r}}{r^3} \times \vec{P} + \frac{m}{M}\frac{Z}{2}\left(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\right) \times \vec{P}(1 + a_e), \end{aligned} \tag{14}$$

$$Q_D^{ij}\left(\frac{m}{M}, a_e\right) = \frac{1}{4}\left(\frac{\delta^{ij}}{r^3} - 3\frac{r^i r^j}{r^5}\right)(1 + a_e)^2. \tag{15}$$

The upper index in $H^{(4+)}$ indicates that this Hamiltonian includes operators of order $m\alpha^4$ and higher (due to the presence of a_e and m/M). We also need the Hamiltonian that contains only $m\alpha^4$ operators, which is obtained from the above equations by setting $a_e \to 0$ and $m/M \to 0$,

$$H^{(4)} = Q_A + \vec{Q}_B \cdot \frac{(\vec{\sigma}_1 + \vec{\sigma}_2)}{2} + \vec{Q}_C \cdot \frac{(\vec{\sigma}_1 - \vec{\sigma}_2)}{2} + Q_D^{ij}\, \sigma_1^i\, \sigma_2^j, \tag{16}$$

where we assume the short-hand notation $Q_i \equiv Q_i(0, 0)$.

The relativistic corrections to the nonrelativistic energy are given by

$$E^{(4,0)} = \langle H^{(4)} \rangle, \tag{17}$$

$$E^{(4,1)} = 2\left\langle H^{(4)} \, \frac{1}{(E-H)'} \, \delta_M H \right\rangle + \langle \delta_M H^{(4)} \rangle, \tag{18}$$

where $\delta_M H^{(4)}$ is the M-dependent part of $H^{(4+)}$ (with $a_e \to 0$). The higher-order (in the mass ratio) terms can be neglected for the D states.

In practical calculations of $E^{(4,0)}$ it is convenient to use instead of Q_A its regularized form of $Q_{A\mathrm{reg}}$, given by Eq. (46), which has the same expectation value on eigenstates of the (nonrecoil) nonrelativistic Hamiltonian.

The expectation values of spin-dependent operators on the eigenstates of J^2 and J_z ($\vec{J} = \vec{L} + \vec{S}$, where $\vec{S} = \vec{s}_1 + \vec{s}_2$) are calculated with help of the following formulas:

$$\langle {}^3D_J|\vec{Q}\cdot\vec{\sigma}_a|{}^3D_J\rangle = \langle {}^3D_J|\vec{Q}\cdot\vec{S}|{}^3D_J\rangle = u_J\, i\,\epsilon^{jli}\,\langle {}^3D^{jk}|Q^l|{}^3D^{ik}\rangle, \tag{19}$$

$$\langle {}^3D_J|Q^{ij}\,\sigma_1^i\,\sigma_2^j|{}^3D_J\rangle = 2\,\langle {}^3D_J|Q^{ij}\,S^i\,S^j|{}^3D_J\rangle = 2\,v_J\,\langle {}^3D^{ik}|Q^{ij}|{}^3D^{jk}\rangle, \tag{20}$$

where Q^i is an arbitrary vector, Q^{ij} is an arbitrary symmetric and traceless tensor operator, $|{}^3D^{ik}\rangle \equiv |\phi^{ik}({}^3D)\rangle$ is the spacial part of the wave function (8), and

$$u_J = (1, 1/3, -2/3), \tag{21}$$

$$v_J = (-1, 1, -2/7), \tag{22}$$

for $J = 1, 2, 3$, respectively. The above formulas were derived by taking into account that

$$\langle D_J|Q|D_J\rangle = \frac{1}{2J+1}\sum_{M_J}\langle D_{JM_J}|Q|D_{JM_J}\rangle = \frac{1}{2J+1}\sum_{M_J}\mathrm{Tr}[Q\,|D_{JM_J}\rangle\langle D_{JM_J}|], \tag{23}$$

(where $M_J = -J, \ldots, J$ is the angular momentum projection) and then evaluating traces with help of Eqs. (C3)–(C9).

IV. LEADING-ORDER QED

The leading QED correction to energy levels is of order $m\alpha^5$ and can be expressed by

$$E^{(5,0)} = \langle H^{(5)}\rangle, \tag{24}$$

$$E^{(5,1)} = 2\left\langle H^{(5)}\,\frac{1}{(E-H)'}\,\delta_M H\right\rangle + \langle \delta_M H^{(5)}\rangle. \tag{25}$$

The effective $m\alpha^5$ Hamiltonian is [11,12]

$$H^{(5)} = \sum_a\left(\frac{19}{30} + \ln(\alpha^{-2}) - \ln k_0\right)\frac{4Z}{3}\,\delta^3(r_a) + \left(\frac{164}{15} + \frac{14}{3}\,\ln\alpha\right)\delta^3(r) - \frac{7}{6\pi}\left(\frac{1}{r^3}\right)_\epsilon + H^{(5)}_{\mathrm{fs}}, \tag{26}$$

where the index $a = 1, 2$ numerates the electrons and the spin-dependent operator $H^{(5)}_{\mathrm{fs}}$ is the nuclear-mass-independent $m\alpha^5$ part of $H^{(4+)}$ in Eq. (11). Further notations are as follows: $\ln k_0$ is the Bethe logarithm defined as

$$\ln k_0 = \frac{\left\langle \sum_a \vec{p}_a\,(H-E)\,\ln[2\,(H-E)]\,\sum_b \vec{p}_b\right\rangle}{2\,\pi\,Z\left\langle \sum_c \delta^3(r_c)\right\rangle}, \tag{27}$$

and $(1/r^3)_\epsilon$ is the so-called Araki-Sucher term, defined by its matrix elements as

$$\left\langle\frac{1}{r^3}\right\rangle_\epsilon = \lim_{\epsilon\to 0}\int \mathrm{d}^3r\,\phi^*(\vec{r})\left[\frac{1}{r^3}\,\Theta(r-\epsilon) + 4\pi\,\delta^3(r)\times(\gamma + \ln\epsilon)\right]\phi(\vec{r}). \tag{28}$$

The recoil addition to the $m\alpha^5$ Hamiltonian is given by [13]

$$\delta_M H^{(5)} = \sum_a\left[\left(\frac{62}{3} + \ln(\alpha^{-2}) - 8\,\ln k_0 - \frac{4}{Z}\,\delta_M \ln k_0\right)\times\frac{Z^2}{3}\,\delta^3(r_a) - \frac{7\,Z^2}{6\,\pi}\left(\frac{1}{r_a^3}\right)_\epsilon\right] + \delta_M H^{(5)}_{\mathrm{fs}}, \tag{29}$$

where $\delta_M H^{(5)}_{\mathrm{fs}}$ is the nuclear-mass-dependent $m\alpha^5$ part of $H^{(4+)}$ in Eq. (11) and $\delta_M \ln k_0$ is the correction to the Bethe logarithm $\ln k_0$ induced by the nonrelativistic kinetic energy operator $\delta_M H$ in Eq. (4).

In numerical calculations, it is sometimes convenient to separate $\delta_M H$ into the reduced-mass and mass-polarization parts according to Eq. (5). The former can be parametrized analytically by introducing the reduced mass, whereas the latter needs to be calculated numerically. The separation of Eq. (5) leads to

$$\delta_M\left\langle\frac{1}{r^3}\right\rangle_\epsilon = \delta_{p_1p_2}\left\langle\frac{1}{r^3}\right\rangle_\epsilon - 3\left\langle\frac{1}{r^3}\right\rangle_\epsilon + \langle 4\pi\delta^3(r)\rangle, \tag{30}$$

$$\delta_M \ln k_0 = \delta_{p_1p_2}\ln k_0 + 1, \tag{31}$$

where $\delta_{p_1p_2}$ denotes the perturbation due to the mass polarization operator $\vec{p}_1\cdot\vec{p}_2$.

In this work we performed direct numerical calculations of the Bethe logarithm for the $1s3d$ states, with the method described in Ref. [10]. Our numerical results are presented in Table I. They are in good agreement with previous results [14] obtained by the numerical method developed by Drake and Goldman [15]. We also performed calculations of the Bethe logarithm with the mass polarization term included into the Hamiltonian. We found that the mass polarization contribution

TABLE I. Numerical results for the Bethe logarithm $\beta \equiv \ln(k_0/Z^2)$ for the $3\,{}^1D$ and $3\,{}^3D$ states of helium. $\delta\beta = \beta - \beta_{1s}$, where β_{1s} is the Bethe logarithm for the hydrogenic $1s$ state, $\beta_{1s} = 2.984\,128\,555\,765\,498$ [16]. For each state, the upper line presents results for the infinitely massive nucleus; the lower line presents results with inclusion of the mass polarization contribution $(m/M)\,\vec{p}_1\cdot\vec{p}_2$.

State		β	$10^6\delta\beta$	$10^6\delta\beta$
$3\,{}^1D$		2.984 119 109 (7)	−9.447 (7)	−9.38 (7)[a]
	$\vec{p}_1\cdot\vec{p}_2$	2.984 119 106 (7)	−9.449 (7)	
$3\,{}^3D$		2.984 125 886 (2)	−2.670 (2)	−2.64 (11)[a]
	$\vec{p}_1\cdot\vec{p}_2$	2.984 125 891 (2)	−2.665 (2)	

[a]Ref. [14].

to the Bethe logarithm is very small and cannot be clearly identified at the level of our present numerical accuracy of a few parts in 10^{-9}.

V. SINGLET-TRIPLET MIXING

The correction due to mixing of the $3\,^1D$ and $3\,^3D$ states is formally of order $m\alpha^6$ but it is strongly enhanced due to a small energy difference between these states. For this reason we consider this contribution separately.

We calculate the mixing correction by forming an effective Hamiltonian matrix in the subspace of the two strongly mixing states,

$$H_{\rm eff} = \begin{pmatrix} E_{\rm dia}(\,^3D_2) & E_{\rm off} \\ E_{\rm off} & E_{\rm dia}(\,^1D_2) \end{pmatrix}, \tag{32}$$

where

$$E_{\rm dia} = m\alpha^2\,[E^{(2)} + \alpha^2\,E^{(4)} + \alpha^3\,E^{(5)}], \tag{33}$$

$$\begin{aligned} E_{\rm off} &= m\alpha^4\,\langle\,^3D_{2M_J}|H_C|\,^1D_{1M_J}\rangle \\ &= m\alpha^4\,\langle\,^1D_{2M_J}|H_C|\,^3D_{1M_J}\rangle, \end{aligned} \tag{34}$$

and $H_C = \vec{Q}_C(a_e, m/M)\cdot(\vec{\sigma}_1 - \vec{\sigma}_2)/2$ is the part of the Breit Hamiltonian $H^{(4+)}$ that mixes the triplet and singlet states. The mixing correction is obtained by diagonalizing the effective Hamiltonian (32), with the result

$$E_{\rm MIX}(\,^1D_2) = -E_{\rm MIX}(\,^3D_2) = \frac{1}{2}\sqrt{(\Delta E)^2 + 4E_{\rm off}^2} - \frac{1}{2}\Delta E, \tag{35}$$

where $\Delta E = E_{\rm dia}(3\,^1D_2) - E_{\rm dia}(3\,^3D_2) > 0$ and the square of the off-diagonal term is evaluated as

$$|\langle\,^3D_{2M_J}|H_C|\,^1D_{1M_J}\rangle|^2 = \tfrac{2}{3}\,\langle\,^3D^{ik}|\epsilon^{klj}\,i\,Q_C^l|\,^1D^{ij}\rangle^2. \tag{36}$$

VI. $m\alpha^6$ QED

The $m\alpha^6$ correction to the energy levels was derived in Refs. [17,18]. It can be represented as a sum of the first-order and second-order perturbation corrections induced by various effective Hamiltonians,

$$\begin{aligned} E^{(6)} = {} & E_Q + E_H + E_{R1} + E_{R2} + E_{LG} + E_{\rm fs,DK} + E_{\rm fs,amm} \\ & + E_{\rm sec}, \end{aligned} \tag{37}$$

where

$$\begin{aligned} E_Q = \Big\langle & -\frac{E^3}{2} - \frac{1}{8}EZQ_1 + \frac{Q_2}{8} + \frac{1}{8}Z(1-2Z)Q_3 + \frac{3}{16}ZQ_4 - \frac{1}{4}ZQ_5 + \frac{Q_{6S}}{24} - \frac{(\mathcal{S}+3)}{96}Q_{6T} + \frac{1}{4}(E^2 + 2E^{(4,0)})Q_7 \\ & - \frac{(5\mathcal{S}+31)}{32}EQ_8 + \frac{(5\mathcal{S}+23)}{32}Q_9 + \frac{1}{2}EZ^2Q_{11} + EZ^2Q_{12} - EZQ_{13} - Z^2Q_{14} + Z^3Q_{15} - \frac{1}{2}Z^2Q_{16} - \frac{(5\mathcal{S}+23)Z}{16}Q_{17} \\ & - \frac{(5\mathcal{S}+13)Z}{32}Q_{18} + \frac{1}{2}ZQ_{19} - \frac{1}{8}Z^2Q_{20} + \frac{1}{4}Z^2Q_{21} + \frac{1}{4}Z^2Q_{22} + \frac{(5\mathcal{S}+47)}{32}Q_{23} + \frac{1}{2}ZQ_{24} + \frac{(\mathcal{S}-3)}{192}Q_{25} - \frac{1}{4}ZQ_{26} \\ & - \frac{1}{8}EQ_{27} - \frac{1}{2}ZQ_{28} + \frac{Q_{29}}{4} + \frac{Q_{30}}{8}\Big\rangle, \end{aligned} \tag{38}$$

where $\mathcal{S} = \vec{\sigma}_1\cdot\vec{\sigma}_2$, $\langle\mathcal{S}\rangle = -3$ for singlet and $\langle\mathcal{S}\rangle = 1$ for triplet states, and operators Q_i are defined in Table II. E_H is the high-energy contribution induced by the forward three-photon exchange scattering amplitude,

$$E_H = \left[-\frac{39\zeta(3)}{\pi^2} + \frac{32}{\pi^2} - 6\ln 2 + \frac{7}{3}\right]\frac{\pi}{4}\langle\delta(r)\rangle, \tag{39}$$

and E_{LG} is the logarithmic contribution,

$$E_{LG} = -\pi\,\ln\alpha\,\langle\delta(r)\rangle. \tag{40}$$

E_{R1} and E_{R2} are the radiative one-loop and two-loop contributions, respectively:

$$E_{R1} = Z^2\left[\frac{427}{96} - 2\,\ln 2\right]\pi\,\langle\delta^3(r_1) + \delta^3(r_2)\rangle + \left[\frac{6\,\zeta(3)}{\pi^2} - \frac{697}{27\,\pi^2} - 8\,\ln 2 + \frac{1099}{72}\right]\pi\,\langle\delta^3(r)\rangle, \tag{41}$$

$$E_{R2} = Z\left[-\frac{9\,\zeta(3)}{4\,\pi^2} - \frac{2179}{648\,\pi^2} + \frac{3\,\ln 2}{2} - \frac{10}{27}\right]\pi\,\langle\delta^3(r_1) + \delta^3(r_2)\rangle + \left[\frac{15\,\zeta(3)}{2\,\pi^2} + \frac{631}{54\,\pi^2} - 5\,\ln 2 + \frac{29}{27}\right]\pi\,\langle\delta^3(r)\rangle. \tag{42}$$

$E_{\rm fs,DK}$ is the Douglas-Kroll correction to the fine structure,

$$\begin{aligned} E_{\rm fs,DK} = {} & -\frac{3Z}{8}R_1 - ZR_2 + \frac{Z}{2}R_3 + \frac{1}{2}R_4 - \frac{1}{2}R_5 + \frac{5}{8}R_6 - \frac{3}{4}R_7 - \frac{1}{4}R_8 - \frac{3}{4}R_9 + \frac{3}{8}R_{10} - \frac{3}{16}R_{11} - \frac{1}{16}R_{12} + \frac{3}{2}R_{13} - \frac{1}{4}R_{14} \\ & + \frac{1}{8}R_{15}, \end{aligned} \tag{43}$$

TABLE II. Expectation values of operators Q_i with $i = 1, \ldots, 30$ for the $3\,^1D$ and $3\,^3D$ states, $\vec{p} = (\vec{p}_1 - \vec{p}_2)/2$, $\vec{P} = \vec{p}_1 + \vec{p}_2$.

		$3\,^1D$	$3\,^3D$
Q_1	$4\pi\,\delta^3(r_1)$	15.99824880	15.99784093
Q_2	$4\pi\,\delta^3(r)$	0.00002874	0
Q_3	$4\pi\,\delta^3(r_1)/r_2$	1.78124709	1.78249111
Q_4	$4\pi\,\delta^3(r_1)\,p_2^2$	1.78492102	1.78746694
Q_5	$4\pi\,\delta^3(r)/r_1$	0.00002428	0
Q_{6S}	$4\pi\;\delta^3(r)\,P^2$	0.00018470	0
Q_{6T}	$4\pi\;\vec{p}\,\delta^3(r)\,\vec{p}$	0	0.00019375
Q_7	$1/r$	0.11121606	0.11129738
Q_8	$1/r^2$	0.01496643	0.01497321
Q_9	$1/r^3$	0.00258825	0.00257961
Q_{10}	$1/r^4$	0.00058978	0.00065795
Q_{11}	$1/r_1^2$	4.00705950	4.00698329
Q_{12}	$1/(r_1 r_2)$	0.22267879	0.22284220
Q_{13}	$1/(r_1 r)$	0.11870346	0.11879759
Q_{14}	$1/(r_1 r_2 r)$	0.02973688	0.02979293
Q_{15}	$1/(r_1^2 r_2)$	0.46021055	0.46055487
Q_{16}	$1/(r_1^2 r)$	0.44649022	0.44680978
Q_{17}	$1/(r_1 r^2)$	0.01618262	0.01620066
Q_{18}	$(\vec{r}_1 \cdot \vec{r})/(r_1^3 r^3)$	0.00039491	0.00039799
Q_{19}	$(\vec{r}_1 \cdot \vec{r})/(r_1^3 r^2)$	0.00678471	0.00679459
Q_{20}	$r_1^i r_2^j (r^i r^j - 3\delta^{ij} r^2)/(r_1^3 r_2^3 r)$	0.00244330	0.00231961
Q_{21}	p_2^2/r_1^2	0.47602349	0.47671633
Q_{22}	$\vec{p}_1 (1/r_1^2)\,\vec{p}_1$	16.00022730	15.99977930
Q_{23}	$\vec{p}_1 (1/r^2)\,\vec{p}_1$	0.03192362	0.03210149
Q_{24}	$p_1^i\,(r^i r^j + \delta^{ij} r^2)/(r_1 r^3)\,p_2^j$	−0.00025389	−0.00024600
Q_{25}	$P^i\,(3r^i r^j - \delta^{ij} r^2)(1/r^5)\,P^j$	−0.00054572	−0.00051388
Q_{26}	$p_2^k\,r_1^i\,(1/r_1^3)(\delta^{jk} r^i/r - \delta^{ik} r^j/r - \delta^{ij} r^k/r - r^i r^j r^k/r^3)\,p_2^j$	0.00081210	0.00036806
Q_{27}	$p_1^2\,p_2^2$	0.44630062	0.44689565
Q_{28}	$p_1^2\,(1/r_1)\,p_2^2$	1.37356243	1.37554162
Q_{29}	$\vec{p}_1 \times \vec{p}_2\,(1/r)\,\vec{p}_1 \times \vec{p}_2$	0.04578880	0.04728700
Q_{30}	$p_1^k\,p_2^l\,(-\delta^{jl} r^i r^k/r^3 - \delta^{ik} r^j r^l/r^3 + 3r^i r^j r^k r^l/r^5)\,p_1^i\,p_2^j$	−0.02301349	−0.02388848

where R_i are defined in Table III, and $E_{\mathrm{fs,amm}}$ is the amm correction to the fine structure, which is the $m\alpha^6$ part of the Breit Hamiltonian $H^{(4+)}$ in Eq. (11).

E_{sec} is the second-order correction induced by the Breit Hamiltonian. After the separation of divergences, it is represented as

$$E_{\mathrm{sec}} = \left\langle H_{\mathrm{reg}}^{(4)} \frac{1}{(E-H)''} H_{\mathrm{reg}}^{(4)} \right\rangle, \tag{44}$$

where $H_{\mathrm{reg}}^{(4)}$ is the regularized Breit Hamiltonian defined below. The double prime on the electron propagator $1/(E - H)''$ indicates that one should exclude from the summation over the Schrödinger spectrum not only the reference state (as is the case in all second-order corrections), but also the state with the opposite spin coupling. More specifically, for the $3\;^{2S+1}D$ reference states relevant for this work, we exclude *both* the $3\;^1D$ and $3\;^3D$ states from the summation over the spectrum. We note that the intermediate state with the opposite spin coupling (triplet for singlet, and vice versa) is already accounted for in the mixing contribution discussed in Sec. V.

The regularized Breit Hamiltonian is given by [17]

$$H_{\mathrm{reg}}^{(4)} = Q_{A\mathrm{reg}} + \vec{Q}_B \cdot \frac{(\vec{\sigma}_1 + \vec{\sigma}_2)}{2} + \vec{Q}_C \cdot \frac{(\vec{\sigma}_1 - \vec{\sigma}_2)}{2} + Q_D^{ij}\,\sigma_1^i\,\sigma_2^j, \tag{45}$$

where

$$Q_{A\mathrm{reg}} = -\frac{1}{2}(E-V)^2 - p_1^i \frac{1}{2r}\left(\delta^{ij} + \frac{r^i r^j}{r^2}\right) p_2^j + \frac{1}{4}\vec{\nabla}_1^2 \vec{\nabla}_2^2 - \frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3} \cdot \vec{\nabla}_1 + \frac{\vec{r}_2}{r_2^3} \cdot \vec{\nabla}_2\right), \tag{46}$$

and $V = -Z/r_1 - Z/r_2 + 1/r$. The operator $\vec{\nabla}_1^2 \vec{\nabla}_2^2$ in the above expression is non-Hermitian and requires an explicit definition. Its action on a trial function ϕ on the right should be understood as a plain differentiation (omitting $\delta^3(r)$; no

TABLE III. Expectation values of spin-dependent $m\alpha^6$ operators for the 3^3D_J states.

R_1	$p_1^2\,(\vec{r}_1/r_1^3)\times\vec{p}_1\cdot\vec{\sigma}_1$	$-0.001359311\ u_J$
R_2	$(\vec{r}_1/r_1^3)\times(\vec{r}/r^3)\cdot\vec{\sigma}_1\,(\vec{r}\cdot\vec{p}_2)$	$-0.002475817\ u_J$
R_3	$(\vec{r}/r^3)\cdot\vec{\sigma}_1\,(\vec{r}_1/r_1^3)\cdot\vec{\sigma}_2$	$-0.000693482\ 2\ v_J$
R_4	$(\vec{r}/r^4)\times\vec{p}_2\cdot\vec{\sigma}_1$	$0.000921565\ u_J$
R_5	$(\vec{r}/r^6)\cdot\vec{\sigma}_1\,\vec{r}\cdot\vec{\sigma}_2$	$0.000197304\ 2\ v_J$
R_6	$p_1^2\,(\vec{r}/r^3)\times\vec{p}_1\cdot\vec{\sigma}_1$	$-0.001250197\ u_J$
R_7	$p_1^2\,(\vec{r}/r^3)\times\vec{p}_2\cdot\vec{\sigma}_1$	$0.014880254\ u_J$
R_8	$i\,p_1^2\,(1/r)\,\vec{\sigma}_1\cdot(\vec{p}_1\times\vec{p}_2)$	$0.001726521\ u_J$
R_9	$i\,p_1^2\,(\vec{r}/r^3)\cdot\vec{p}_2\,\vec{r}\times\vec{p}_1\cdot\vec{\sigma}_1$	$-0.001924622\ u_J$
R_{10}	$i\,(\vec{r}/r^5)\times(\vec{r}\cdot\vec{p}_2)\,\vec{p}_1\cdot\vec{\sigma}_1$	$-0.000041310\ u_J$
R_{11}	$(\vec{r}/r^5)\times(\vec{r}\times\vec{p}_1\cdot\vec{\sigma}_1)\,\vec{p}_2\cdot\vec{\sigma}_2$	$-0.000088519\ 2\ v_J$
R_{12}	$(1/r^3)\,\vec{p}_1\cdot\vec{\sigma}_2\,\vec{p}_2\cdot\vec{\sigma}_1$	$0.000182341\ 2\ v_J$
R_{13}	$p_1^2\,(\vec{r}/r^5)\cdot\vec{\sigma}_1\,\vec{r}\cdot\vec{\sigma}_2$	$0.001782698\ 2\ v_J$
R_{14}	$i\,p_1^2\,(\vec{r}/r^3)\cdot\vec{\sigma}_1\,\vec{p}_1\cdot\vec{\sigma}_2$	$0.001084191\ 2\ v_J$
R_{15}	$i\,p_1^2\,(1/r^3)\,[\vec{r}\cdot\vec{\sigma}_1\,\vec{p}_2\cdot\vec{\sigma}_2+\vec{r}\cdot\vec{\sigma}_2\,\vec{p}_2\cdot\vec{\sigma}_1-(3/r^2)\vec{r}\cdot\vec{\sigma}_1\,\vec{r}\cdot\vec{\sigma}_2\,(\vec{r}\cdot\vec{p}_2)]$	$-0.005402678\ 2\ v_J$

differentiation by parts is allowed in the matrix element). We note that the expectation value of the regularized Breit Hamiltonian on the eigenfunctions of the (nonrecoil) nonrelativistic Hamiltonian is the same as that of $H^{(4)}$:

$$\left\langle H^{(4)}_{\rm reg}\right\rangle = \langle H^{(4)}\rangle = E^{(4,0)}. \tag{47}$$

The second-order $m\alpha^6$ correction involves numerous contributions from many different symmetries of intermediate states. The angular momentum algebra is performed in Cartesian coordinates as explained in Appendix B, with the explicit formulas listed in Appendix D.

VII. HIGHER-ORDER QED CORRECTION

We estimate the $m\alpha^7$ correction to the ionization energy of $1snd$ states as

$$E^{(7)} = \left[Z^3(L^2A_{62}+LA_{61}+A_{60})+\frac{Z^2}{\pi}B_{50}+\frac{Z}{\pi^2}C_{40}\right] \times\left[\langle\delta(\vec{r}_1)+\delta(\vec{r}_2)\rangle-\frac{Z^3}{\pi}\right], \tag{48}$$

where $L=\ln[(Z\alpha)^{-2}]$ and A_{ij}, B_{ij}, and C_{ij} are the coefficients of the $Z\alpha$ expansion of one-loop, two-loop, and three-loop

TABLE IV. $m\alpha^6$ corrections for ionization energies, in units of $10^{-3}\,m\alpha^6$. Conversion factor to MHz is 0.018658054. $S=0$, 1 denotes the spin of the reference state, whereas $S'=1-S$ denotes the opposite spin state (triplet for singlet and vice versa).

Contribution	Intermediate states symmetry	$3\,^1D$	$3\,^3D$ $J=1$	$3\,^3D$ $J=2$	$3\,^3D$ $J=3$
E_Q		19.711	19.853	19.853	19.853
E_H		−0.006			
E_{R1}		−10.667	−13.220	−13.220	−13.220
E_{R2}		−0.098	−0.118	−0.118	−0.118
E_{LG}		0.035			
$E_{\rm fs,DK}$			−6.395	0.377	2.471
$E_{\rm fs,amm}$			−0.050	0.051	−0.015
$E_{\rm sec}$	$^{2S'+1}P$	−0.018	−0.025		
	$^{2S'+1}D$	−1.156		−1.158	
	$^{2S'+1}F$	−0.057			−0.039
	^{2S+1}S		0.148		
	^{2S+1}P		−0.021	−0.145	
	^{2S+1}D	−0.156 (2)	0.705 (8)	0.233 (2)	0.313 (6)
	^{2S+1}F			−0.056	−0.057
	^{2S+1}G				−0.013
Total		7.589 (2)	0.873 (8)	5.816 (2)	9.175 (6)
Total (MHz)		0.142	0.016	0.109	0.171

TABLE V. Theoretical ionization energies of the $1s3d$ states of ^{4}He, in MHz. The values of fundamental constants used are $R_\infty c = 3\,289\,841\,960.355$ MHz, $\alpha^{-1} = 137.035\,999\,139$, $M/m = 7294.29954136$. Uncertainties of fundamental constants do not influence the numerical results presented.

	$3\,^1D_2$	$3\,^3D_1$	$3\,^3D_2$	$3\,^3D_3$
$E^{(2,0)}$	−365 966 841.606	−366 069 330.717	−366 069 330.717	−366 069 330.717
$E^{(2,1)}$	49 946.656	50 208.515	50 208.515	50 208.515
$E^{(2,2+)}$	−13.886	−13.652	−13.652	−13.652
$E^{(4,0)}$	−851.144	259.290	−1 039.409	−1 141.056
$E^{(4,1)}$	0.154	−0.465	0.081	0.143
$E^{(5,0)}$	−13.962	−15.707	−17.705	−16.413
$E^{(5,1)}$	−0.004	0.003	0.004	0.004
$E_{\rm MIX}$	24.967 (5)	0.0	−24.967 (5)	0.0
$E^{(6,0)}$	0.142	0.016	0.109	0.171
$E^{(7,0)}$	0.019 (19)	0.023 (23)	0.023 (23)	0.023 (23)
$E_{\rm FNS}$	−0.008	−0.009	−0.009	−0.009
Total theory	−365 917 748.673 (20)	−366 018 892.702 (23)	−366 020 217.728 (24)	−366 020 292.992 (23)
Previous theory [9]	−365 917 749.02 (2)	−366 018 892.97 (2)	−366 020 218.09 (2)	−366 020 293.41 (2)
Difference	0.35 (3)	0.27 (3)	0.36 (3)	0.42 (3)

QED effects for the $1s$ hydrogenic state, respectively. The numerical values of the coefficients are $A_{62} = -1$, $A_{61} = 5.286040$, $A_{60} = -31.501041$, $B_{50} = -21.5544$, and $C_{40} = 0.417504$ [19]. Having in mind that in order $m\alpha^6$ the radiative QED correction is one of the largest but not the dominant contribution, we ascribe the uncertainty of 100% to this approximation of $E^{(7)}$.

VIII. RESULTS AND DISCUSSION

The results of our numerical calculations of the $m\alpha^6$ corrections are listed in Table IV. The numerical values presented are corrections to the ionization energy; i.e., the corresponding hydrogenic $1s$ contributions are subtracted from E_Q, E_{R1}, E_{R2}, and $E_{\rm sec}(^{2S+1}D)$. The subtraction of the hydrogenic contribution leads to a cancellation of about five decimal figures, which makes calculations rather demanding, especially for the $E_{\rm sec}(^{2S+1}D)$ correction. Specifically, for the $3\,^1D_2$ reference state, the numerical value of −0.156 (2) quoted in Table IV for the $E(3\,^1D_2|\,^1D)$ arises as $-16\,000.156\,(2) + 16\,000$, where the latter term is the hydrogenic $1s$ contribution.

The interesting feature about the obtained $m\alpha^6$ results is that the one-loop radiative correction E_{R1} is *not* dominant. The remaining, nonradiative $m\alpha^6$ contribution is larger than the radiative, and of the opposite sign. As a result, the total $m\alpha^6$ correction is quite small numerically and differs significantly from the previous estimations [9]. The nonradiative part of $m\alpha^6$ correction, which has not been accounted for in the previous calculation [9], shifts the $3\,^1D_2$ and $3\,^3D_1$ ionization energies by 0.34 and 0.27 MHz, respectively.

Table V presents a summary of individual contributions to the ionization energy of the $3\,^1D_2$ and $3\,^3D_J$ states of the ^{4}He atom. Our theoretical values of the ionization energies differ from the previous results of Morton *et al.* [9] by about 0.3 MHz, or 10σ. The main reason for such a large deviation is the nonradiative part of the $m\alpha^6$ correction described in the preceding paragraph. Moreover, our final uncertainty is similar to that of Morton *et al.*, but in our case it comes from the higher-order $m\alpha^7$ contribution, which is estimated by scaling the known result for the hydrogenic radiative corrections. Since we found that in order $m\alpha^6$ the radiative correction is not dominant, we have to assume that a similar situation can occur in the next order, so we estimate the uncertainty as 100% of the radiative effects. For the fine-structure and the singlet-triplet separation intervals, we keep the same uncertainty as for the individual ionization energies, since we assume that the nonradiative $m\alpha^7$ effects could contribute on the same level as the radiative ones.

Tables VI and VII present comparisons of theoretical predictions with experimental results for the fine-structure intervals and various transition frequencies for the ^{4}He atom. The result for the $3\,^1D_2$–$3\,^3D_1$ transition is obtained by combining together four measurements [3,20–22]:

$$E(3\,^1D_2 - 3\,^3D_1) = E(3\,^1D_2 - 2\,^1S_0) + E(2\,^1S_0 - 2\,^3S_1) - E(2\,^3P_0 - 2\,^3S_1) - E(3\,^3D_1 - 2\,^3P_0). \tag{49}$$

For the fine structure, we observe deviations of both sets of theoretical predictions, ours and those of Morton *et al.*, from the experimental results on the level of 2–3 of experimental σ. The experiments are rather old and their accuracy is lower than what could be achievable nowadays, so it is desirable to verify them before any definite conclusions are drawn.

The comparison of theory and experiment for transition frequencies presented in Table VII is quite surprising. We

TABLE VI. Fine-structure energy differences of the $3\,^3D_J$ states of ^{4}He, in MHz.

ν_{32}	ν_{21}	ν_{31}	
−75.264 (24)	−1325.026 (24)	−1400.290 (23)	This work
−75.32 (2)	−1325.12 (2)	−1400.44 (2)	Theory [9]
−76.15 (30)	−1324.50 (35)	−1400.65 (37)	Expt. [23]
−75.97 (23)		−1400.67 (29)	Expt. [24]

TABLE VII. Comparison of different theoretical predictions with experimental results for various transition energies in ^{4}He, in MHz. Theoretical ionization energies of the $n = 2$ states in the column "Present theory" are taken from Ref. [5].

	Experiment	Ref.	Present theory	Difference from experiment	Other theory [9]	Difference from experiment
			$3L'$–$2L$ transitions			
$3\,^1D_2$–$2\,^1S_0$	594 414 291.803 (13)	[20]	594 414 289.3 (1.9)	2.5 (1.9)	594 414 292. (5.)	0. (5.)
$3\,^3D_1$–$2\,^3S_1$	786 823 850.002 (56)	[25]	786 823 848.7 (1.3)	1.3 (1.3)	786 823 845. (7.)	4. (7.)
$3\,^3D_1$–$2\,^3P_0$	510 059 755.352 (28)	[22]	510 059 754.2 (0.7)	1.2 (0.7)	510 059 749. (2.)	6. (2.)
$3\,^1D_2$–$2\,^1P_1$	448 791 399.113 (268)	[26]	448 791 397.8 (0.4)	1.3 (0.5)	448 791 400.5 (2)	−1.4 (2)
			$2L'$–$2L$ transitions			
$2\,^3P_0$–$2\,^3S_1$	276 764 094.657 2 (14)	[3]	276 764 094.5 (2.0)	0.2 (2.0)	276 764 096. (7.)	2. (7.)
$2\,^1S_0$–$2\,^3S_1$	192 510 702.148 72 (20)	[21]	192 510 703.4 (0.8)	−1.3 (0.8)	192 510 697. (9.)	5. (9.)
$2\,^1P_1$–$2\,^1S_0$	145 622 892.886 (183)	[27]	145 622 891.5 (2.3)	1.4 (2.3)	145 622 892. (5.)	0. (5.)
$2\,^1P_1$–$2\,^3S_1$	338 133 594.4 (5)	[28]	338 133 594.9 (1.4)	−0.5 (2.2)	338 133 589. (7.)	5. (7.)
			$3L'$–$3L$ transitions			
$3\,^1D_2$–$3\,^3D_1$	101 143.943 (31)	[3,20–22]	101 144.029 (23)	0.086 (37)	101 143.95 (3)	0.01 (4)

observe good agreement between theory and experiment for all measured $2L'$–$2L$ transitions. For the $3D$–$2L$ intervals, however, all experimental transition frequencies are about 1 MHz larger than the theoretical predictions. Since different experimental results are supposed to be uncorrelated, a reason for the systematic discrepancy should be on the theoretical side. An unaccounted-for contribution of 1 MHz could hardly come from the $3D$ ionization energy since two independent calculations (ours and that of Drake and co-workers [9]) agree on this level of accuracy. This would mean that an unknown, nearly L-independent contribution of about 1 MHz is present for all $n = 2$ ionization energies. Assuming the standard $1/n^3$ scaling of QED effects, this implies an unknown contribution of $10/n^3$ MHz for an arbitrary state.

Having in mind that theoretical energies of the $n = 2$ states of helium have been independently checked on the level of the $m\alpha^5$ effects [10,29], possible sources of unaccounted contributions could be a mistake in the evaluation of the $m\alpha^6$ corrections or an underestimation of $m\alpha^7$ effects. The latter possibility will be checked when our ongoing project of calculating all $m\alpha^7$ effects to the $2\,^3S$ and $2\,^3P$ ionization energies [4] is completed.

On the experimental side, it is desirable to conduct more measurements of transitions between states from different shells, as this will allow to confirm and study further the systematic deviation of experimental results from theoretical predictions.

In summary, we performed detailed calculations of ionization energies of the $1s3d$ states in the ^{4}He atom, including the complete evaluation of the $m\alpha^6$ QED effects. The nonradiative $m\alpha^6$ corrections, which have not been accounted for in the previous calculations, turned out to be much larger than previously anticipated, shifting the theoretical predictions by about 10σ. However, this was not sufficient to explain the previously reported systematic discrepancies between the theoretical and experimental results for the $3D$-$2L$ transitions. These discrepancies could possibly indicate the presence of some unaccounted-for contributions of order $m\alpha^6$ or underestimation of higher-order effects.

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APPENDIX A: WAVE FUNCTIONS IN CARTESIAN COORDINATES

Since we use the explicitly correlated basis functions, it is convenient to represent the angular part of the wave function in Cartesian coordinates. In this section we list the explicit expressions for wave functions of symmetries relevant for this work. We denote by $(\cdots)^{(n)}$ the traceless and symmetric rank-n tensor and $\vec{R} \equiv \vec{r}_1 \times \vec{r}_2$.

The $L = 0$ wave function of a definite exchange symmetry is of the form

$$\phi(^{1,3}S^e) = F \pm (1 \leftrightarrow 2), \tag{A1}$$

where F is a scalar function of r_1, r_2 and $r \equiv |\vec{r}_1 - \vec{r}_2|$, the upper sign corresponds to the singlet, and the lower sign to the triplet state.

The $L = 1$ odd and even wave functions are

$$\vec{\phi}(^{1,3}P^o) = \vec{r}_1 F \pm (1 \leftrightarrow 2), \tag{A2}$$

$$\vec{\phi}(^{1,3}P^e) = \vec{R} F \pm (1 \leftrightarrow 2). \tag{A3}$$

The $L = 2$ odd and even wave functions are

$$\phi^{ij}(^{1,3}D^o) = \left(r_1^i R^j + r_1^j R^i\right) F \pm (1 \leftrightarrow 2), \tag{A4}$$

$$\phi^{ij}(^{1,3}D^e) = \left(r_1^i r_1^j\right)^{(2)} F + \left(r_1^i r_2^j\right)^{(2)} G \pm (1 \leftrightarrow 2), \tag{A5}$$

where

$$\left(r_1^i r_1^j\right)^{(2)} = r_1^j r_1^j - \tfrac{1}{3}\,\delta^{ij}\,r_1^2, \tag{A6}$$

$$\left(r_1^i r_2^j\right)^{(2)} = \tfrac{1}{2}\left(r_1^j r_2^j + r_2^j r_1^j - \tfrac{2}{3}\,\delta^{ij}\,\vec{r}_1\cdot\vec{r}_2\right). \tag{A7}$$

The $L = 3$ odd and even wave functions are

$$\phi^{ijk}({}^{1,3}F^o) = \left(r_1^i r_1^j r_1^k\right)^{(3)} F + \left(r_1^i r_1^j r_2^k\right)^{(3)} G \pm (1 \leftrightarrow 2), \tag{A8}$$

$$\phi^{ijk}({}^{1,3}F^e) = \left(r_1^i r_1^j R^k\right)^{(3)} F + \left(r_1^i r_2^j R^k\right)^{(3)} G \pm (1 \leftrightarrow 2), \tag{A9}$$

where

$$\left(r_1^i r_1^j r_1^k\right)^{(3)} = r_1^i r_1^j r_1^k - \frac{r_1^2}{5}\left(\delta^{ij} r_1^k + \delta^{ik} r_1^j + \delta^{jk} r_1^i\right), \tag{A10}$$

$$\left(r_1^i r_1^j r_2^k\right)^{(3)} = \frac{1}{3}\left[r_1^i r_1^j r_2^k + r_1^i r_2^j r_1^k + r_2^i r_1^j r_1^k - \frac{r_1^2}{5}\left(\delta^{ij} r_2^k + \delta^{ik} r_2^j + \delta^{jk} r_2^i\right) - \frac{2\,\vec{r}_1\cdot\vec{r}_2}{5}\left(\delta^{ij} r_1^k + \delta^{ik} r_1^j + \delta^{jk} r_1^i\right)\right], \tag{A11}$$

$$\left(r_1^i r_1^j R^k\right)^{(3)} = \frac{1}{3}\left[r_1^i r_1^j R^k + r_1^i R^j r_1^k + R^i r_1^j r_1^k - \frac{r_1^2}{5}(\delta^{ij} R^k + \delta^{ik} R^j + \delta^{jk} R^i)\right], \tag{A12}$$

$$\left(r_1^i r_2^j R^k\right)^{(3)} = \frac{1}{6}\left[r_1^i r_2^j R^k + r_1^i R^j r_2^k + R^i r_1^j r_2^k + r_2^i r_1^j R^k + r_2^i R^j r_1^k + R^i r_2^j r_1^k - \frac{2\,\vec{r}_1\cdot\vec{r}_2}{5}(\delta^{ij} R^k + \delta^{ik} R^j + \delta^{jk} R^i)\right]. \tag{A13}$$

The $L = 4$ even wave function is

$$\phi^{ijkl}({}^{1,3}G^e) = \left(r_1^i r_1^j r_1^k r_1^l\right)^{(4)} F + \left(r_1^i r_1^j r_1^k r_2^l\right)^{(4)} G + \left(r_1^i r_1^j r_2^k r_2^l\right)^{(4)} H \pm (1 \leftrightarrow 2), \tag{A14}$$

where

$$\left(r_1^i r_1^j r_1^k r_1^l\right)^{(4)} = r_1^i r_1^j r_1^k r_1^l - \frac{r_1^2}{8}\left(\delta^{ij} r_1^k r_1^l + \delta^{ik} r_1^j r_1^l + \delta^{il} r_1^j r_1^k + \delta^{jk} r_1^i r_1^l + \delta^{jl} r_1^i r_1^k + \delta^{kl} r_1^i r_1^j\right), \tag{A15}$$

$$\left(r_1^i r_1^j r_1^k r_2^l\right)^{(4)} = \tfrac{1}{4}\left[r_1^i r_1^j r_1^k r_2^l + r_1^i r_1^j r_2^k r_1^l + r_1^i r_2^j r_1^k r_1^l + r_2^i r_1^j r_1^k r_1^l - \tfrac{1}{8}(\delta^{ij} S^{kl} + \delta^{ik} S^{jl} + \delta^{il} S^{jk} + \delta^{jk} S^{il} + \delta^{jl} S^{ik} + \delta^{kl} S^{ij})\right], \tag{A16}$$

$$S^{kl} = r_1^2\left(r_1^k r_2^l + r_2^k r_1^l\right) + 2\,\vec{r}_1\cdot\vec{r}_2\, r_1^k r_1^l, \tag{A17}$$

$$\begin{aligned}\left(r_1^i r_1^j r_2^k r_2^l\right)^{(4)} = \tfrac{1}{6}\big[&r_1^i r_1^j r_2^k r_2^l + r_1^i r_2^j r_1^k r_2^l + r_1^i r_2^j r_2^k r_1^l + r_2^i r_1^j r_1^k r_2^l + r_2^i r_1^j r_2^k r_1^l + r_2^i r_2^j r_1^k r_1^l \\ &- \tfrac{1}{8}(\delta^{ij} P^{kl} + \delta^{ik} P^{jl} + \delta^{il} P^{jk} + \delta^{jk} P^{il} + \delta^{jl} P^{ik} + \delta^{kl} P^{ij})\big],\end{aligned} \tag{A18}$$

$$P^{kl} = r_1^2 r_2^k r_2^l + r_2^2 r_1^k r_1^l + 2\,\vec{r}_1\cdot\vec{r}_2\left(r_1^k r_2^l + r_2^k r_1^l\right). \tag{A19}$$

APPENDIX B: TENSOR DECOMPOSITION IN CARTESIAN COORDINATES

In order to perform the angular momentum algebra in Cartesian coordinates, one requires decompositions of products of various operators into traceless and symmetric tensors. First, we decompose the product of a traceless and symmetric tensor D^{ij} and an arbitrary vector Q^k,

$$\begin{aligned}D^{ij}\,Q^k = \;& T^{ijk} + \epsilon^{ikl}\,T^{lj} + \epsilon^{jkl}\,T^{li} + \delta^{ik}\,T^j + \delta^{jk}\,T^i \\ &- \tfrac{2}{3}\,\delta^{ij}\,T^k,\end{aligned} \tag{B1}$$

where

$$T^{ijk} = (D^{ij}\,Q^k)^{(3)}, \tag{B2}$$

$$T^{ij} = \tfrac{1}{6}\,(\epsilon^{jkl} D^{ik}\,Q^l + \epsilon^{ikl} D^{jk}\,Q^l), \tag{B3}$$

$$T^i = \tfrac{3}{10}\,D^{ij} Q^j. \tag{B4}$$

This decomposition was used in calculations of various second-order matrix elements and in the evaluation of the Bethe logarithm. In the latter case, with $Q^k = p^k$, we obtain

$$\begin{aligned}\langle D^{ij} p^k \hat{R} p^k D^{ij}\rangle &= \langle D^{ij}\,p^k\,\hat{R}\,(D^{ij}\,p^k)^+\rangle \\ &= \langle (D^{ij} p^k)^{(3)}\,\hat{R}\,(D^{ij}\,p^k)^{(3)+}\rangle + 6\,\langle T^{ij}\,\hat{R}\,T^{ij+}\rangle \\ &\quad + \tfrac{20}{3}\,\langle T^i\,\hat{R}\,T^{i+}\rangle,\end{aligned} \tag{B5}$$

where $\hat{R} = 1/(E - H)$ and "+" denotes the Hermitian conjugate.

The second decomposition we need is that of the product of two traceless and symmetric tensors D^{ij} and Q^{ij},

$$\begin{aligned}D^{ij}\,Q^{kl} = \;& T^{ijkl} + \epsilon^{ika} T^{jal} + \epsilon^{jka} T^{ial} + \epsilon^{ila} T^{jak} + \epsilon^{jla} T^{iak} \\ &+ \delta^{ik} T^{jl} + \delta^{il} T^{jk} + \delta^{jk} T^{il} + \delta^{jl} T^{ik} - \tfrac{4}{3}\,\delta^{ij} T^{kl}\end{aligned}$$

$$- \tfrac{4}{3}\,\delta^{kl} T^{ij} + T^a\,(\epsilon^{ika}\delta^{jl} + \epsilon^{ila}\delta^{jk} + \epsilon^{jka}\delta^{il} + \epsilon^{jla}\delta^{ik}) + T\left(\delta^{ik}\delta^{jl} + \delta^{il}\,\delta^{jk} - \tfrac{2}{3}\,\delta^{ij}\delta^{kl}\right), \quad \text{(B6)}$$

where

$$T^{ijkl} = (D^{ij}\,Q^{kl})^{(4)}, \quad \text{(B7)}$$

$$T^{jbl} = \tfrac{1}{4}\,(\epsilon^{ikb}\,D^{ij}\,Q^{kl})^{(3)}, \quad \text{(B8)}$$

$$T^{jl} = \tfrac{3}{7}\,(D^{ij}\,Q^{il})^{(2)}, \quad \text{(B9)}$$

$$T^{b} = \tfrac{1}{10}\,\epsilon^{jlb}\,D^{ij}\,Q^{il}, \quad \text{(B10)}$$

$$T = \tfrac{1}{10}\,D^{ij}\,Q^{ij}. \quad \text{(B11)}$$

APPENDIX C: SPIN-ANGULAR REPRESENTATION OF *D* STATES

Let $\vec{S}$ be the angular momentum operator for $S = 1$ that satisfies the commutator relation

$$[S^i, S^j] = i\,\epsilon^{ijk}\,S^k, \quad \text{(C1)}$$

then in the fundamental representation

$$S^i\,S^j\,S^k = \frac{i}{2}\,\epsilon^{ijk}\,\vec{S}^2 + \delta^{jk}\,S^i + i\,\epsilon^{ika}\,S^j\,S^a \quad \text{(C2)}$$

and

$$\mathrm{Tr}\,S^i\,S^j = 2\,\delta^{ij}, \quad \text{(C3)}$$

$$\mathrm{Tr}\,S^i\,S^j\,S^k = i\,\epsilon^{ijk}, \quad \text{(C4)}$$

$$\mathrm{Tr}\,S^i\,S^j\,S^k\,S^l = \delta^{ij}\,\delta^{kl} + \delta^{jk}\,\delta^{il}. \quad \text{(C5)}$$

Assuming the explicit representation of the spin operator in terms of Pauli matrices, $\vec{S} = (\vec{\sigma}_1 + \vec{\sigma}_2)/2$, we obtain the following identities:

$$\frac{1}{5}\sum_M |\,^1D_{2M}\rangle\,\langle\,^1D_{2M}| = |\,^1D^{ij}\rangle\langle\,^1D^{ij}|\left(1 - \frac{\vec{S}^2}{2}\right), \quad \text{(C6)}$$

$$\frac{1}{3}\sum_M |\,^3D_{1M}\rangle\,\langle\,^3D_{1M}| = |\,^3D^{ik}\rangle\langle\,^3D^{jk}|\left(\delta^{ij}\,\frac{\vec{S}^2}{2} - S^j\,S^i\right), \quad \text{(C7)}$$

$$\frac{1}{5}\sum_M |\,^3D_{2M}\rangle\,\langle\,^3D_{2M}| = |\,^3D^{ik}\rangle\langle\,^3D^{jk}|\left(-\frac{1}{3}\,\delta^{ij}\,\frac{\vec{S}^2}{2} + \frac{2}{3}\,S^i\,S^j + \frac{1}{3}\,S^j\,S^i\right), \quad \text{(C8)}$$

$$\frac{1}{7}\sum_M |\,^3D_{3M}\rangle\,\langle\,^3D_{3M}| = |\,^3D^{ik}\rangle\langle\,^3D^{jk}|\left(\frac{11}{21}\,\delta^{ij}\,\frac{\vec{S}^2}{2} - \frac{10}{21}\,S^i\,S^j + \frac{4}{21}\,S^j\,S^i\right). \quad \text{(C9)}$$

APPENDIX D: EXPLICIT FORMULAS FOR THE SECOND-ORDER CORRECTIONS

In this section we present explicit calculation formulas for the second-order corrections, for the singlet ($S = 0$) and triplet ($S = 1$) reference states. For each reference state, there are four different symmetries of intermediate states contributing, with rational weight factors that are determined by the angular momentum algebra method illustrated in the previous sections. The results are as follows. For $S = 1$ and $J = 1$,

$$E_{\rm sec}(\,^3D_1) = E(\,^3D_1|\,^1P^e) + E(\,^3D_1|\,^3S) + E(\,^3D_1|\,^3P^e) + E(\,^3D_1|\,^3D), \quad \text{(D1)}$$

$$E(\,^3D_1|\,^1P^e) = \sum_n \frac{1}{E - E_n}\,\langle\,^3D^{ij}|i\,Q^j_C|\,^1P^i_n\rangle^2, \quad \text{(D2)}$$

$$E(\,^3D_1|\,^3S) = \frac{4}{3}\sum_n \frac{1}{E - E_n}\,\langle\,^3D^{ij}|Q^{ij}_D|\,^3S_n\rangle^2, \quad \text{(D3)}$$

$$E(\,^3D_1|\,^3P^e) = \frac{1}{2}\sum_n \frac{1}{E - E_n}\,\langle\,^3D^{kj}|i\,\delta^{ki}\,Q^j_B - 2\,\epsilon^{jli}Q^{kl}_D|\,^3P^i_n\rangle^2, \quad \text{(D4)}$$

$$E(\,^3D_1|\,^3D) = \sum_n{}'' \frac{1}{E - E_n}\,\langle\,^3D^{ik}|\delta^{kj}\,Q_{\rm Areg} + i\,\epsilon^{klj}Q^l_B - 2\,Q^{kj}_D|\,^3D^{ij}_n\rangle^2. \quad \text{(D5)}$$

For $S = 1$ and $J = 2$,

$$E_{\rm sec}(^3D_2) = E(^3D_2|\,^1D) + E(^3D_2|^3P^e) + E(^3D_2|^3D) + E(^3D_2|\,^3F^e), \quad \text{(D6)}$$

$$E(^3D_2|\,^1D) = \frac{2}{3}\sum_n{}'' \frac{1}{E - E_n}\,\langle\,^3D^{ik}|\epsilon^{klj}i\,Q^l_C|\,^1D^{ij}_n\rangle^2, \quad \text{(D7)}$$

$$E(\,^3D_2|\,^3P^e) = \frac{1}{10}\sum_n \frac{1}{E - E_n}\,\langle\,^3D^{kj}|3\,i\,\delta^{ki}\,Q^j_B + 2\,\epsilon^{jli}Q^{kl}_D|\,^3P^i_n\rangle^2, \quad \text{(D8)}$$

$$E(\,^3D_2|\,^3D) = \sum_n{}'' \frac{1}{E-E_n}\,\langle\,^3D^{ik}|\delta^{jk}\,Q_{\rm Areg} + \frac{i}{3}\,\epsilon^{klj}Q_B^l + 2\,Q_D^{kj}\,|\,^3D_n^{ij}\rangle^2, \tag{D9}$$

$$E(\,^3D_2|\,^3F^e) = \frac{2}{3}\sum_n \frac{1}{E-E_n}\,\langle\,^3D^{ia}|i\,\delta^{ja}\,Q_B^k - 2\,\epsilon^{abj}Q_D^{bk}\,|\,^3F_n^{ijk}\rangle^2. \tag{D10}$$

For $S = 1$ and $J = 3$,

$$E_{\rm sec}(\,^3D_3) = E(\,^3D_3|\,^1F^e) + E(\,^3D_3|\,^3D) + E(\,^3D_3|\,^3F^e) + E(\,^3D_3|\,^3G), \tag{D11}$$

$$E(\,^3D_3|\,^1F^e) = \frac{5}{7}\sum_n \frac{1}{E-E_n}\,\langle\,^3D^{ij}|i\,Q_C^k\,|\,^1F_n^{ijk}\rangle^2, \tag{D12}$$

$$E(\,^3D_3|\,^3D) = \sum_n{}'' \frac{1}{E-E_n}\,\langle\,^3D^{ik}|\delta^{jk}\,Q_{\rm Areg} - \frac{2}{3}\,i\,\epsilon^{klj}Q_B^l - \frac{4}{7}\,Q_D^{kj}\,|\,^3D_n^{ij}\rangle^2, \tag{D13}$$

$$E(\,^3D_3|\,^3F^e) = \frac{20}{21}\sum_n \frac{1}{E-E_n}\,\langle\,^3D^{ia}|i\,\delta^{ja}\,Q_B^k + \epsilon^{abj}Q_D^{bk}\,|\,^3F_n^{ijk}\rangle^2, \tag{D14}$$

$$E(\,^3D_3|\,^3G) = \frac{20}{7}\sum_n \frac{1}{E-E_n}\,\langle\,^3D^{ij}|Q_D^{kl}\,|\,^3G_n^{ijkl}\rangle^2. \tag{D15}$$

For $S = 0$ and $J = 2$,

$$E_{\rm sec}(\,^1D_2) = E(\,^1D_2|\,^1D) + E(\,^1D_2|\,^3P^e) + E(\,^1D_2|\,^3D) + E(\,^1D_2|\,^3F^e), \tag{D16}$$

$$E(\,^1D_2|\,^1D) = \sum_n{}'' \frac{1}{E-E_n}\,\langle\,^1D^{ij}|Q_{\rm Areg}\,|\,^1D_n^{ij}\rangle^2, \tag{D17}$$

$$E(\,^1D_2|\,^3P^e) = \frac{3}{5}\sum_n \frac{1}{E-E_n}\,\langle\,^1D^{ij}|iQ_C^j\,|\,^3P_n^i\rangle^2, \tag{D18}$$

$$E(\,^1D_2|\,^3D) = \frac{2}{3}\sum_n{}'' \frac{1}{E-E_n}\,\langle\,^1D^{ik}|i\epsilon^{klj}Q_C^l\,|\,^3D_n^{ij}\rangle^2, \tag{D19}$$

$$E(\,^1D_2|\,^3F^e) = \sum_n \frac{1}{E-E_n}\,\langle\,^1D^{ij}|iQ_C^k\,|\,^3F_n^{ijk}\rangle^2. \tag{D20}$$

In the formulas above, the double prime on the sum means that the singlet and triplet $3D$ states are excluded from the summation over the spectrum.

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