# Quantum electrodynamics $m\alpha^6$ and $m\alpha^7 \ln\alpha$ corrections to the fine splitting in Li and $Be^+$

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We derive quantum electrodynamics corrections to the fine structure in three-electron atomic systems at $m\alpha^6$ and $m\alpha^7 \ln\alpha$ orders and present their numerical evaluations for the Li atom and $Be^+$ ion.

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## I. INTRODUCTION

The fine splitting is a difference between energies of $P_{3/2}$ and $P_{1/2}$ states. For hydrogenic systems it can be obtained from the Dirac equation, while for many electron systems one needs quantum electrodynamic (QED) theory to consistently describe correlations with relativistic effects. The most common many-electron Dirac-like methods [1–4] are able to achieve two significant digits at most, while experimental precision is about 6 significant digits [5, 6]. A much more accurate description of light few-electron systems relies on nonrelativistic version of QED, called NRQED theory. Relativistic, retardation, electron self-interaction, and vacuum polarization effects can all be accounted for perturbatively by expansion of energy levels in powers of the fine structure constant $\alpha$,

$$E(\alpha) = m\,\alpha^2\,\mathcal{E}^{(2)} + m\,\alpha^4\,\mathcal{E}^{(4)} + m\,\alpha^5\,\mathcal{E}^{(5)} + m\,\alpha^6\,\mathcal{E}^{(6)} + \ldots \tag{1}$$

where expansion coefficients $\mathcal{E}^{(i)}$ may include powers of $\ln\alpha$. Since these expansion coefficients are expressed in terms of the first- and second-order matrix elements of some operators with the nonrelativistic wave function, the accuracy of the numerical calculation strongly depends on the quality of this function. For example, MCHF calculations [7–9] are accurate only to three digits because the wave function is a combination of Slater determinants and does not satisfy the cusp condition. A much more accurate nonrelativistic wave function can be obtained by using an explicitly correlated basis such as Hylleraas functions [10–13]. However, three-electron integrals with explicitly correlated functions are much more complicated than two-electron ones. Moreover, the required number of basis functions has to be much larger in order to achieve similar accuracy as for two-electron systems. So the extension of QED calculations to a three-electron system is not a simple task. In our recent works [6, 14] we performed complete calculations of higher-order $m\alpha^6$ and $m\,\alpha^7\,\ln\alpha$ corrections to Li and $Be^+$ $2P_{3/2} - 2P_{1/2}$ fine splitting. Here we aim to present in more detail the computational methods.

The fine structure splitting at the leading order $E^{(4)}_{\rm fs}$ is given by the expectation value

$$E^{(4)}_{\rm fs} = \langle H^{(4)}_{\rm fs} \rangle \tag{2}$$

of spin-dependent operators from the Breit-Pauli Hamiltonian [15],

$$\begin{aligned} H^{(4)}_{\rm fs} &= \sum_a \frac{Z\,\alpha}{4\,m^2\,r_a^3}\,\vec{\sigma}_a\left[(g-1)\,\vec{r}_a\times\vec{p}_a\right] \\ &+ \sum_{a\neq b}\frac{\alpha}{4\,m^2\,r_{ab}^3}\,\vec{\sigma}_a\left[g\,\vec{r}_{ab}\times\vec{p}_b - (g-1)\,\vec{r}_{ab}\times\vec{p}_a\right], \end{aligned} \tag{3}$$

where $g$ is the exact electron g-factor. The mean value in Eq. (2), $\langle\ldots\rangle \equiv \langle\Phi|\ldots|\Phi\rangle$ is calculated using the wave function $\Phi$ from the stationary Schrödinger equation

$$(H-E)\Phi = 0 \tag{4}$$

with the nonrelativistic Hamiltonian $H$ in the infinite nuclear mass limit

$$H = \sum_a \frac{\vec{p}_a^{\,2}}{2\,m} + V \tag{5}$$

$$V \equiv \sum_a -\frac{Z\,\alpha}{r_a} + \sum_{a>b}\frac{\alpha}{r_{ab}} \tag{6}$$

The Li and $Be^+$ fine structure in the leading order, including finite nuclear mass corrections, has been calculated by using the Hylleraas functions in Refs. [10, 13]. rThe high accuracy is achieved by the use of a relatively large number (about 14 000) of these functions. All matrix elements are expressed in terms of standard and extended Hylleraas integrals, which are obtained with the help of recursion relations [16, 17].

The situation is different with matrix elements of $m\,\alpha^6$ and higher-order operators in the Hylleraas basis, where additional classes of complicated integrals appear, for which no efficient numerical algorithms are known. Other difficulties arise in the evaluation of the second-order matrix element with nearly singular operators. The Green function, or equivalently the sum over pseudo-states, requires large values of nonlinear parameters. This causes severe problems with the numerical stability of recursive algorithms with Hylleraas integrals. We overcome this problem by the application of another basis set, which consists of the explicitly correlated Gaussian functions. We have found [18, 19] that the second-order matrix elements can be calculated with high precision when nonlinear parameters are globally optimized and a large number of Gaussian functions is employed.

## II. HIGHER-ORDER FINE STRUCTURE

The $m\alpha^6$ correction $E^{(6)}_{\rm fs}$ to the fine structure can be expressed as the sum of the first- and second-order matrix ele-

ments with the nonrelativistic wave function,

$$E^{(6)}_{\rm fs} = \left\langle H^{(4)}\,\frac{1}{(E-H)'}\,H^{(4)}\right\rangle + \langle H^{(6)}_{\rm fs}\rangle, \tag{7}$$

where the Breit-Pauli Hamiltonian $H^{(4)}$ is of the form [15]

$$H^{(4)} = H^{(4)}_A + H^{(4)}_B + H^{(4)}_C \tag{8}$$

$$H^{(4)}_A = \sum_a\left\{-\frac{\vec{p}_a^{\,4}}{8}+\frac{\pi\,Z}{2}\,\delta^3(r_a)\right\} + \sum_{a<b}\left\{\pi\,\delta^3(r_{ab})-\frac{1}{2}\,p_a^i\left(\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)p_b^j\right\}. \tag{9}$$

$$H^{(4)}_B = \sum_a\frac{Z}{4\,r_a^3}\,\vec{\sigma}_a\cdot\vec{r}_a\times\vec{p}_a + \sum_{a\neq b}\frac{1}{4\,r_{ab}^3}\vec{\sigma}_a\left(2\,\vec{r}_{ab}\times\vec{p}_b-\vec{r}_{ab}\times\vec{p}_a\right). \tag{10}$$

$$H^{(4)}_C = \sum_{a<b}\frac{\sigma_a^i\,\sigma_b^j}{4\,r_{ab}^3}\left(\delta^{ij}-3\,\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\right). \tag{11}$$

The potentially singular second-order quadratic term with $H^{(4)}_A$ in Eq. (7) does not contribute to fine splitting, and thus is excluded from further consideration. $H^{(6)}_{\rm fs}$ is an effective Hamiltonian of order $m\,\alpha^6$. Following the derivation in Refs. [20] and [13], $H^{(6)}_{\rm fs}$ can be represented in the following form

$$H^{(6)}_{\rm fs} = \sum_{i=1,7}\delta H_i\,, \tag{12}$$

$$\delta H_1 = \sum_a\frac{3}{16\,m^4}\,p_a^2\,e\,\vec{\mathcal{E}}_a\times\vec{p}_a\cdot\vec{\sigma}_a \tag{13}$$

$$\delta H_2 = \sum_{a\neq b}-\frac{i\,\pi}{8\,m^4}\,\vec{\sigma}_a\cdot\vec{p}_a\times\delta^3(r_{ab})\,\vec{p}_a \tag{14}$$

$$\delta H_4 = \sum_a\frac{e}{4\,m^3}\left[2\,p_a^2\,\vec{p}_a\cdot\vec{\mathcal{A}}_a+p_a^2\,\vec{\sigma}_a\cdot\nabla_a\times\vec{\mathcal{A}}_a\right] \tag{15}$$

$$\delta H_5 = \sum_a\frac{e^2}{2\,m^2}\,\vec{\sigma}_a\cdot\vec{\mathcal{E}}_a\times\vec{\mathcal{A}}_a + \frac{i\,e}{16\,m^3}\left[\vec{\mathcal{A}}_a\times\vec{p}_a\cdot\vec{\sigma}_a-\vec{\sigma}_a\cdot\vec{p}_a\times\vec{\mathcal{A}}_a\,,p_a^2\right] \tag{16}$$

$$\delta H_6 = \sum_a\frac{e^2}{2\,m^2}\,\vec{\mathcal{A}}_a^2 \tag{17}$$

$$\delta H_7 = \sum_{a\neq b}\frac{\alpha}{4\,m^2}\left\{-i\left[\vec{\sigma}_a\times\frac{\vec{r}_{ab}}{r_{ab}},\frac{p_a^2}{2\,m}\right]e\,\vec{\mathcal{E}}_b + \left[\frac{p_b^2}{2\,m},\left[\vec{\sigma}_a\times\frac{\vec{r}_{ab}}{r_{ab}},\frac{p_a^2}{2\,m}\right]\right]\vec{p}_b\right\} \tag{18}$$

where $\mathcal{E}_a$ is the static electric field at the position of particle $a$

$$e\,\vec{\mathcal{E}}_a \equiv -\nabla_a V = -Z\,\alpha\,\frac{\vec{r}_a}{r_a^3}+\sum_{b\neq a}\alpha\,\frac{\vec{r}_{ab}}{r_{ab}^3} \tag{19}$$

and $\mathcal{A}_a^i$ is the vector potential at the position of particle $a$, which is produced by all other particles

$$e\,\mathcal{A}_a^i \equiv \sum_{b\neq a}\frac{\alpha}{2\,r_{ab}}\left(\delta^{ij}+\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\right)\frac{p_b^j}{m}+\frac{\alpha}{2\,m}\,\frac{\left(\vec{\sigma}_b\times\vec{r}_{ab}\right)^i}{r_{ab}^3}\,, \tag{20}$$

In order to further improve theoretical predictions, the higher-order $m\,\alpha^7$ contribution is not neglected but instead is approximated by the numerically dominating logarithmic part. It is obtained from the analogous correction to the helium fine structure [21, 22] by dropping the $\sigma^i\,\sigma^j$ terms because they do not contribute for states with the total electron spin $S=1/2$,

$$E^{(7)}_{\rm fs,log} = \langle H^{(7)}_{\rm fs,log}\rangle + 2\left\langle H^{(4)}_B\,\frac{1}{(E_0-H_0)'}\,H^{(5)}_{\rm log}\right\rangle \tag{21}$$

$$H^{(5)}_{\rm log} = \alpha^2\ln[(Z\,\alpha)^{-2}]\left[\frac{4Z}{3}\,\sum_a\delta^3(r_a)-\frac{7}{3}\sum_{b<a}\delta^3(r_{ab})\right] \tag{22}$$

$$H^{(7)}_{\rm fs,log} = \alpha^2\ln[(Z\,\alpha)^{-2}]\left[\frac{Z}{3}\,\sum_a i\,\vec{p}_a\times\delta^3(r_a)\,\vec{p}_a\cdot\vec{\sigma}_a - \frac{3}{4}\sum_{b\neq a}i\,\vec{p}_a\times\delta^3(r_{ab})\,\vec{p}_a\cdot\vec{\sigma}_a\right]. \tag{23}$$

The neglected higher-order corrections are the nonlogarithmic $m\,\alpha^7$ term and the finite nuclear mass corrections to the $m\,\alpha^6$ contribution. They will limit the accuracy of our theoretical predictions for Li and $Be^+$ fine structure.

## III. TRANSFORMATION OF MATRIX ELEMENTS

The expectation value of $H^{(6)}_{\rm fs}$ in Eq. (12) is transformed initially to a form convenient for numerical calculations with ${}^2P$-states

$$\delta H_1 = = \frac{3}{16}\left(-Z\,Q_1+Q_2\right) \tag{24}$$

$$\delta H_2 = -\frac{\pi}{8}\,D_2 \tag{25}$$

$$\delta H_4 = -\frac{1}{4}\left(Q_3+Q_4\right) \tag{26}$$

$$\delta H_5 = \frac{1}{4}\left[-Z(Q_5+Q_6)+Q_7+Q_8\right]+\frac{1}{8}\left(-ZP_1+P_2\right) + \frac{1}{8}\left(Q_9-Q_{10}-Q_3\right)-\frac{1}{16}\,P_3 \tag{27}$$

$$\delta H_6 = -\frac{1}{4}\left(Q_{11}+Q_{12}\right)+\frac{1}{16}\,P_4 \tag{28}$$

$$\delta H_7 = \frac{Z}{4}\left(Q_{14}-Q_{15}\right)-\frac{1}{4}\left(Q_{17}+Q_{18}\right) + \frac{1}{4}\left(-Q_4+Q_{19}-Q_{20}\right) \tag{29}$$

where $Q_i$ and $P_i$ are defined in Table I. Additionally, operators $Q_1$, $Q_2$, and $Q_4$ are transformed into the sum of the singular D-term with the Dirac-$\delta$ operator and the regular R-part.

Matrix elements with D-terms are calculated with Hylleraas, while Gaussian functions are used for R-terms, which ensures high numerical precision.

The second-order contribution is split into parts coming from intermediate states with specified angular momentum and spin,

$$\left\langle H^{(4)}\,\frac{1}{(E-H)'}\,H^{(4)}\right\rangle = \left\langle H^{(4)}\,\frac{1_{2,4}S_o + 1_{2,4}P + 1_{2,4}D_o + 1_4F}{(E-H)'}\,H^{(4)}\right\rangle = X_{2S_o} + X_{4S_o} + X_{2P} + X_{4P} + X_{2D_o} + X_{4D_o} + X_{4F} \tag{30}$$

where $1_{2,4}X$ is a projection into doublet or quartet state $X$, respectively. These contributions are also defined in Table II. Most of them can be calculated as they stand. Only the non-symmetric $\langle H_B^{(4)}/(E-H)'\,H_A^{(4)}\rangle$ matrix element needs numerical regularization due to the high singularity of $H_A^{(4)}$. This is done as follows: $H_A^{(4)}$ is transformed to the regular form by the following transformations

$$4\pi\,\delta^3(r_a) = 4\pi\,[\delta^3(r_a)]_r - \left\{\frac{2}{r_a}, E-H\right\} \tag{31}$$

$$4\pi\,[\delta^3(r_a)]_r = \frac{4}{r_a}(E-V) - 2\sum_b \vec{p}_b\,\frac{1}{r_a}\,\vec{p}_b \tag{32}$$

$$4\pi\,\delta^3(r_{ab}) = 4\pi\,[\delta^3(r_{ab})]_r - \left\{\frac{1}{r_{ab}}, E-H\right\} \tag{33}$$

$$4\pi\,[\delta^3(r_{ab})]_r = \frac{2}{r_{ab}}(E-V) - \sum_c \vec{p}_c\,\frac{1}{r_{ab}}\,\vec{p}_c \tag{34}$$

$$\sum_a p_a^4 = \sum_a [p_a^4]_r + 4\left\{V, E-H\right\} \tag{35}$$

$$\sum_a [p_a^4]_r = 4\,(E-V)^2 - 2\sum_{a<b}\vec{p}_a^{\,2}\,\vec{p}_b^{\,2} \tag{36}$$

The overall regularized form of $H_A^{(4)}$ is

$$H_A^{(4)} = [H_A^{(4)}]_r + \left\{Q_A, E-H\right\}, \tag{37}$$

where

$$Q_A = \frac{Z}{4}\sum_a \frac{1}{r_a} - \frac{1}{2}\sum_{a<b}\frac{1}{r_{ab}}. \tag{38}$$

The expectation value of the regularized operator is the same as that without regularization. What has changed is the second-order matrix element

$$\left\langle H_B^{(4)}\,\frac{1}{(E-H)'}\,H_A^{(4)}\right\rangle = \left\langle H_B^{(4)}\,\frac{1}{(E-H)'}\,[H_A^{(4)}]_r\right\rangle + \frac{\delta X_{2P}}{2} \tag{39}$$

where

$$\begin{aligned}\delta X_{2P} &= 2\left(\langle H_B^{(4)} Q_A\rangle - \langle H_B^{(4)}\rangle\langle Q_A\rangle\right) \\ &= \frac{Z}{8}\Big(Z\,\langle Q_{21}\rangle + 2\,\langle Q_{23}\rangle - \langle Q_{22}\rangle\Big) \\ &\quad -\frac{1}{4}\Big(Z\,\langle Q_{24}\rangle + 2\,\langle Q_{26}\rangle - \langle Q_{25}\rangle\Big) \\ &\quad -\left(\frac{Z}{4}\,\langle Q_{29}\rangle + \frac{1}{2}\,\langle Q_{31}\rangle - \frac{1}{4}\,\langle Q_{30}\rangle\right) \\ &\quad \times\left(\frac{Z}{2}\langle Q_{27}\rangle - \langle Q_{28}\rangle\right)\end{aligned} \tag{40}$$

These additional $Q_i$ operators together with their expectation value are presented in Table III.

The last considered term, the $m\,\alpha^7\,\ln\alpha$ correction from Eq. (21), is represented as

$$E_{\rm log}^{(7)} = \ln[(Z\,\alpha)^{-2}]\,\left[\frac{Z}{3}\,\langle D_1\rangle - \frac{3}{4}\,\langle D_2\rangle + 2\left(\frac{4Z}{3}\,Y_1 - \frac{7}{3}\,Y_2\right)\right] \tag{41}$$

where $D_i$ are defined in Table I and $Y_i$ in Table II. The second-order matrix element $Y$ requires numerical regularization, similarly to the one in Eq. (39), and is transformed into the following form

$$Y_1 = \left\langle H_B^{(4)}\,\frac{1}{(E-H)'}\,\sum_a [\delta^3(r_a)]_r\right\rangle + \delta Y_1 \tag{42}$$

$$Y_2 = \left\langle H_B^{(4)}\,\frac{1}{(E-H)'}\,\sum_{b<a} [\delta^3(r_{ab})]_r\right\rangle + \delta Y_2 \tag{43}$$

where

$$\begin{aligned}\delta Y_1 &= -\frac{1}{2\,\pi}\sum_a\left(\left\langle\frac{1}{r_a}\,H_B^{(4)}\right\rangle - \langle H_B^{(4)}\rangle\left\langle\frac{1}{r_a}\right\rangle\right) \\ &= \frac{1}{8\,\pi}\Big(-Z\,\langle Q_{21}\rangle + \langle Q_{22}\rangle - 2\,\langle Q_{23}\rangle \\ &\quad +\langle Q_{27}\rangle\,(Z\,\langle Q_{29}\rangle - \langle Q_{30}\rangle + 2\,\langle Q_{31}\rangle)\Big)\end{aligned} \tag{44}$$

$$\begin{aligned}\delta Y_2 &= -\frac{1}{\pi}\sum_{b<a}\left(\left\langle\frac{1}{r_{ab}}\,H_B^{(4)}\right\rangle - \langle H_B^{(4)}\rangle\left\langle\frac{1}{r_{ab}}\right\rangle\right) \\ &= \frac{1}{4\,\pi}\Big(-Z\,\langle Q_{24}\rangle + \langle Q_{25}\rangle - 2\,\langle Q_{26}\rangle \\ &\quad +\langle Q_{28}\rangle\,(Z\,\langle Q_{29}\rangle - \langle Q_{30}\rangle + 2\,\langle Q_{31}\rangle)\Big)\end{aligned} \tag{45}$$

are expressed in terms of $Q_i$ from Table III.

## IV. SPIN REDUCTION OF MATRIX ELEMENTS

The wave function $\Phi^i$ of the $^2$P state in a three-electron system is of the form

$$\Phi^i = \frac{1}{\sqrt{6}}\,\mathcal{A}\big[\phi^i(\vec{r}_1,\vec{r}_2,\vec{r}_3)\,[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]\,\alpha(3)\big], \tag{46}$$

TABLE I: Expectation values of operators for Li and $Be^+$ $2^2P_J$ states, $\langle Q\rangle = K_J\,V$ with the additional prefactor $K_J = \{1, -1/2\}$ for $J = 1/2, 3/2$, correspondingly. All digits are significant.

| Operator | $V_{\rm Li}$ | $V_{\rm Be^+}$ |
|---|---|---|
| $Q_1 = \sum_a \vec\sigma_a\, p_a^2\, \frac{\vec r_a}{r_a^3} \times \vec p_a = -2\,\pi\, D_1 - R_1$ | −0.695 207 | −14.464 31 |
| $D_1 = \sum_a i\,\vec\sigma_a\, \vec p_a \times \delta^3(r_a)\vec p_a$ | 0.097 730 | 2.010 13 |
| $R_1 = \sum_a i\,\vec\sigma_a\, p_a^k\, \vec p_a \times \frac{1}{r_a}\vec p_a\, p_a^k$ | 0.082 895 | 1.834 29 |
| $Q_2 = \sum_{a,b\neq a} \vec\sigma_a\, p_a^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_a = -2\,\pi\, D_2 - R_2$ | −0.502 754 | −11.065 87 |
| $D_2 = \sum_{a,b\neq a} i\,\vec\sigma_a\, \vec p_a \times \delta^3(r_{ab})\vec p_a$ | 0.044 668 | 0.980 97 |
| $R_2 = \sum_{a,b\neq a} i\,\vec\sigma_a\, p_a^k\, \vec p_a \times \frac{1}{r_{ab}}\vec p_a\, p_a^k$ | 0.222 098 | 4.902 28 |
| $Q_3 = \sum_{a,b\neq a} \vec\sigma_a\, p_a^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_b = 2\,\pi\, D_3 + R_3$ | 0.000 421 | 0.737 15 |
| $D_3 = \sum_{a,b\neq a} i\,\vec\sigma_a\, \vec p_b \times \delta^3(r_{ab})\vec p_b$ | 0.017 545 | 0.369 31 |
| $R_3 = \sum_{a,b\neq a} i\,\vec\sigma_a\, p_b^k\, \vec p_b \times \frac{1}{r_{ab}}\vec p_b\, p_b^k$ | −0.109 834 | −1.583 29 |
| $Q_4 = \sum_{a,b\neq a} \vec\sigma_a\, p_b^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_b = 2\,\pi\, D_3 + R_4$ | 0.281 276 | 5.677 45 |
| $R_4 = \sum_{a,b\neq a} i\,\vec\sigma_a\, p_b^k\, \vec p_b \times \frac{1}{r_{ab}}\vec p_b\, p_b^k$ | 0.171 036 | 3.357 01 |
| $Q_5 = \sum_{a,b\neq a} \vec\sigma_a\, \frac{1}{r_{ab}}\, \frac{\vec r_a}{r_a^3} \times \vec p_b$ | 0.161 022 | 2.122 84 |
| $Q_6 = \sum_{a,b\neq a} \vec\sigma_a\, \frac{\vec r_a \times \vec r_{ab}}{r_a^3\, r_{ab}^3}\, (\vec r_{ab}\cdot\vec p_b)$ | 0.068 423 | 0.858 67 |
| $Q_7 = \sum_{a,b\neq a,c\neq a} \vec\sigma_a\, \frac{1}{r_{ac}}\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_c$ | 0.189 027 | 2.559 31 |
| $Q_8 = \sum_{a,b\neq a,c\neq a} \vec\sigma_a\, \frac{\vec r_{ab} \times \vec r_{ac}}{r_{ab}^3\, r_{ac}^3}\, (\vec r_{ac}\cdot\vec p_c)$ | 0.052 774 | 0.675 94 |
| $P_1 = \sum_{a,b\neq a} (\vec\sigma_a \times \vec\sigma_b)\, \frac{\vec r_a \times \vec r_{ab}}{r_a^3\, r_{ab}^3}$ | −0.066 977 | −0.904 13 |
| $P_2 = \sum_{a,b\neq a,c\neq a} (\vec\sigma_a \times \vec\sigma_b)\, \frac{\vec r_{ac} \times \vec r_{ab}}{r_{ac}^3\, r_{ab}^3}$ | −0.059 905 | −0.821 17 |
| $P_3 = \sum_{a,b\neq a} (\vec\sigma_a \times \vec\sigma_b)\, i\, p_a^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_a$ | 0.102 287 | 1.841 14 |
| $Q_9 = \sum_{a,b\neq a} i\,\vec\sigma_a\, p_a^2\, \frac{1}{r_{ab}}\, \vec p_a \times \vec p_b$ | −0.126 256 | −3.131 89 |
| $Q_{10} = \sum_{a,b\neq a} i\,\vec\sigma_a\, p_a^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times (\vec r_{ab}\cdot\vec p_b)\, \vec p_a$ | −0.396 739 | −8.005 14 |
| $Q_{11} = \sum_{a,b\neq a,c\neq b} \vec\sigma_a\, \frac{1}{r_{bc}}\, \frac{\vec r_{ab}}{r_{ab}^3} \times \vec p_c$ | −0.114 547 | −1.441 91 |
| $Q_{12} = \sum_{a,b\neq a,c\neq b} \vec\sigma_a\, \frac{\vec r_{ab} \times \vec r_{bc}}{r_{ab}^3\, r_{bc}^3}\, (\vec r_{bc}\cdot\vec p_c)$ | 0.053 650 | 0.682 88 |
| $P_4 = \sum_{a,b\neq a,c\neq a} (\vec\sigma_a \times \vec\sigma_b)\, \frac{\vec r_{ac} \times \vec r_{bc}}{r_{ac}^3\, r_{bc}^3}$ | 0.059 905 | 0.821 17 |
| $Q_{14} = \sum_{a,b\neq a} \vec\sigma_a\, \frac{1}{r_{ab}}\, \frac{\vec r_b}{r_b^3} \times \vec p_a$ | −0.041 132 | 0.033 59 |
| $Q_{15} = \sum_{a,b\neq a} \vec\sigma_a\, \frac{\vec r_b \times \vec r_{ab}}{r_b^3\, r_{ab}^3}\, (\vec r_{ab}\cdot\vec p_a)$ | −0.144 617 | −1.287 70 |
| $Q_{17} = \sum_{a,b\neq a,c\neq b} \vec\sigma_a\, \frac{1}{r_{ab}}\, \frac{\vec r_{bc}}{r_{bc}^3} \times \vec p_a$ | 0.171 163 | 2.362 41 |
| $Q_{18} = \sum_{a,b\neq a,c\neq b} \vec\sigma_a\, \frac{\vec r_{ab} \times \vec r_{bc}}{r_{ab}^3\, r_{bc}^3}\, (\vec r_{ab}\cdot\vec p_a)$ | 0.065 529 | 0.700 97 |
| $Q_{19} = \sum_{a,b\neq a} i\,\vec\sigma_a\, p_b^2\, \frac{1}{r_{ab}}\, \vec p_a \times \vec p_b$ | −0.224 280 | −3.050 65 |
| $Q_{20} = \sum_{a,b\neq a} i\,\vec\sigma_a\, p_b^2\, \frac{\vec r_{ab}}{r_{ab}^3} \times (\vec r_{ab}\cdot\vec p_a)\, \vec p_b$ | −0.506 006 | −8.526 97 |

where $\mathcal{A}$ denotes antisymmetrization and $\phi^i(\vec r_1, \vec r_2, \vec r_3)$ is a spatial function with Cartesian index $i$ that comes from any of the electron coordinates. The normalization we assume is

$$\sum_i \langle \Phi'^i | \Phi^i \rangle = \sum_i \left\langle \phi'^{\,i}(r_1,\, r_2,\, r_3) | \mathcal{P}[c_{123}\, \phi^i(r_1, r_2, r_3)] \right\rangle = 1 \tag{47}$$

where $\mathcal{P}$ denotes the sum of all permutations of 1,2, and 3. The $^2P_{1/2}$ and $^2P_{3/2}$ wave functions are constructed using Clebsch-Gordon coefficients. Expectation values with these wave functions can be reduced to spatial expectation values with algebraic prefactor $K_J$ for $J = 1/2, 3/2$. Namely, the first-order matrix elements with auxiliary notation $\{K_{1/2}, K_{3/2}\}$ take the form

$$\langle \Phi' | O | \Phi \rangle = \{1, 1\} \left\langle \phi'^{\,i}(r_1,\, r_2,\, r_3) | Q\, \mathcal{P}[c_{123}\, \phi^i(r_1, r_2, r_3)] \right\rangle \tag{48}$$

$$\langle \Phi' | \sum_a \vec\sigma_a \cdot \vec Q_a | \Phi \rangle \;=\; \{1, -1/2\}\, i\, \epsilon^{ijk} \sum_a \left\langle \phi'^{\,i}(r_1,\, r_2,\, r_3) | Q_a^j\, \mathcal{P}\Big[c_{123}^{Fa}\, \phi^k(r_1, r_2, r_3)\Big] \right\rangle \tag{49}$$

$$\langle \Phi' | \sum_{a\neq b} \vec\sigma_a \times \vec\sigma_b \cdot \vec Q_{ab} | \Phi \rangle \;=\; \{1, -1/2\}\, (-2\,\epsilon^{ijk}) \sum_{ab=12,23,31} \left\langle \phi'^{\,i}(r_1,\, r_2,\, r_3) | \,(Q_{ab}^j - Q_{ba}^j)\, \mathcal{P}\Big[c_{123}^{P}\, \phi^k(r_1, r_2, r_3)\Big] \right\rangle \tag{50}$$

where $c_{klm}$ coefficients are defined in Table IV.

The spin reduction of the second-order matrix elements is more complicated. We shall first introduce the following aux-

TABLE II: Second-order contributions to Li and $Be^+$ fine splitting $X = (K_{3/2} - K_{1/2})\,V$, the additional prefactor $\{K_{1/2}\,K_{3/2}\}$ is for $J = 1/2, 3/2$, correspondingly. The numerical uncertainties are about $10^{-4}$

| Contribution | $\{K_{1/2}, K_{3/2}\}$ | $V_{\rm Li}$ | $V_{\rm Be^+}$ |
|---|---|---|---|
| $X_{^2S_o} = \langle\Phi\vert H_B^{(4)}\,\frac{^1\!2_{S_o}}{E-H}\,H_B^{(4)}\vert\Phi\rangle$ | $\{1, 0\}$ | $-0.293\,49$ | $-1.051\,4(2)$ |
| $X_{^4S_o} = \langle\Phi\vert H_B^{(4)}\,\frac{^1\!4_{S_o}}{E-H}\,H_B^{(4)}\vert\Phi\rangle$ | $\{0, 2/3\}$ | $-0.443\,91(3)$ | $-1.625\,3$ |
| $X_{^2P} = \langle\Phi\vert H_B^{(4)}\,\frac{^1\!2_{P}}{(E-H)'}\,(2H_A^{(4)} + H_B^{(4)})\vert\Phi\rangle$ | | | |
| $\langle\Phi\vert H_B^{(4)}\,\frac{^1\!2_{P}}{(E-H)'}\,[H_A^{(4)}]_r\vert\Phi\rangle$ | $\{1, -1/2\}$ | $-0.0217(6)$ | $-1.435(8)$ |
| $\delta X_{^2P}$ | $\{1, -1/2\}$ | $-0.086\,80$ | $-2.169\,0$ |
| $\langle\Phi\vert H_B^{(4)}\,\frac{^1\!2_{P}}{(E-H)'}\,H_B^{(4)}\vert\Phi\rangle$ | $\{1, 1/4\}$ | $-0.719\,6(6)$ | $-5.803(4)$ |
| $X_{^4P} = \langle\Phi\vert(H_B^{(4)} + H_C^{(4)})\,\frac{^1\!4_{P}}{E-H}\,(H_B^{(4)} + H_C^{(4)})\vert\Phi\rangle$ | | | |
| $\langle\Phi\vert H_B^{(4)}\,\frac{^1\!4_{P}}{E-H}\,H_B^{(4)}\vert\Phi\rangle$ | $\{1/3, 5/6\}$ | $-0.901\,2(4)$ | $-3.475\,5(6)$ |
| $\langle\Phi\vert H_C^{(4)}\,\frac{^1\!4_{P}}{E-H}\,H_C^{(4)}\vert\Phi\rangle$ | $\{3, 3/10\}$ | $-0.002\,31$ | $-0.033\,2$ |
| $\langle\Phi\vert H_B^{(4)}\,\frac{^1\!4_{P}}{E-H}\,H_C^{(4)}\vert\Phi\rangle$ | $\{-1, 1/2\}$ | $0.006\,97$ | $0.102\,5$ |
| $X_{^2D_o} = \langle\Phi\vert H_B^{(4)}\,\frac{^1\!2_{D_o}}{E-H}\,H_B^{(4)}\vert\Phi\rangle$ | $\{0, 3/2\}$ | $-0.500\,75$ | $-1.885\,6(4)$ |
| $X_{^4D_o} = \langle\Phi\vert(H_B^{(4)} + H_C^{(4)})\,\frac{^1\!4_{D_o}}{E-H}\,(H_B^{(4)} + H_C^{(4)})\vert\Phi\rangle$ | | | |
| $\langle\Phi\vert H_B^{(4)}\,\frac{^1\!4_{D_o}}{E-H}\,H_B^{(4)}\vert\Phi\rangle$ | $\{2, 1\}$ | $-0.733\,27(2)$ | $-2.625\,6(2)$ |
| $\langle\Phi\vert H_C^{(4)}\,\frac{^1\!4_{D_o}}{E-H}\,H_C^{(4)}\vert\Phi\rangle$ | $\{2, 1\}$ | $0.000\,08$ | $0.000\,9$ |
| $\langle\Phi\vert H_B^{(4)}\,\frac{^1\!4_{D_o}}{E-H}\,H_C^{(4)}\vert\Phi\rangle$ | $\{2, -1\}$ | $0.000\,00$ | $0.000\,1$ |
| $X_{^4F} = \langle\Phi\vert H_C^{(4)}\,\frac{^1\!4_{F}}{E-H}\,H_C^{(4)}\vert\Phi\rangle$ | $\{0, 3\}$ | $-0.000\,71$ | $-0.009\,6$ |
| $Y_1 = \langle\Phi\vert H_B^{(4)}\,\frac{1}{(E-H)'}\,\sum_a \delta^3(r_a)\vert\Phi\rangle$ | | | |
| $\langle\Phi\vert H_B^{(4)}\,\frac{1}{(E-H)'}\,\sum_a [\delta^3(r_a)]_r\vert\Phi\rangle$ | $\{1, -1/2\}$ | $-0.028\,95$ | $-0.647\,1$ |
| $\delta Y_1$ | $\{1, -1/2\}$ | $0.007\,99$ | $0.186\,0$ |
| $Y_2 = \langle\Phi\vert H_B^{(4)}\,\frac{1}{(E-H)'}\,\sum_{b<a} \delta^3(r_{ab})\vert\Phi\rangle$ | | | |
| $\langle\Phi\vert H_B^{(4)}\,\frac{1}{(E-H)'}\,\sum_{b<a} [\delta^3(r_{ab})]_r\vert\Phi\rangle$ | $\{1, -1/2\}$ | $0.001\,07$ | $-0.002\,5$ |
| $\delta Y_2$ | $\{1, -1/2\}$ | $-0.003\,66$ | $0.053\,5$ |

iliary functions,

$$\Psi^i = Q\,\mathcal{P}[c_{123}\,\phi^i(r_1, r_2, r_3)] \quad (51)$$

$$\Psi^{ij} = \sum_a Q_a^i\,\mathcal{P}\Big[c_{123}^{Fa}\,\phi^j(r_1, r_2, r_3)\Big] \quad (52)$$

$$\Psi_A^{ij} = \mathcal{P}\Big[c_{123}^{A}\,(Q_1^i - Q_2^i)\,\phi^j(r_1, r_2, r_3)\Big] \quad (53)$$

$$\Psi_A^{ijk} = \mathcal{P}\Big[c_{123}^{A}\,(Q_{13}^{ij} - Q_{23}^{ij})\,\phi^k(r_1, r_2, r_3)\Big] \quad (54)$$

Then, the spin-reduced second-order matrix elements are

$$\langle\Phi|\sum_a \vec{\sigma}_a\cdot\vec{Q}_a\,\frac{^1\!2_{S_o}}{E-H}\,\sum_b \vec{\sigma}_b\cdot\vec{Q}_b|\Phi\rangle = \frac{\{1,0\}}{6}\left\langle\Psi^{ii}\,\frac{^1\!2_{S_o}}{E-H}\,\Psi^{jj}\right\rangle \quad (55)$$

$$\langle\Phi|\sum_a \vec{\sigma}_a\cdot\vec{Q}_a\,\frac{^1\!4_{S_o}}{E-H}\,\sum_b \vec{\sigma}_b\cdot\vec{Q}_b|\Phi\rangle = \frac{\{0,2/3\}}{6}\left\langle\Psi_A^{ii}\frac{^1\!4_{S_o}}{E-H}\Psi_A^{jj}\right\rangle \quad (56)$$

$$\langle\Phi|Q\,\frac{^1\!2_{P_o}}{(E-H)'}\,Q|\Phi\rangle = \frac{\{1,1\}}{6}\left\langle\Psi^{i}\,\frac{^1\!2_{P_o}}{(E-H)'}\,\Psi^{i}\right\rangle \quad (57)$$

TABLE III: Expectation values of additional operators arising from reduction of the second-order matrix elements, $\langle Q\rangle = K_J\,V$ with the additional prefactor $K_J = \{1, -1/2\}$ for $J = 1/2, 3/2$, correspondingly. All digits are significant.

| Operator | $V_{\rm Li}$ | $V_{\rm Be^+}$ |
|---|---|---|
| $Q_{21} = \sum_{a,c} \vec{\sigma}_a \frac{1}{r_c}\frac{\vec{r}_a}{r_a^3} \times \vec{p}_a$ | −0.849 430 | −9.552 24 |
| $Q_{22} = \sum_{a,b\neq a,c} \vec{\sigma}_a \frac{1}{r_c}\frac{\vec{r}_{ab}}{r_{ab}^3} \times \vec{p}_a$ | −1.432 170 | −15.223 86 |
| $Q_{23} = \sum_{a,b\neq a,c} \vec{\sigma}_a \frac{1}{r_c}\frac{\vec{r}_{ab}}{r_{ab}^3} \times \vec{p}_b$ | 0.242 656 | 3.250 48 |
| $Q_{24} = \sum_{a,c<d} \vec{\sigma}_a \frac{1}{r_{cd}}\frac{\vec{r}_a}{r_a^3} \times \vec{p}_a$ | −0.400 085 | −4.721 57 |
| $Q_{25} = \sum_{a,b\neq a,c<d} \vec{\sigma}_a \frac{1}{r_{cd}}\frac{\vec{r}_{ab}}{r_{ab}^3} \times \vec{p}_a$ | −0.766 998 | −8.959 65 |
| $Q_{26} = \sum_{a,b\neq a,c<d} \vec{\sigma}_a \frac{1}{r_{cd}}\frac{\vec{r}_{ab}}{r_{ab}^3} \times \vec{p}_b$ | 0.159 671 | 2.209 81 |
| $Q_{27} = \sum_a \frac{1}{r_a}$ | 5.638 906 | 7.898 02 |
| $Q_{28} = \sum_{a<b} \frac{1}{r_{ab}}$ | 2.096 405 | 3.233 41 |
| $Q_{29} = \sum_a \vec{\sigma}_a \frac{\vec{r}_a}{r_a^3} \times \vec{p}_a$ | −0.125 946 | −0.969 13 |
| $Q_{30} = \sum_{a,b\neq a} \vec{\sigma}_a \frac{\vec{r}_{ab}}{r_{ab}^3} \times \vec{p}_a$ | −0.224 641 | −1.659 49 |
| $Q_{31} = \sum_{a,b\neq a} \vec{\sigma}_a \frac{\vec{r}_{ab}}{r_{ab}^3} \times \vec{p}_b$ | 0.038 474 | 0.360 85 |

TABLE IV: Symmetrization coefficients in matrix elements

| $(k,l,m)$ | $c_{klm}$ | $c^A_{klm}$ | $c^{F1}_{klm}$ | $c^{F2}_{klm}$ | $c^{F3}_{klm}$ | $c^P_{klm}$ |
|---|---|---|---|---|---|---|
| $(1,2,3)$ | 2 | 1 | 0 | 0 | 2 | 0 |
| $(1,3,2)$ | -1 | -1 | 1 | -1 | -1 | 1 |
| $(2,1,3)$ | 2 | 1 | 0 | 0 | 2 | 0 |
| $(2,3,1)$ | -1 | -1 | -1 | 1 | -1 | -1 |
| $(3,1,2)$ | -1 | 1 | 1 | -1 | -1 | 1 |
| $(3,2,1)$ | -1 | -1 | -1 | 1 | -1 | -1 |

$$\langle\Phi|Q\,\frac{1_{^2P_o}}{(E-H)'}\sum_a \vec{\sigma}_a\cdot\vec{Q}_a|\Phi\rangle \;=\; \frac{\{1,-1/2\}}{6}\left\langle \Psi^i\,\frac{1_{^2P_o}}{(E-H)'}\,i\,\epsilon^{ijk}\,\Psi^{jk}\right\rangle \tag{58}$$

$$\langle\Phi|\sum_a \vec{\sigma}_a\cdot\vec{Q}_a\,\frac{1_{^2P_o}}{(E-H)'}\sum_b \vec{\sigma}_b\cdot\vec{Q}_b|\Phi\rangle \;=\; \frac{\{1,1/4\}}{6}\left\langle i\,\epsilon^{ijk}\Psi^{ij}\,\frac{1_{^2P_o}}{(E-H)'}\,i\,\epsilon^{lmk}\Psi^{lm}\right\rangle \tag{59}$$

$$\langle\Phi|\sum_a \vec{\sigma}_a\cdot\vec{Q}_a\,\frac{1_{^4P_o}}{E-H}\sum_b \vec{\sigma}_b\cdot\vec{Q}_b|\Phi\rangle \;=\; \frac{\{1/3,5/6\}}{6}\left\langle i\,\epsilon^{ijk}\Psi_A^{ij}\,\frac{1_{^4P_o}}{E-H}\,i\,\epsilon^{lmk}\Psi_A^{lm}\right\rangle \tag{60}$$

$$\langle\Phi|\sum_{a<b}\sigma_a^i\sigma_b^j\,Q_{ab}^{ij}\,\frac{1_{^4P_o}}{E-H}\sum_{c<d}\sigma_c^i\sigma_d^j\,Q_{cd}^{ij}|\Phi\rangle \;=\; \frac{\{3,3/10\}}{6}\left\langle \Psi_A^{ijj}\,\frac{1_{^4P_o}}{E-H}\Psi_A^{ikk}\right\rangle \tag{61}$$

$$\langle\Phi|\sum_a \vec{\sigma}_a\cdot\vec{Q}_a\,\frac{1_{^4P_o}}{E-H}\sum_{b<c}\sigma_b^i\sigma_c^j\,Q_{bc}^{ij}|\Phi\rangle \;=\; \frac{\{-1,1/2\}}{6}\left\langle i\,\epsilon^{jml}\Psi_A^{ml}\,\frac{1_{^4P_o}}{E-H}\Psi_A^{jkk}\right\rangle \tag{62}$$

$$\langle\Phi|\sum_a \vec{\sigma}_a\cdot\vec{Q}_a\,\frac{1_{^2D_o}}{E-H}\sum_b \vec{\sigma}_b\cdot\vec{Q}_b|\Phi\rangle \;=\; \frac{\{0,3/2\}}{6}\left\langle \Psi^{ji}\,\frac{1_{^2D_o}}{E-H}\Psi^{ij}\right\rangle \tag{63}$$

$$\langle\Phi|\sum_a \vec{\sigma}_a\cdot\vec{Q}_a\,\frac{1_{^4D_o}}{E-H}\sum_b \vec{\sigma}_b\cdot\vec{Q}_b|\Phi\rangle \;=\; \frac{\{2,1\}}{6}\left\langle \Psi_A^{ji}\,\frac{1_{^4D_o}}{E-H}\Psi_A^{ij}\right\rangle \tag{64}$$

$$\langle\Phi|\sum_{a<b}\sigma_a^i\sigma_b^j\,Q_{ab}^{ij}\,\frac{1_{^4D_o}}{E-H}\sum_{c<d}\sigma_c^i\sigma_d^j\,Q_{cd}^{ij}|\Phi\rangle \;=\; \frac{\{2,1\}}{6}\left\langle i\,\epsilon^{ijk}\Psi_A^{lij}\frac{1_{^4D_o}}{E-H}\,i\,\epsilon^{mnk}\Psi_A^{lmn}\right\rangle \tag{65}$$

$$\langle\Phi|\sum_{a}\vec{\sigma}_a\cdot\vec{Q}_a\,\frac{1_{^4D_o}}{E-H}\sum_{b<c}\sigma_b^i\sigma_c^j\,Q_{bc}^{ij}|\Phi\rangle \;=\; \frac{\{2,-1\}}{6}\left\langle \Psi_A^{lk}\frac{1_{^4D_o}}{E-H}\,i\,\epsilon^{kmn}\Psi_A^{lmn}\right\rangle \tag{66}$$

$$\langle\Phi|\sum_{a<b}\sigma_a^i\sigma_b^j\,Q_{ab}^{ij}\,\frac{1_{^4F_o}}{E-H}\sum_{c<d}\sigma_c^i\sigma_d^j\,Q_{cd}^{ij}|\Phi\rangle \;=\; \frac{\{0,3\}}{6}\left\langle \Psi_A^{kji}\frac{1_{^4F_o}}{E-H}\Psi_A^{ijk}\right\rangle \tag{67}$$

These formulas, including $K_J$ coefficients, have been obtained with a computer symbolic program.

## V. NUMERICAL CALCULATIONS

The spatial function $\phi$ in Eq. (46) is represented as a linear combination of the Hylleraas [23] or the explicitly correlated Gaussians functions [24]

$$\phi \;=\; \begin{cases} e^{-\alpha_1 r_1^2-\alpha_2 r_2^2-\alpha_3 r_3^2-\alpha_{12} r_{12}^2-\alpha_{13} r_{13}^2-\alpha_{23} r_{23}^2} \\ e^{-\alpha_1 r_1-\alpha_2 r_2-\alpha_3 r_3}\; r_{23}^{n_1}\, r_{31}^{n_2}\, r_{23}^{n_3}\, r_1^{n_4}\, r_2^{n_5}\, r_3^{n_6} \end{cases} \tag{68}$$

In the Hylleraas basis we use six sectors with different values of nonlinear parameters $w_i$ and a maximum value of $\Omega \equiv n_1+n_2+n_3+n_4+n_5 = 12$; details are presented in Refs. [10, 13]. In Gaussian basis we use $N = 256, 512, 1024$, and $2048$ functions with well-optimized nonlinear parameters for each basis function separately. The accuracy achieved for nonrelativistic energies is about $10^{-13}$ in Hylleraas and $10^{-11}$ in Gaussian bases.

These nonrelativistic wave functions are used in evaluation of matrix elements. Most of the $Q$ and $P$ operators in Tables I and III are intractable with present algorithms with Hylleraas functions due to difficulties with integrals with inverse powers of electron distances, but also due to very lengthy expressions in terms of Hylleraas integrals. Thus, we calculate them using Gaussian functions; however, with some exceptions. There are operators $Q_1$, $Q_2$, and $Q_4$, the expectation value of which is very slowly convergent. Namely, the accuracy achieved is as low as $10^{-2}-10^{-3}$ with as many as 2048 well-optimized Gaussian functions. So, to avoid loss of numerical accuracy, we represent these operators as the sum of the singular $D$-part and the regular $R$-part. The singular D-part, numerically dominating, is calculated with Hylleraas functions, while the regular R-part, free of singularities, is calculated with a Gaussian basis. This leads to significant improvements in accuracy, so the numerical uncertainties do not affect theoretical predictions for the fine structure. Numerical results for all first-order matrix elements obtained with the largest basis are presented in Table I and III. The achieved precision is at least $10^{-5}$, which is one digit better in comparison to second-order matrix elements described in the following.

The evaluation of second-order matrix elements is much more computationally demanding. First of all, they are obtained only in the Gaussian basis, due to its high flexibility. The resolvent $1/(E-H)$ for each angular momentum is represented in terms of functions with the appropriate Cartesian prefactor, as follows

$$\phi_{S_o} = \epsilon_{ijk} r_a^i r_b^j r_c^k\;\phi \tag{69}$$

$$\phi_{P_o}^i = r_a^i\;\phi \tag{70}$$

$$\phi_{D_o}^{ij} = \left[\frac{\epsilon_{ikl}}{2}\,r_c^j + \frac{\epsilon_{jkl}}{2}\,r_c^i - \frac{\delta^{ij}}{3}\epsilon_{mkl}\,r_c^m\right] r_a^k\, r_b^l\phi \tag{71}$$

$$\begin{aligned}\phi_{F_o}^{ijk} \;=\; &\left[\frac{r_a^i}{6}(r_b^j r_c^k + r_c^j r_b^k) + \frac{r_b^i}{6}(r_a^j r_c^k + r_c^j r_a^k)\right.\\ &+\frac{r_c^i}{6}(r_a^j r_b^k + r_b^j r_a^k)\\ &-\frac{\delta^{jk}}{15}\left(r_a^i r_b^l r_c^l + r_b^i r_a^l r_c^l + r_c^i r_a^l r_b^l\right)\\ &-\frac{\delta^{ki}}{15}\left(r_a^j r_b^l r_c^l + r_b^j r_a^l r_c^l + r_c^j r_a^l r_b^l\right)\\ &\left.-\frac{\delta^{ij}}{15}\left(r_a^k r_b^l r_c^l + r_b^k r_a^l r_c^l + r_c^k r_a^l r_b^l\right)\right]\phi\end{aligned} \tag{72}$$

where subscripts $a, b$, and $c$ refer to any of the electrons including the same one. Nonlinear parameters for intermediate states are extensively optimized for each second-order symmetric matrix element. Moreover, one takes all possible representations of angular factors for intermediate states in appropriate proportions to ensure the completeness of the basis. Most importantly, the number of Gaussian functions for intermediate states is chosen to be sufficiently high to saturate the matrix element. Namely, for a given size $N$ of the external wave function, we use $3/2\,N$ elements for all $D_o$- and quartet $F_o$-states, $N$ elements for quartet $P_o$-states, and $1/2\,N$ for $S_o$-states. Among all matrix elements, the most demanding in terms of optimization was that with intermediate states of symmetry $^2P_o$, as the external wave function. Here, the basis set for the resolvent is divided into two sectors. The first sector is built of the known basis functions with the nonlinear parameters determined in the minimization of $E(2^2P)$. For this purpose we took one of the previously generated basis sets of $\Psi$ of size equal to $N/2$. The nonlinear parameters of

this basis remain fixed during the optimization in order to ensure the accurate representation of the states orthogonal to $\Psi$. The second sector, of size equal to $3/2N$ or $N$ for the matrix element involving $H_B$ or $[H_A]_r$, respectively, consists of basis functions that undergo optimization. For the asymmetric matrix elements the basis is combined from two corresponding symmetric ones.

The most computationally demanding matrix element was the $\langle [H_A]_r\, 1/(E-H)'\, H_B\rangle$ term, and it has the slowest numerical convergence in the Gaussian basis. Numerical results for matrix elements are summarized in Table II. The achieved precision is about $10^{-4}$, one digit less than the first-order matrix elements. In addition, we observe significant cancellations between $S = 1/2$ and $S = 3/2$ intermediate states, and between the first- and second-order terms, see Table V. The final numerical result for the $m\,\alpha^6$ contribution in Table V is relatively quite small. Regarding the $m\,\alpha^7$ contribution, the second-order term $Y$ is numerically dominant, and contributions from $D_i$ terms are an order of magnitude smaller. Altogether this correction is only three times smaller than the $m\,\alpha^6$ contribution, which is certainly not negligible.

TABLE V: Summary of $m\,\alpha^6$ contributions to fine splitting.

| Contribution | Li | $Be^+$ |
|---|---|---|
| $X_{^2S_o}$ | 0.293 49 | 1.051 4(3) |
| $X_{^4S_o}$ | −0.295 94(2) | −1.083 5(1) |
| $X_{^2P_o}$ | 0.735 0(18) | 11.912(24) |
| $X_{^4P_o}$ | −0.423 5(2) | −1.340 5(3) |
| $X_{^2D_o}$ | −0.751 13(2) | −2.828 4(6) |
| $X_{^4D_o}$ | 0.733 34(2) | 2.625 7(2) |
| $X_{^4F_o}$ | −0.002 13 | −0.028 9(1) |
| total second order | 0.289 16(19) | 10.308(24) |
| $\delta H_1$ | −0.445 2(16) | −13.160(3) |
| $\delta H_2$ | 0.026 31 | 0.577 8 |
| $\delta H_4$ | 0.105 63 | 2.405 5(1) |
| $\delta H_5$ | 0.150 52 | 3.186 6 |
| $\delta H_6$ | −0.011 60 | −0.130 7 |
| $\delta H_7$ | −0.027 83 | −0.757 8(3) |
| total first order | −0.202 1(16) | −7.879(3) |
| total $m\,\alpha^6$ | 0.087 1(24) | 2.429(24) |

## VI. SUMMARY

We have performed accurate calculations of the fine structure in Li and $Be^+$ using the nonrelativistic QED approach combined with explicitly correlated basis functions. Relativistic and QED corrections are represented in terms of matrix elements of effective operators, which are calculated with a highly accurate nonrelativistic wave function. Numerical results are summarized in Table VI. We observe an agreement with the experimental values. However, our result for Li lies below, while for $Be^+$ above experiments of [5] and [6] respectively. As the sign of all corrections is the same for Li and $Be^+$, this may suggest that one of these experiments underestimated its uncertainty.

The extension of presented computational approach to other systems with more electrons is problematic, due to a lack of formulas for the four-electron Hylleraas integrals. Therefore, achieving similar accuracy for the four electron systems would be very challenging.

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TABLE VI: Fine splitting of 2P-states in Li and $Be^+$ in units of MHz. $\delta E_{\rm fs}$ is the hyperfine mixing correction. The uncertainty due to neglected terms is estimated to be 50% of $E^{(7,0)}_{\rm fslog}$

| | $^7$Li | Ref. | $^9Be^+$ | Ref. |
|---|---|---|---|---|
| $E^{(4,0)}_{\rm fs}$ | 10 053.707(8) | [13] | 197 039.15(8) | [13] |
| $E^{(4,1)}_{\rm fs}$ | −2.389 | [13] | −21.27 | [13] |
| $E^{(6,0)}_{\rm fs}$ | 1.63(5) | [14] | 45.4(4) | |
| $E^{(7,0)}_{\rm fslog}$ | 0.15(7) | | 4.6(2.3) | |
| $\delta E_{\rm fs}$ | 0.159 | [13] | 0.03 | [13] |
| $E_{\rm fs}$(theo) | 10 053.25(9) | [14] | 197 068.0(2.4) | [6] |
| $E_{\rm fs}$(theo) | 10 052.(43) | Yan *et al.* [11] | 197 024.(150) | Yan *el al.* [11] |
| $E_{\rm fs}$(exp) | 10 053.310(17) | Brown *et al.* [5] | 197 063.48(52) | Nörtershäuser *et al.*[6] |
| $E_{\rm fs}$(exp) | 10 053.24(22) | Brog *et al.* [25] | 197 144. | Ralchenko *et al.*[28] |
| $E_{\rm fs}$(exp) | 10 053.184(58) | Orth *et al.* [26] | 197 150.(64) | Bollinger *et al.* [29] |
| $E_{\rm fs}$(exp) | 10 053.119(58) | Noble *et al.* [27] | | |

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### Appendix A: Quantum mechanics of three identical particles

Consider a wave function of three identical particles $\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3)$. Eigenstates of the nonrelativistic Hamiltonian can be classified by representation of the permutation group $S_3$. Two of them, *id* and *sgn*, are one dimensional, and the third is two dimensional. The wave functions corresponding to one-dimensional representations are

$$\psi_S(\vec{r}_1,\vec{r}_2,\vec{r}_3) = \frac{1}{\sqrt{6}}\left[\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3)+\phi(\vec{r}_2,\vec{r}_3,\vec{r}_1)+ \phi(\vec{r}_3,\vec{r}_1,\vec{r}_2)+\phi(\vec{r}_2,\vec{r}_1,\vec{r}_3)+\phi(\vec{r}_3,\vec{r}_2,\vec{r}_1)+\phi(\vec{r}_1,\vec{r}_3,\vec{r}_2)\right] \quad \text{(A1)}$$

and

$$\psi_A(\vec{r}_1,\vec{r}_2,\vec{r}_3) = \frac{1}{\sqrt{6}}\left[\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3)+\phi(\vec{r}_2,\vec{r}_3,\vec{r}_1)+ \phi(\vec{r}_3,\vec{r}_1,\vec{r}_2)-\phi(\vec{r}_2,\vec{r}_1,\vec{r}_3)-\phi(\vec{r}_3,\vec{r}_2,\vec{r}_1)-\phi(\vec{r}_1,\vec{r}_3,\vec{r}_2)\right] \quad \text{(A2)}$$

In order to construct the wave functions corresponding to the two-dimensional representation, let us consider the spin-dependent wave function for a three-electron system for the total spin $S=1/2$

$$\begin{aligned}\Phi &= \frac{1}{\sqrt{6}}\,\mathcal{A}\big[\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3)\,[\alpha(1)\,\beta(2)-\beta(1)\,\alpha(2)]\,\alpha(3)\big] \\ &= \frac{1}{\sqrt{6}}[\alpha(1)\,\beta(2)\,\alpha(3)\,\psi_1+\beta(1)\,\alpha(2)\,\alpha(3)\,\psi_2+ \\ &\quad \alpha(1)\,\alpha(2)\,\beta(3)\,\psi_3] \qquad \text{(A3)}\end{aligned}$$

where $\mathcal{A}$ denotes antisymmetrization, and

$$\begin{aligned}\psi_1 &= \phi(\vec{r}_1,\vec{r}_2,\vec{r}_3)-\phi(\vec{r}_2,\vec{r}_3,\vec{r}_1)+\phi(\vec{r}_2,\vec{r}_1,\vec{r}_3)- \\ &\quad \phi(\vec{r}_3,\vec{r}_2,\vec{r}_1) \qquad \text{(A4)} \\ \psi_2 &= \phi(\vec{r}_3,\vec{r}_1,\vec{r}_2)-\phi(\vec{r}_2,\vec{r}_1,\vec{r}_3)-\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3)+ \\ &\quad \phi(\vec{r}_1,\vec{r}_3,\vec{r}_2) \qquad \text{(A5)} \\ \psi_3 &= \phi(\vec{r}_2,\vec{r}_3,\vec{r}_1)-\phi(\vec{r}_3,\vec{r}_1,\vec{r}_2)+\phi(\vec{r}_3,\vec{r}_2,\vec{r}_1)- \\ &\quad \phi(\vec{r}_1,\vec{r}_3,\vec{r}_2) \qquad \text{(A6)}\end{aligned}$$

$\psi_i$ functions form a two-dimensional representation of $S_3$, $\sum_i \psi_i = 0$.

Let us denote the standard matrix element

$$\langle\phi'|\phi\rangle_S = \left\langle \phi'^{\,i}(r_1,\,r_2,\,r_3)|\mathcal{P}[c_{123}\,\phi^i(r_1,r_2,r_3)]\right\rangle \quad \text{(A7)}$$

where $\mathcal{P}$ denotes the sum of all permutations of 1,2, and 3. Then

$$\langle\Phi'|\Phi\rangle = \langle\phi'|\phi\rangle_S \quad \text{(A8)}$$

and the scalar products between $\psi_i$ is

$$\langle\psi_i'|\psi_j\rangle = \langle\phi'|\phi\rangle_S\,(-1+3\,\delta_{ij}) \quad \text{(A9)}$$

The two orthogonal and normalized functions can be chosen as $\psi_I=\psi_1/\sqrt{2}$ and $\psi_{II}=(\psi_2-\psi_3)/\sqrt{6}$.

The first-order matrix elements of the spin-independent operator $Q$ are

$$\langle\Phi|Q|\Phi\rangle = \frac{1}{6}\langle\psi_i|Q|\psi_i\rangle = \langle\phi|Q|\phi\rangle_S, \quad \text{(A10)}$$

and the second-order matrix elements with $Q_1$ and $Q_2$ are

$$\begin{aligned}\langle\Phi|Q_1\,\frac{1}{E-H}\,Q_2|\Phi\rangle &= \frac{1}{6}\langle\psi_i|Q_1\,\frac{1}{E-H}\,Q_2|\psi_i\rangle \\ &= \langle\phi|Q_1\frac{1}{E-H}\,Q_2|\phi\rangle_S \quad \text{(A11)}\end{aligned}$$

In the numerical evaluation of second-order matrix elements with doublet $S = 1/2$ intermediate states, the resolvent $1/(E-H)$ is represented on the basis of functions of proper $S_3$ symmetry, namely $\psi_I$ and $\psi_{II}$

$$\begin{aligned}\langle\psi_I^k|E-H|\psi_I^l\rangle &= \langle\psi_{II}^k|E-H|\psi_{II}^l\rangle \quad \text{(A12)} \\ &= \langle\phi^k|E-H|\phi^l\rangle_S = E\,\mathcal{N}_{kl} - \mathcal{H}_{kl}\end{aligned}$$

Hence, the second-order matrix element using Eq. (A7) becomes

$$\begin{aligned}\langle\Phi|Q_1\,\frac{1}{E-H}\,Q_2|\Phi\rangle &= \frac{1}{6}\langle\psi_i|Q_1|\psi_I^k\rangle\,(E\,\mathcal{N}-\mathcal{H})^{-1}_{kl}\,\langle\psi_I^l|Q_2|\psi_i\rangle + \frac{1}{6}\langle\psi_i|Q_1|\psi_{II}^k\rangle\,(E\,\mathcal{N}-\mathcal{H})^{-1}_{kl}\,\langle\psi_{II}^l|Q_2|\psi_i\rangle \quad \text{(A13)} \\ &= \langle\phi|Q_1|\phi^k\rangle_S\,(E\,\mathcal{N}-\mathcal{H})^{-1}_{kl}\,\langle\phi^l|Q_2|\phi\rangle_S \\ &= \langle\mathcal{P}[c_{123}\,\phi(r_1,r_2,r_3)|Q_1|\phi^k\rangle\,(E\,\mathcal{N}-\mathcal{H})^{-1}_{kl}\,\langle\phi^l|Q_2|\mathcal{P}[c_{123}\,\phi(r_1,r_2,r_3)\rangle\end{aligned}$$

and the last form is used in the numerical calculations.