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Analytical expressions of non-relativistic static multipole polarizabilities for hydrogen-like ions*

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Analytical formulas for the static multipole polarizabilities of hydrogen-like ions are derived by using the analytical wave functions and the reduced Green function and by applying a numerical fitting procedure. Our results are then applied to the studies of blackbody radiation shifts to atomic energy levels at different temperatures. Our analytical results can be served as a benchmark for other theoretical methods.

Keywords: polrizabilities, analytical formula, hydrogen-like ions

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1. Introduction

Hydrogen is one of the most studied atomic systems. Hydrogen is also a prototype for studying alkali atoms and highly charged hydrogen-like ions. The static polarizabilities of hydrogen-like systems are very important for high-precision spectroscopy experiments. Different computational methods have been developed for evaluating the static polarizabilities of simple atomic systems.[1–4] The analytical expressions for both the Schrödinger and Dirac–Green functions of hydrogen have been derived by Swainson and Drake.[5–7] In their approach, the wave functions and the Green functions are expressed as infinite series involving Laguerre functions, which is a Sturmian form in essence. A formal scheme for deriving the dipole polarizabilities of hydrogen has been given by Krylovetsky *et al.*,[8] where the Sturmian polynomials are also used in their work to describe the wave functions and the Green function. Analytical expressions for the dipole polarizabilities of hydrogen in an arbitrary atomic state have been obtained by Baye.[9] The analytical asymptotic behavior of dipole polarizabilities in Rydberg state for helium has also been studied by different methods.[1,10] However, analytical results for multipole polarizabilities of hydrogen are still less investigated, which will be the main focus of the present work. This paper is organized as follows. In Section 2, we introduce the theoretical formalism. In Section 3, we demonstrate our fitting procedure for obtaining analytical expressions of the static multipole polarizabilities. In Section 4, we apply our results to the calculations of the blackbody radiation shifts of the hydrogen atom.

2. Formalism

In spherical coordinates, the wave function for a spherically symmetric potential $V(r)$ can be written in the form

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi), \tag{1}$$

where $R_{nl}(r)$ is the radial part and $Y_{lm}(\theta,\phi)$ is the spherical harmonics. In atomic units, the radial equation for $R_{nl}(r)$ is

$$\left\{\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right) - \frac{l(l+1)}{r^2} + 2[E-V(r)]\right\}R_{nl}(r) = 0. \tag{2}$$

For hydrogen, $V(r) = -1/r$ and the energy eigenvalue is $-1/(2n^2)$.

When an external electric field exists, the atomic energy levels will be shifted due to the Stark effect. We can treat the electric field as a perturbation if it is weak. The energy shift ΔE can then be expanded in terms of the external field $\mathcal{E}$ according to Ref. [11]

$$\Delta E = -\frac{1}{2}\alpha_{\mathrm{d}}\mathcal{E}^2 - \frac{1}{6}\alpha_{\mathrm{q}}(\partial\mathcal{E})^2 + \cdots, \tag{3}$$

where α_{d} and α_{q} are the dipole and quadrupole polarizabilities, respectively. Considering a multipole electric polarizability, a general expression for a two-photon process can be written as

$$\alpha_\mu^{(\lambda)} = \langle\psi|Q_\mu^{(\lambda)}\left(\frac{1}{E_0-H_0}\right)'Q_\mu^{*(\lambda)} + Q_\mu^{*(\lambda)}\left(\frac{1}{E_0-H_0}\right)'Q_\mu^{(\lambda)}|\psi\rangle. \tag{4}$$

Equation (4) attributes to the two-photon process, which means that the electron absorbs one photon and then emits

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one photon or vice versa. Or it is derived from the second-perturbation theory of energy shift. $Q_\mu^{(\lambda)}$ is the multipole operator defined by[12]

$$Q_\mu^{(\lambda)} = \sqrt{4\pi/(2\lambda+1)}r^\lambda Y_{\lambda\mu}(\theta,\phi),$$

where λ is the multiplicity, such as $\lambda=1$ for dipole, $\lambda=2$ for quadrupole, and so on. And μ is the component notation corresponding to the spheric harmonic expansion, whose possible values are $-\lambda,-\lambda+1,\ldots,\lambda$. The validity condition of the multipole expansion of an external field is when the external field wavelength is much longer than the characteristic length of the atom. The prime notation on $1/(E_0-H_0)$ indicates that it is the reduced Green function, where H_0 is the nonrelativistic Hamiltonian of hydrogen and E_0 is its eigenvalue. Rewriting Eq. (4) in the spatial representation, we have

$$\begin{aligned}\alpha_{nl}^{(\lambda)\mu} &= \int \psi_{nlm}^\dagger(\boldsymbol{r}_1)\left[\hat{Q}_\mu^{(\lambda)}G'(\boldsymbol{r}_1,\boldsymbol{r}_2;E_n)\hat{Q}_\mu^{*(\lambda)}\right.\\ &\left.+\hat{Q}_\mu^{*(\lambda)}G'(\boldsymbol{r}_1,\boldsymbol{r}_2;E_n)\hat{Q}_\mu^{(\lambda)}\right]\psi_{nlm}(\boldsymbol{r}_2)\,\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2, \quad (5)\end{aligned}$$

where $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are different positions of electrons due to the propagation, $G'(\boldsymbol{r}_1,\boldsymbol{r}_2;E_n)$ is the reduced Green function in the position representation.

Following Refs. [5,7], the radial part of the nonrelativistic wave function can be written as

$$R_{nl}(r) = N_{nl}(2r/n)^l\,\mathrm{e}^{-r/n}L_{n-l-1}^{2l+1}(2r/n), \quad (6)$$

where $L_n^l(z)$ is the generalized Laguerre function and N_{nl} is the normalization factor

$$N_{nl} = \left(2/n^2\right)\sqrt{(n-l-1)!/(n+l)!}.$$

The reduced Green function in the spherical coordinates can be expressed as

$$G'(\boldsymbol{r}_1,\boldsymbol{r}_2;E_n) = \sum_{l'm'} g_{l'}(r_1,r_2;E_n)Y_{l'm'}(\theta_1,\phi_1)Y_{l'm'}^*(\theta_2,\phi_2), \quad (7)$$

where the radial function $g_{l'}(r_1,r_2;E_n)$ can be expressed as a Sturmian polynomial

$$\begin{aligned}&g_{l'}(r_1,r_2;E_n)\\ &= 2\left(\frac{2}{n}\right)^{2l'+1}(r_1r_2)^{l'}\,\mathrm{e}^{-(r_1+r_2)/n}\\ &\times\left\{\sum_{k=0}^{\infty}\frac{k!}{(2l'+1+k)!\,(l'+1+k-n)}L_k^{2l'+1}\left(\frac{2r_1}{n}\right)\right.\\ &\times L_k^{2l'+1}\left(\frac{2r_2}{n}\right)+\frac{(n-l'-1)!}{2n\,(n+l')!}\left\{L_{n-l'-1}^{2l'+1}\left(\frac{2r_1}{n}\right)\right.\\ &\times\left[(n-l')L_{n-l'}^{2l'+1}\left(\frac{2r_2}{n}\right)-(n+l')L_{n-l'-2}^{2l'+1}\left(\frac{2r_2}{n}\right)\right]\\ &+L_{n-l'-1}^{2l'+1}\left(\frac{2r_1}{n}\right)L_{n-l'-1}^{2l'+1}\left(\frac{2r_2}{n}\right)\\ &+\left[(n-l')L_{n-l'}^{2l'+1}\left(\frac{2r_1}{n}\right)-(n+l')L_{n-l'-2}^{2l'+1}\left(\frac{2r_1}{n}\right)\right]\\ &\left.\left.\times L_{n-l'-1}^{2l'+1}\left(\frac{2r_2}{n}\right)\right\}\right\}. \quad (8)\end{aligned}$$

With these expressions, we can rewrite Eq. (5) in the form of separated radial and angular parts

$$\begin{aligned}\alpha_{nl}^{(\lambda)\mu} &= \frac{8\pi}{2\lambda+1}\sum_{l'}\left[\int \mathrm{d}r_1\mathrm{d}r_2 r_1^{2+\lambda}r_2^{2+\lambda}\right.\\ &\times R_{nl}(r_1)g_{l'}(r_1,r_2;E_n)R_{nl}(r_2)\\ &\times\sum_{m'}\int \mathrm{d}\Omega_1\mathrm{d}\Omega_2 Y_{\lambda\mu}^*(\Omega_1)Y_{lm}^*(\Omega_1)Y_{l'm'}(\Omega_1)\\ &\left.\times Y_{\lambda\mu}(\Omega_2)Y_{l'm'}^*(\Omega_2)Y_{lm}(\Omega_2)\right]. \quad (9)\end{aligned}$$

The treatment of the angular part is quite straightforward by using

$$\begin{aligned}&\int \mathrm{d}\Omega Y_{\lambda\mu}(\Omega)Y_{lm}(\Omega)Y_{l'm'}(\Omega)\\ &= \sqrt{\frac{(\lambda,l,l')}{4\pi}}\begin{pmatrix}\lambda & l & l'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\lambda & l & l'\\ \mu & m & -m'\end{pmatrix}, \quad (10)\end{aligned}$$

where $(\lambda,l,l')\equiv(2\lambda+1)(2l+1)(2l'+1)$. The angular part thus becomes

$$(-1)^\mu\frac{(\lambda,l,l')}{4\pi}\begin{pmatrix}\lambda & l & l'\\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix}\lambda & l & l'\\ \mu & m & -m'\end{pmatrix}^2. \quad (11)$$

In the case of scalar polarizability, we should sum over magnetic quantum numbers m and m' and average over m. Using the relation

$$\begin{aligned}&\sum_{m_1,m_2}\begin{pmatrix}l_1 & l_2 & l_3\\ m_1 & m_2 & m_3\end{pmatrix}\begin{pmatrix}l_1 & l_2 & l_3'\\ m_1 & m_2 & m_3'\end{pmatrix}\\ &= \frac{1}{2l_3+1}\delta(l_3,l_3')\,\delta(m_3,m_3'),\end{aligned}$$

we can obtain the final expression of the angular part

$$\mathcal{A}_{ll'}^{(\lambda)\mu} = (-1)^\mu\frac{(2l'+1)}{4\pi}\begin{pmatrix}\lambda & l & l'\\ 0 & 0 & 0\end{pmatrix}^2. \quad (12)$$

Let us now consider the radial part in Eq. (9). Introducing the following integral:

$$\begin{aligned}\mathcal{M}_{nll'}^{(\lambda)} &= \frac{8\pi}{2\lambda+1}|N_{nl}|^2\int_0^\infty r_1^{\lambda+2}R_{nl}(r_1)g_{l'}(r_1,r_2;E_0)\\ &\times r_2^{\lambda+2}R_{nl}(r_2)\,\mathrm{d}r_1\mathrm{d}r_2, \quad (13)\end{aligned}$$

the scalar polarizability can be written in the form

$$\alpha_{nl}^{(\lambda)\mu} = \sum_{l'}\mathcal{M}_{nll'}^{(\lambda)}\mathcal{A}_{ll'}^{(\lambda)\mu}. \quad (14)$$

It is noted that the range of l' in the above is from $|l-\lambda|$ to $l+\lambda$ with step 2. Recalling the Sturmian form of the wave function and the reduced Green function Eqs. (6) and (8), the radial integral $\mathcal{M}_{nll'}^{(\lambda)}$ can be reduced as a series of the basic integral[18]

$$\int_0^\infty x^\rho\,\mathrm{e}^{-x}L_\nu^\beta(x)L_{\nu'}^{\beta'}(x)\,\mathrm{d}x$$

$$= (-1)^{\nu+\nu'}\Gamma(\rho+1)\sum_k \binom{\rho-\beta}{\nu-k}\binom{\rho-\beta'}{\nu'-k}\binom{\rho+k}{k}, \quad (15)$$

where $\binom{\rho}{k} = \frac{\rho!}{(\rho-k)!k!}$. Thus $\mathcal{M}^{(\lambda)}_{nll'}$ should be a polynomial of the principal quantum number n and angular quantum number l. Therefore, we can assume that the polarizability can be written in the following general form:

$$\alpha_s^{(\lambda)} = \sum_i C_i^{(\lambda)}(l) n^{x_i},$$
$$C_i^{(\lambda)}(l) = \sum_j D_{ij}^{(\lambda)} l^{y_{ij}}, \quad (16)$$

where $C_i^{(\lambda)}(l)$ and $D_{ij}^{(\lambda)}$ are the expansion coefficients that need to be determined.

3. Scalar polarizabilities

3.1. Dipole polarizability

We first discuss the dipole polarizability when $\lambda = 1$ and the corresponding dipole operator is $Q_\mu^{(1)} = \sqrt{4\pi/3}\, rY_{1\mu}(\theta,\phi)$. According to Eq. (14), the dipole polarizability is

$$\alpha_{nl}^{(1)\mu} = \sum_{l'} \mathcal{M}^{(1)}_{nll'} \mathcal{A}^{(1)\mu}_{ll'}. \quad (17)$$

For each l', we fit our expression to an analytical formula and then sum over l' to obtain a final expression.

We first consider the radial integral

$$\mathcal{M}^{(1)}_{nll'} = \frac{8\pi}{3}|N_{nl}|^2 \int_0^\infty r_1^3 R_{nl}(r_1)\, g_{l'}(r_1,r_2;E_0) \times r_2^3 R_{nl}(r_2)\, \mathrm{d}r_1 \mathrm{d}r_2. \quad (18)$$

According to Eqs. (6), (8), and (15), $\mathcal{M}^{(1)}_{nll'}$ in the above equation can be easily evaluated numerically or analytically. It should be noted that, since the binomial coefficient $\binom{m}{n}$ requires both m and n to be non-negative integrals, the range of k in Eq. (8) is actually finite. We choose the upper limit of k to be 100, which is sufficient for this work. The radial integral $\mathcal{M}^{(1)}_{nll'}$ can be written in a similar form as Eq. (16) but with different coefficients

$$\mathcal{M}^{(1)}_{nll'} = \sum_i c_i^{(1)}(l) n^{x_i}, \quad c_i^{(1)}(l) = \sum_j d_{ij}^{(1)} l^{y_{ij}}. \quad (19)$$

We set l from 1 to 20, and for each of them, we take 20 allowed principal quantum numbers n. Since in the dipole case, l' is $|l-1|$ and $l+1$, we have two cases of radial integrals $\mathcal{M}^{(1)}_{nl,|l-1|}$ and $\mathcal{M}^{(1)}_{nl,l+1}$. Thus these radial integrals can form a matrix of 20×20 with respect to n and l, with their matrix elements denoted by $\mathcal{M}^{(1)}_{nl}(n,l)$. Recalling the simultaneous equation (19), our task is to determine the coefficients $c_i^{(1)}$ and $d_{ij}^{(1)}$ by a fitting procedure. In order to do this, we must first make some appropriate assumptions. We assume that the power index of n has a pattern of $2\lambda+2i$, $(i=1,2,\ldots,20)$. In the dipole case, it is $4,6,8,\ldots$. Then we have an initial form for this radial integral as $c_1^{(1)}n^4 + c_2^{(1)}n^6 + c_3^{(1)}n^8 + \cdots$. The maximum value of x_i is still unknown at this stage and we temporarily set it to be 20. We first fit $c_i^{(1)}$ to the exact values by solving the following equations:

$$\mathcal{M}^{(1)}_{nl}(n_j,l_k) = \sum_{i=1}^{20} c_i^{(1)} n_j^{x_i}, \quad j,k = 1,2,\ldots,20, \quad (20)$$

where $\mathcal{M}^{(1)}_{nl}(n_j,l_k)$ are the matrix elements evaluated numerically according to Eq. (18). For given l_k, we select 20 values of n_j and solve the resulting equations simultaneously. We show the results of $c_i^{(1)}$ in Table 3 of Appendix A to demonstrate the fitting process. We can see that only the coefficients $c_1^{(1)}$ and $c_2^{(1)}$ are non-zero in the dipole case. The fitted values of $c_i^{(1)}$ can be written in two 20×20 matrices

$$c^{(1)}\left(l' = l+1\right) = \begin{pmatrix} \frac{3}{2} & \frac{21}{4} & 0 & 0 & \cdots & 0 & 0 \\ \frac{17}{8} & \frac{127}{8} & 0 & 0 & \cdots & 0 & 0 \\ \frac{11}{4} & \frac{139}{4} & 0 & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{97}{8} & \frac{22703}{8} & 0 & 0 & \cdots & 0 & 0 \\ \frac{51}{4} & \frac{13179}{4} & 0 & 0 & \cdots & 0 & 0 \\ \frac{107}{8} & \frac{30385}{8} & 0 & 0 & \cdots & 0 & 0 \end{pmatrix},$$

$$c^{(1)}(l' = |l-1|) = \begin{pmatrix} \frac{1}{4} & \frac{-1}{4} & 0 & 0 & \cdots & 0 & 0 \\ -\frac{3}{8} & \frac{3}{8} & 0 & 0 & \cdots & 0 & 0 \\ -1 & \frac{1}{4} & 0 & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ -\frac{83}{8} & -\frac{12973}{8} & 0 & 0 & \cdots & 0 & 0 \\ -11 & -\frac{7759}{4} & 0 & 0 & \cdots & 0 & 0 \\ -\frac{93}{8} & -\frac{18375}{8} & 0 & 0 & \cdots & 0 & 0 \end{pmatrix},$$

where the row and column indexes are l and n, respectively. After determining $c_i^{(1)}$, we further solve the following equations to obtain $d_{ij}^{(1)}$:

$$c^{(1)}(l_i,x_k) = \sum_{j=1}^{20} d_j^{(1)} l_i^{y_j}, \quad (i,k = 1,2,\ldots 20), \quad (21)$$

where $c^{(1)}(l_i,x_k)$ are matrix elements. At this stage, we assume that y_j are non-negative integers and l is from 1 to 20, the same as the $c_i^{(1)}$ fitting. After finishing the above fitting process, we substitute $d_{ij}^{(1)}$ into Eq. (19) and obtain the following radial analytical expressions:

$$\mathcal{M}^{(1)}_{nl,|l-1|} = \frac{8\pi}{3}\left[\left(-\frac{3l^3}{8} + \frac{15l^2}{8} - \frac{19l}{8} + \frac{5}{8}\right)n^4 + \left(\frac{7}{8} - \frac{5l}{8}\right)n^6\right],$$
$$\mathcal{M}^{(1)}_{nl,l+1} = \frac{8\pi}{3}\left[\left(\frac{3l^3}{8} + 3l^2 + \frac{29l}{4} + \frac{21}{4}\right)n^4\right.$$

$$+\left(\frac{5l}{8}+\frac{3}{2}\right)n^6\Bigg]. \tag{22}$$

By including the following angular coefficients defined in Eq. (12) with $\mu=0$:

$$\mathcal{A}^{(1)0}_{l,|l-1|}=\frac{1}{4\pi}\frac{l}{2l+1},\quad \mathcal{A}^{(1)0}_{l,l+1}=\frac{1}{4\pi}\frac{l+1}{2l+1}, \tag{23}$$

we finally obtain the analytical expression for the scalar dipole polarizability denoted by $\alpha_{\rm s}^{(1)}$,

$$\begin{aligned}\alpha_{\rm s}^{(1)} &= \mathcal{M}^{(1)}_{nl,|l-1|}\mathcal{A}^{(1)0}_{l,|l-1|}+\mathcal{M}^{(1)}_{nl,l+1}\mathcal{A}^{(1)0}_{l,l+1}\\ &= \frac{7}{4}\left(l^2+l+2\right)n^4+n^6,\end{aligned} \tag{24}$$

which agrees with Ref. [9].

3.2. Multipole polarizabilities

The expressions for the higher-order polarizabilities can be obtained in a similar way. In this work, we mainly deal with the quadrupole ($\lambda=2$) and octupole ($\lambda=3$) polarizabilities. Again, we focus on the scalar polarizabilities. For the quadrupole case, $Q^{(2)}_{\mu}=\sqrt{4\pi/5}\ r^2Y_{2\mu}(\theta,\phi)$ and the orbital quantum number l' of the intermediate states takes 3 different values: $|l-2|$, l, $l+2$. The radial integral is now

$$\begin{aligned}\mathcal{M}^{(2)}_{nll'} &= \frac{8\pi}{5}|N_{nl}|^2\int_0^\infty r_1^4R_{nl}(r_1)\,g_{l'}(r_1,r_2;E_0)\\ &\quad\times r_2^4R_{nl}(r_2)\,{\rm d}r_1{\rm d}r_2.\end{aligned} \tag{25}$$

By applying the same fitting procedure used above, we obtain

$$\begin{aligned}\mathcal{M}^{(2)}_{nl,|l-2|} &= \frac{8\pi}{5}\Bigg[\left(\frac{35l^5}{12}-\frac{1085l^4}{48}+\frac{415l^3}{8}\right.\\ &\quad\left.-\frac{1495l^2}{48}-\frac{193l}{24}+\frac{7}{4}\right)n^6\\ &\quad+\left(\frac{5l^3}{4}+15l^2-\frac{745l}{12}+\frac{2135}{48}\right)n^8\\ &\quad+\left(\frac{541}{48}-\frac{14l}{3}\right)n^{10}\Bigg],\\ \mathcal{M}^{(2)}_{nl,l+2} &= \frac{8\pi}{5}\Bigg[\left(-\frac{35l^5}{12}-\frac{595l^4}{16}-\frac{4115l^3}{24}\right.\\ &\quad\left.-\frac{5625l^2}{16}-\frac{2519l}{8}-\frac{395}{4}\right)n^6\\ &\quad+\left(-\frac{5l^3}{4}+\frac{45l^2}{4}+\frac{265l}{3}+\frac{1925}{16}\right)n^8\\ &\quad+\left(\frac{14l}{3}+\frac{255}{16}\right)n^{10}\Bigg],\\ \mathcal{M}^{(2)}_{nl,l} &= \frac{8\pi}{5}\Bigg[\left(-\frac{21l^4}{16}-\frac{21l^3}{8}-\frac{147l^2}{16}-\frac{63l}{8}+\frac{7}{4}\right)n^6\\ &\quad+\left(-\frac{45l^2}{8}-\frac{45l}{8}+\frac{345}{16}\right)n^8+\frac{143n^{10}}{16}\Bigg].\end{aligned} \tag{26}$$

Inserting the angular parts in Eq. (12) with $\mu=0$, we have the scalar quadrupole polarizability denoted by $\alpha_{\rm s}^{(2)}$,

$$\begin{aligned}\alpha_{\rm s}^{(2)} &= \sum_{l'}\mathcal{M}^{(2)}_{nl,l'}\mathcal{A}^{(2)0}_{l,l'}\\ &= \mathcal{M}^{(2)}_{nl,l-2}\mathcal{A}^{(2)0}_{l,l-2}+\mathcal{M}^{(2)}_{nl,l}\mathcal{A}^{(2)0}_{l,l}+\mathcal{M}^{(2)}_{nl,l+2}\mathcal{A}^{(2)0}_{l,l+2}\\ &= \left[-\frac{399}{40}l^2(l+1)^2-\frac{1581}{20}l(l+1)-\frac{79}{2}\right]n^6\\ &\quad+\left[3l(l+1)+\frac{385}{8}\right]n^8+\frac{51}{8}n^{10}.\end{aligned} \tag{27}$$

In the octupole case, l' takes $|l-3|$, $|l-1|$, $l+1$, $l+3$, and $Q^{(3)}_{\mu}=\sqrt{4\pi/7}\ r^3Y_{3\mu}(\theta,\phi)$. The radial integrals are given by

$$\begin{aligned}\mathcal{M}^{(3)}_{nl,l-3} &= \Bigg[\left(-\frac{3605l^7}{256}+\frac{44765l^6}{256}-\frac{198485l^5}{256}+\frac{381605l^4}{256}\right.\\ &\quad\left.-\frac{153139l^3}{128}+\frac{44233l^2}{128}-\frac{4209l}{64}+\frac{405}{32}\right)n^8\\ &\quad+\left(\frac{2975l^5}{256}-\frac{68005l^4}{256}+\frac{504245l^3}{384}\right.\\ &\quad\left.-\frac{273525l^2}{128}+\frac{406735l}{384}-\frac{27265}{128}\right)n^{10}\\ &\quad+\left(\frac{19859l^3}{768}+\frac{3619l^2}{256}-\frac{433307l}{768}+\frac{185885}{256}\right)n^{12}\\ &\quad+\left(\frac{20805}{256}-\frac{6075l}{256}\right)n^{14}\Bigg]\times\frac{8\pi}{7},\\ \mathcal{M}^{(3)}_{nl,l-1} &= \Bigg[\left(-\frac{135l^7}{256}+\frac{765l^6}{128}-\frac{1935l^5}{128}+\frac{45l^4}{32}\right.\\ &\quad\left.+\frac{24161l^3}{256}-\frac{3909l^2}{128}-\frac{6699l}{64}+\frac{621}{32}\right)n^8\\ &\quad+\left(-\frac{315l^5}{256}-\frac{165l^4}{128}+\frac{1015l^3}{8}\right.\\ &\quad\left.-\frac{2915l^2}{16}-\frac{87465l}{256}+\frac{32395}{128}\right)n^{10}\\ &\quad+\left(\frac{2219l^3}{256}-\frac{6461l^2}{128}-\frac{21777l}{128}+\frac{10829}{32}\right)n^{12}\\ &\quad+\left(\frac{7365}{128}-\frac{2025l}{256}\right)n^{14}\Bigg]\times\frac{8\pi}{7},\\ \mathcal{M}^{(3)}_{nl,l+1} &= \Bigg[\left(\frac{135l^7}{256}+\frac{2475l^6}{256}+\frac{15885l^5}{256}+\frac{47385l^4}{256}\right.\\ &\quad\left.+\frac{6413l^3}{32}-\frac{1707l^2}{32}-\frac{3801l}{32}+\frac{355}{16}\right)n^8\\ &\quad+\left(\frac{315l^5}{256}+\frac{1245l^4}{256}-\frac{15325l^3}{128}\right.\\ &\quad\left.-\frac{71455l^2}{128}-\frac{12875l}{32}+\frac{2285}{8}\right)n^{10}\\ &\quad+\left(-\frac{2219l^3}{256}-\frac{19579l^2}{256}+\frac{11053l}{256}+\frac{115045}{256}\right)n^{12}\\ &\quad+\left(\frac{2025l}{256}+\frac{16755}{256}\right)n^{14}\Bigg]\times\frac{8\pi}{7},\\ \mathcal{M}^{(3)}_{nl,l+3} &= \Bigg[\left(\frac{3605l^7}{256}+\frac{4375l^6}{16}+\frac{135695l^5}{64}+\frac{67865l^4}{8}\right.\\ &\quad\left.+\frac{4839023l^3}{256}+\frac{188405l^2}{8}+\frac{490659l}{32}+\frac{65205}{16}\right)n^8\end{aligned}$$

$$+\left(-\frac{2975l^5}{256}-\frac{1295l^4}{4}-\frac{239225l^3}{96}-\frac{249165l^2}{32}-\frac{7981925l}{768}-\frac{159985}{32}\right)n^{10}+\left(-\frac{19859l^3}{768}-\frac{1015l^2}{16}+\frac{98861l}{192}+\frac{40915}{32}\right)n^{12}+\left(\frac{6075l}{256}+105\right)n^{14}\Bigg]\times\frac{8\pi}{7}. \quad (28)$$

The scalar octupole polarizability denoted by $\alpha_s^{(3)}$ is thus

$$\begin{aligned}\alpha_s^{(3)} &= \sum_{l'}\mathcal{M}^{(3)}_{nl,l'}\mathcal{A}^{(3)0}_{l,l'}\\ &=\Bigg[\frac{10005}{224}l^3(l+1)^3+\frac{503775}{448}l^2(l+1)^2+\frac{94335}{32}l(l+1)+\frac{9315}{8}\Bigg]n^8\\ &+\Bigg[-\frac{24855}{448}l^2(l+1)^2-\frac{18845}{14}l(l+1)-\frac{22855}{16}\Bigg]n^{10}\\ &+\Bigg[\frac{5845}{16}-\frac{595}{32}l(l+1)\Bigg]n^{12}+30n^{14}. \quad (29)\end{aligned}$$

For the higher-order polarizabilities, we simply list the results for the cases of $\lambda=4$ and $\lambda=5$

$$\begin{aligned}\alpha_s^{(4)} &= \Bigg[-\frac{2225}{12}l^4(l+1)^4-\frac{1152875}{96}l^3(l+1)^3-\frac{10350025}{96}l^2(l+1)^2-\frac{3003935}{16}l(l+1)-\frac{124299}{2}\Bigg]n^{10}\\ &+\Bigg[\frac{9835}{24}l^3(l+1)^3+\frac{8539195}{384}l^2(l+1)^2+\frac{7460075}{64}l(l+1)+\frac{2737085}{32}\Bigg]n^{12}\\ &+\Bigg[-\frac{18165}{128}l^2(L+1)^2-\frac{398055}{32}l(l+1)-\frac{3012009}{128}\Bigg]n^{14}\\ &+\Bigg[\frac{137235}{64}-\frac{13545}{64}l(l+1)\Bigg]n^{16}+\frac{16495}{128}n^{18}, \quad (30)\\ \alpha_s^{(5)} &= \Bigg[\frac{525315}{704}l^5(l+1)^5+\frac{595596225}{5632}l^4(l+1)^4+\frac{3466632645}{1408}l^3(l+1)^3+\frac{18923161215}{1408}l^2(l+1)^2+\frac{6365941155}{352}l(l+1)+\frac{42728175}{8}\Bigg]n^{12}\\ &+\Bigg[-\frac{13401675}{5632}l^4(l+1)^4-\frac{192584175}{704}l^3(l+1)^3-\frac{6068288037}{1408}l^2(l+1)^2-\frac{868148127}{64}l(l+1)-\frac{973745157}{128}\Bigg]n^{14}\\ &+\Bigg[\frac{34965}{16}l^3(l+1)^3+\frac{170846235}{704}l^2(l+1)^2+\frac{6106752099}{2816}l(l+1)+\frac{1316905205}{512}\Bigg]n^{16}\\ &+\Bigg[\frac{224721}{704}l^2(l+1)^2-\frac{60183963}{704}l(l+1)-\frac{134357685}{512}\Bigg]n^{18}+\Bigg[\frac{5498955}{512}-\frac{359289}{256}l(l+1)\Bigg]n^{20}+\frac{272713}{512}n^{22}. \quad (31)\end{aligned}$$

As we assumed at the beginning of our fitting process, the scalar polarizabilities can be expressed as a polynomial of the principal quantum number n, written as $\sum_i C_i n^{x_i}$, where C_i are the polynomials of the orbital quantum number l, written as $C_i=\sum_j d_{ij}l^{y_{ij}}$. We can now see that the actual l dependence of C_i is a polynomial of $l(l+1)$.

We now compare our results with the calculations of Tang *et al.*,[4] as listed in Table 1, for the cases of scalar quadrupole, octupole, and hexadecapole polarizabilities of the ground state hydrogen-like systems. It should be noted that the work of Tang *et al.* is based on the Dirac–Coulomb Hamiltonian, which means that their results include relativistic corrections, whereas ours are fully nonrelativistic.

Table 1. Quadrupole, octupole, and hexadecapole polarizabilities.

Z	This work	Ref. [4]
	$\alpha_s^{(2)}$	
1	15	14.998829822856441699
2	0.234375	0.2343018679357912100
5	0.00096	$9.581285372324045392\times10^{-4}$
	$\alpha_s^{(3)}$	
1	131.25	131.237821447844662
2	0.5126953125	0.51250503752377047
5	0.000336	$3.3522106087870162\times10^{-4}$
	$\alpha_s^{(4)}$	
1	2126.25	2126.02867449912883
2	2.076416015625	2.07555154606120519
5	0.000217728	$2.1716184269455411\times10^{-4}$

There is a scaling relation for the multipole polarizabilities of different nuclear charge Z. The multipole polarizability has a general expression $\langle \boldsymbol{r}^\lambda \frac{1}{E-H}\boldsymbol{r}^\lambda\rangle$, where λ is the multiplicity. By noting that $\boldsymbol{r}$ scales as $1/Z$ and $E-H$ scales as Z^2, the term $\langle \boldsymbol{r}^\lambda \frac{1}{E-H}\boldsymbol{r}^\lambda\rangle$ thus scales as $1/Z^{2\lambda+2}$. We therefore have the following relation:

$$\alpha_Z^{(\lambda)}=\frac{\alpha_1^{(\lambda)}}{Z^{2\lambda+2}}, \quad (32)$$

as reflected in Table 1.

As the multiplicity λ increases, the range of the n-power index x_i becomes larger, $2\lambda+2i$, with $i=1,2,\ldots,\lambda+1$. Taking $\lambda=5$ as an example, the n-power indexes are $12,14,16,18,20,22$, which are exactly ranging from $2\lambda+2$ to $2\lambda+2(\lambda+1)$ with a step of 2. For a certain C_i, the $l(l+1)$-power index y_{ij} ranges from 0 to $(x_{\max}-x_i)/2$. Taking $\lambda=5$ as an example again, $x_{\max}=22$, then the coefficient of n^{12} has the terms from $[l(l+1)]^y$ in which y ranges

from 0 to $(22-12)/2=5$. The correspondent coefficient of n^{14} has terms of $[l(l+1)]^y$ $(y=1,2,3,4)$ just because of $(22-14)/2=4$. The highest-order term n^{22} has coefficient with only $[l(l+1)]^0$. This pattern can be tested in different λ cases we listed. However, the pattern of $l(l+1)$ coefficients d_{ij} has not been found, which may be an interesting question.

4. Application on blackbody radiation shift

Blackbody radiation (BBR) shift in an atomic system is due to the AC Stark effect, which is related to the dynamical polarizability of the system. The BBR is isotropic and thus it can be described by the scalar polarizability. Some studies on BBR shifts to atomic energy levels can be found in Refs. [13–17], including relativistic and QED corrections. Here we only focus on the nonrelativistic energy shift due to the BBR, which is given by

$$\Delta E=\frac{-2e^2}{\pi}\int \mathrm{d}\omega \frac{\omega^3}{\mathrm{e}^{\omega/(k_{\mathrm{B}}T)}-1}\left\langle \boldsymbol{r}\frac{(E_0-H_0)}{(E_0-H_0)^2-\omega^2}\boldsymbol{r}\right\rangle, \quad (33)$$

where $[(E_0-H_0)^2-\omega^2]^{-1}$ is the Green function, ω is the photon energy from BBR, and k_{B} is the Boltzmann constant. Usually the photon energy is much smaller than the energy intervals in atom so that we may expand $[(E_0-H_0)^2-\omega^2]^{-1}$ according to

$$\frac{1}{(E_0-H_0)^2-\omega^2}\sim\frac{1}{(E_0-H_0)^2}+\frac{\omega^2}{(E_0-H_0)^4}+\frac{\omega^4}{(E_0-H_0)^6}+\cdots.$$

Then we recast Eq. (33) into the following form:

$$\begin{aligned}\Delta E&=\frac{-2e^2}{\pi}\int_0^\infty \frac{\omega^3}{\mathrm{e}^{\omega/k_{\mathrm{B}}T}-1}\\&\quad\times\left\langle \boldsymbol{r}\left[\frac{1}{(E_0-H_0)}+\frac{\omega^2}{(E_0-H_0)^3}+\cdots\right]\boldsymbol{r}\right\rangle\mathrm{d}\omega\\&=\Delta E^{(1)}+\Delta E^{(2)}+\cdots,\end{aligned} \quad (34)$$

where $(E_0-H_0)^{-1}$ is the reduced Green function shown in Eqs. (7) and (8). We can see that the BBR shift can be expressed in terms of the static polarizabilities. The leading-order BBR shift is

$$\Delta E^{(1)}=\frac{-2e^2}{\pi}\int_0^\infty \mathrm{d}\omega\frac{\omega^3}{\mathrm{e}^{\omega/k_{\mathrm{B}}T}-1}\left\langle \boldsymbol{r}\frac{1}{E_0-H_0}\boldsymbol{r}\right\rangle \quad (35)$$

in natural units, or

$$\begin{aligned}\Delta E^{(1)}&=\frac{-e^2}{2}\frac{\hbar}{\pi^2c^3\varepsilon_0}\int_0^\infty \mathrm{d}\omega\frac{\omega^3}{\mathrm{e}^{\hbar\omega/k_{\mathrm{B}}T}-1}\\&\quad\times\left\langle \boldsymbol{r}\frac{1}{(E_0-H_0)}\boldsymbol{r}\right\rangle\frac{a_0^2}{E_{\mathrm{H}}}\end{aligned} \quad (36)$$

in SI unites, where c is the speed of light, ε_0 is the permittivity, a_0 is the Bohr radius, and E_{H} is the Hartree energy. In the above equation, $\langle \boldsymbol{r}(E_0-H_0)^{-1}\boldsymbol{r}\rangle$ is nothing but the static dipole polarizability, as shown in Eq. (24). The remaining integration over ω can be done and the result is

$$\int_0^\infty \mathrm{d}\omega\frac{\omega^3}{\mathrm{e}^{\hbar\omega/k_{\mathrm{B}}T}-1}=\frac{\pi^4k_{\mathrm{B}}^4T^4}{15\hbar^4}. \quad (37)$$

In Table 2, we list the BBR shifts to the 1S and 2S states of hydrogen. Our results for the 1S state are in good agreements with those in Ref. [13]. For the 2S state, however, there exist significant discrepancies between our results and Ref. [13], especially at low temperatures. We will discuss this issue later.

Table 2. Blackbody radiation shifts (in Hz) to the 1S and 2S states of hydrogen.

Temperature/K	This work	Ref. [13]	Ref. [14]
	1S		
300	-3.8786×10^{-2}	-3.88×10^{-2}	−0.04128
77	-1.6832×10^{-4}	-1.68×10^{-4}	
3	-1.2258×10^{-9}	-1.22×10^{-9}	
	2S		
300	−1.0343	-9.89×10^{-1}	−1.077
77	-4.4887×10^{-3}	-1.44×10^{-3}	
3	-3.2689×10^{-8}	7.79×10^{-7}	

The second-order BBR shift is given by

$$\begin{aligned}\Delta E^{(2)}&=\frac{-e^2}{2}\frac{\hbar}{\pi^2c^3\varepsilon_0}\int_0^\infty \mathrm{d}\omega\frac{\omega^5}{\mathrm{e}^{\hbar\omega/k_{\mathrm{B}}T}-1}\\&\quad\times\left\langle \boldsymbol{r}\frac{1}{(E_0-H_0)^3}\boldsymbol{r}\right\rangle\frac{a_0^2}{E_{\mathrm{H}}^3}.\end{aligned} \quad (38)$$

In the coordinate representation, the key quantity we need to calculate is

$$\begin{aligned}\mathcal{I}^{(3)}_{nll'}&\equiv\int \psi^\dagger_{nlm}(\boldsymbol{r}_1)\,\boldsymbol{r}_1G'_1(\boldsymbol{r}_1,\boldsymbol{r}_2;E_n)\,G'_2(\boldsymbol{r}_2,\boldsymbol{r}_3;E_n)\\&\quad\times G'_3(\boldsymbol{r}_3,\boldsymbol{r}_4;E_n)\,\boldsymbol{r}_4\psi_{nlm}(\boldsymbol{r}_4)\,\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\mathrm{d}\boldsymbol{r}_3\mathrm{d}\boldsymbol{r}_4.\end{aligned}$$

The angular part of this integral can be easily evaluated due to the orthogonality relation of the spherical harmonics. The radial part can be written in the form

$$\begin{aligned}&\int r_1^2\mathrm{d}r_1r_2^2\mathrm{d}r_2r_3^2\mathrm{d}r_3r_4^2\mathrm{d}r_4R_{nl}(r_1)\,g_{l_1}(r_1,r_2;E_n)\\&\times g_{l_2}(r_2,r_3;E_n)\,g_{l_3}(r_3,r_4;E_n)\,R_{nl}(r_4).\end{aligned}$$

Since the angular part contains $\delta_{l_1l_2}$ and δ_{l_2,l_3}, the three radial functions g_{l_i} will have the same intermediate orbital angular quantum numbers, i.e., $|l-1|$ and $l+1$. By applying the same method introduced in Section 2, we can obtain the following expressions:

$$\begin{aligned}\mathcal{M}^{(1,3)}_{nl,|l-1|}&=\left(-\frac{5l^5}{96}+\frac{45l^4}{64}-\frac{163l^3}{48}+\frac{495l^2}{64}-\frac{647l}{96}\right.\\&\quad\left.+\frac{21}{16}\right)n^8+\left(-\frac{35l^3}{96}+\frac{55l^2}{16}-\frac{845l}{96}+\frac{341}{64}\right)n^{10}\\&\quad+\left(\frac{91}{64}-\frac{7l}{12}\right)n^{12},\end{aligned}$$

$$\mathcal{M}^{(1,3)}_{nl,l+1} = \left(\frac{5l^5}{96}+\frac{185l^4}{192}+\frac{323l^3}{48}+\frac{4351l^2}{192}+\frac{1135L}{32} + \frac{319}{16}\right)n^8+\left(\frac{35l^3}{96}+\frac{145l^2}{32}+\frac{805l}{48}+\frac{3443}{192}\right)n^{10} + \left(\frac{7l}{12}+\frac{385}{192}\right)n^{12}. \quad (39)$$

The corresponding angular parts are

$$\mathcal{A}^{(1,3)}_{l,|l-1|} = \frac{l}{6l+3}, \quad \mathcal{A}^{(1,3)}_{l,l+1} = \frac{l+1}{6l+3}. \quad (40)$$

We thus have

$$\mathcal{I}^{(3)}_{nl} = \sum_{l'}\mathcal{I}^{(3)}_{nll'} = \mathcal{M}^{(1,3)}_{nl,l+1}\mathcal{A}^{(1,3)}_{l,l+1}+\mathcal{M}^{(1,3)}_{nl,|l-1|}\mathcal{A}^{(1,3)}_{l,|l-1|} = \left[\frac{55}{96}l^2(l+1)^2+\frac{539}{48}l(l+1)+\frac{319}{24}\right]n^8 + \left[\frac{25}{9}l(l+1)+\frac{3443}{288}\right]n^{10}+\frac{385n^{12}}{288}. \quad (41)$$

The corresponding BBR shift to the 1S state of hydrogen at 300 K is -3.8878×10^{-6} Hz, which is much smaller than the leading-order one and can be omitted in most cases.

In Appendix, we give the analytical expressions for $\langle \boldsymbol{r}(E_0-H_0)^{-2}\boldsymbol{r}\rangle$ and $\langle \boldsymbol{r}(E_0-H_0)^{-4}\boldsymbol{r}\rangle$, which will be useful in higher-order perturbation calculations. For instance, one should calculate $\langle \boldsymbol{r}(E_0-H_0)^{-2}\boldsymbol{r}\rangle$ when considering the second-order perturbation of Eq. (36).

Our approach here is nonrelativistic in nature, which works well for the ground states, as shown in Table 2. However, for the exited nS states, even for $n=2$, the discrepancy appears, especially at lower temperatures. In Ref. [13], the radial wave function is treated under the Schrödinger–Pauli approximation, whereas the angular part is treated using a Dirac spinor and the Dirac angular quantum number. Further, they also consider the Lamb shift and fine-structure contributions. Table 2 also shows that, for the 2S state, the discrepancy between our results and Ref. [13] becomes more significant as the temperature decreases due to the relativistic effect. In the nonrelativistic limit, the BBR shift acts as T^4/Z^4; whereas the relativistic correction acts as $(Z\alpha T)^2$. Therefore, the relativistic correction becomes more important for high Z and/or low T.[13,17]

5. Summary

In this work, based on the analytical wave function and the reduced Green function, we have obtained the analytical expressions for the scalar multipole polarizabilities of hydrogen-like ions through a numerical fitting procedure. These analytical expressions can be expressed as a polynomial of n and $l(l+1)$. We have applied our results to the BBR calculations and found that the relativistic effects are particularly important at low temperatures. Our analytical formulas can be served as a benchmark for other computational methods.

Compared with the known numerical results, it is found that our results are in good agreement with the ground state. We also discuss the influence of relativistic effects in blackbody radiation correction. It is worth mentioning that for simple atoms, the mean velocity of electron will be smaller in the excited states, which means that the higher the excited state, the less significant the relativistic effect of the atom. In this case, the results of our nonrelativistic-based-derivation could be more accurate. However, for the highly charged hydrogen-like ions, the relativistic effects can be more significant. For other systems, like helium in Rydberg states, the analytical asymptotic behavior of the dipole polarizabilities has few similarities with that of the hydrogen-like atoms.[1,10] That is, more details should be studied if we want to use these hydrogen analytical expressions to help describing polarizabilities of other systems.

Appendix A: Supplementary materials

In this appendix, we give Table A1 on the fitting progress to help understanding, and two analytical results of two integrals which could be useful in higher-order perturbation calculations.

Table A1. An example of the c_i fitting. The values of radial integrals in different n are also listed. The coefficients c_i have only non-zero c_1 and c_2. For simplicity, we only list the results of $l=0,1,9$ for $l'=l+1$, and $l=1,2,9$ for $l'=|l-1|$.

$l'=l+1$			
	$l=0$	$l=1$	$l=9$
$\mathcal{M}^{(1)}(n,l)$ $n=1,2,\ldots,20$	{27/4, 180, 6075/4, 7488, 106875/4, 76788, 756315/4, 414720, 3326427/4, 1552500, 10936827/4, 4587840, 29560635/4, 11495988, 69406875/4, 25509888, 146579355/4, 51569460, 285012027/4, 96840000}	{390, 2835, 12768, 43125, 119718, 288120, 622080, 1233468, 2283750, 3996993, 6674400, 10710375, 16610118, 25008750, 36691968, 52618230, 73942470, 102041343, 138540000, 185340393}	{12993750, 21214809, 33444576, 51152751, 76193334, 110868750, 157999104, 220996566, 303944886, 411684039, 549900000, 725219649, 945310806, 1218987396, 1556319744, 1968750000, 2469212694, 3072260421, 3794194656, 4653201699}
$c_i^{(1)}$ $(i=1,\ldots,20)$	$\{3/2,21/4,0,0,\ldots,0\}$	$\{17/8,127/8,0,0,\ldots,0\}$	$\{57/8,4695/8,0,0,\ldots,0\}$

Table A1. (*Continued*).

$l' = \lvert l-1 \rvert$			
	$l=1$	$l=2$	$l=9$
$\mathcal{M}^{(1)}(n,l)$ $n=1,2,\ldots,20$	{12, 162, 960, 3750, 11340, 28812, 64512, 131220, 247500, 439230, 741312, 1199562, 1872780, 2835000, 4177920, 6013512, 8476812, 11728890, 15960000, 21392910}	{–243, –1440, –5625, –17010, –43218, –96768, –196830, –371250, –658845, –1111968, –1799343, –2809170, –4252500, –6266880, –9020268, –12715218, –17593335, –23940000, –32089365, –42429618}	{–6172500, –10497597, –17133120, –26990145, –41229972, –61306875, –89014272, –126534315, –176490900, –242006097, –326760000, –435053997, –571877460, –742977855, –954934272, –1215234375, –1532354772, –1915844805, –2376413760, –2926021497}
$c_i^{(1)}$ $(i=1,\ldots,20)$	$\{1/4,-1/4,0,0,\ldots,0\}$	$\{-3/8,3/8,0,0,\ldots,0\}$	$\{-19/4,-569/4,0,\ldots,0\}$

Here we present the analytical results for the integrals $\langle rG'^2r\rangle$ and $\langle rG'^4r\rangle$. In the coordinate representation, they can be written as

$$\mathcal{I}^{(2)}_{n,ll'} \equiv \int \psi^{\dagger}_{nlm}(\boldsymbol{r}_1)\,\boldsymbol{r}_1 G'_1(\boldsymbol{r}_1,\boldsymbol{r}_2;E_0)\,G'_2(\boldsymbol{r}_2,\boldsymbol{r}_3;E_0)\,\boldsymbol{r}_3\psi_{nlm}(\boldsymbol{r}_3)\,\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\mathrm{d}\boldsymbol{r}_3, \tag{A1}$$

$$\mathcal{I}^{(4)}_{n,ll'} \equiv \int \psi^{\dagger}_{nlm}(\boldsymbol{r}_1)\,\boldsymbol{r}_1 G'_1(\boldsymbol{r}_1,\boldsymbol{r}_2;E_0)\,G'_2(\boldsymbol{r}_2,\boldsymbol{r}_3;E_0)\,G'_2(\boldsymbol{r}_3,\boldsymbol{r}_4;E_0)\,G'_2(\boldsymbol{r}_4,\boldsymbol{r}_5;E_0)\,\boldsymbol{r}_5\psi_{nlm}(\boldsymbol{r}_5)\,\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\mathrm{d}\boldsymbol{r}_3\mathrm{d}\boldsymbol{r}_4\mathrm{d}\boldsymbol{r}_5. \tag{A2}$$

Using Eqs. (6), (8), and (15) and applying the fitting procedure, we can obtain the following analytical expressions after summing over l':

$$\mathcal{I}^{(2)}_{nl} = \left[\frac{5}{48}l^2(l+1)^2+\frac{14}{3}l(l+1)+\frac{163}{24}\right]n^6+\left[\frac{5}{12}(l+1)l+\frac{61}{16}\right]n^8+\frac{7n^{10}}{48}, \tag{A3}$$

$$\begin{aligned}\mathcal{I}^{(4)}_{nl} = {}& \left[\frac{35}{3456}l^3(l+1)^3+\frac{3595}{1728}l^2(l+1)^2+\frac{7385}{288}l(l+1)+\frac{1255}{48}\right]n^{10}\\ &+\left[\frac{385}{3456}l^2(l+1)^2+\frac{40765}{3456}l(l+1)+\frac{58145}{1728}\right]n^{12}+\left[\frac{1393}{3456}l(l+1)+\frac{2779}{384}\right]n^{14}+\frac{491n^{16}}{3456}.\end{aligned} \tag{A4}$$

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