Relativistic and QED corrections for the Beryllium atom

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Complete relativistic and quantum electrodynamics corrections of order $\alpha^2\,\mathrm{Ry}$ and $\alpha^3\,\mathrm{Ry}$ are calculated for the ground state of the beryllium atom and its positive ion. A basis set of correlated Gaussian functions is used, with exponents optimized against nonrelativistic binding energies. The results for Bethe logarithms $\ln k_0(\mathrm{Be}) = 5.750\,34(3)$ and $\ln k_0(\mathrm{Be}^+) = 5.751\,67(3)$ demonstrate the availability of high precision theoretical predictions for energy levels of the beryllium atom and light ions. Our recommended value of the ionization potential 75192.514(80) cm^{-1} agrees with equally accurate available experimental values.

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High precision calculations of atomic energy levels and transition rates allow for accurate QED tests and for determination of fundamental physical constants. Hydrogen, helium, and recently lithium have been a subject of intensive theoretical research. The hydrogen spectrum is known up to order $\alpha^5\,\mathrm{Ry}$ [1, 2], which includes two- and three-loop self energy corrections. At present, the accuracy is limited by the uncertainty in the proton electric charge and magnetic moment distribution. For the helium atom, all corrections up to order $\alpha^4\,\mathrm{Ry}$ have recently been completed for S- and P-states [3–5]. Moreover, for helium fine structure the dominant $\alpha^5\,\mathrm{Ry}$ corrections have been recently evaluated [6, 7], and significant discrepancies with experiments [8, 9] have been observed. For the lithium atom, the nonrelativistic energy and leading relativistic corrections, as well as nuclear recoil effects have been calculated most precisely by Yan and Drake in series of papers [10]. Recently, the leading QED corrections, of order $\alpha^3\,\mathrm{Ry}$ to the binding energy of the lithium ground state have been completed by two groups [11] and [12]. For the beryllium atom theoretical results are much less accurate in comparison to lithium and helium. The accurate nonrelativistic energy of the Be ground state was calculated first by Sims and Hagstrom [13] to be $-14.666\,54$ au, later by Bunge [14] to be $-14.667\,358(28)$ au, and the most accurate energy so far is $-14.667\,355\,627$ au, found by Komasa [15]. Relativistic corrections have been calculated by Liu and Kelly [16], Lindroth *et al.* [17], and the most accurate results have been obtained by Chung *et al.* [18], where additional QED effects have been partially included. In this paper we present a complete calculation of both: relativistic $\alpha^2\,\mathrm{Ry}$ and radiative $\alpha^3\,\mathrm{Ry}$ corrections to the 2^1S_0 ground state of the beryllium atom and $2^2S_{1/2}$ ground state of the singly ionized beryllium ion. The calculational method applied in this work uses a correlated basis set of Gaussian functions (ECG). It is described in detail in our former work on lithium atom [12]. However, a new integral representation of the Bethe logarithm and a new regularized formula for several singular operators, including $P(1/r^3)$ distribution, allowed us to obtain an accurate numerical result for QED effects. The use of the ECG basis set enables essentially exact incorporation of electron correlations and at the same time all matrix elements can be calculated analytically. The only approximations performed are expansions in α and in the electron-nucleus mass ratio. The first terms of the α-expansion of binding energy are the relativistic and radiative (QED) corrections

$$E = \frac{\mu}{m}\,E_0 + \alpha^2\,E_{\mathrm{REL}} + \alpha^3\,E_{\mathrm{QED}} + \alpha^4\,\delta E_{\mathrm{QED}}, \qquad (1)$$

where E_0 is the nonrelativistic energy corresponding to the Hamiltonian (in atomic units)

$$H_0 = -\sum_i\left(\frac{\boldsymbol{\nabla}_i^2}{2} + \frac{Z}{r_i}\right) + \sum_{i>j}\left(\frac{1}{r_{ij}} - \frac{\mu}{M}\,\boldsymbol{\nabla}_i\boldsymbol{\nabla}_j\right), \qquad (2)$$

where M and μ are the nuclear and the reduced mass, respectively. The relativistic correction E_{REL} is the expectation value of the Breit-Pauli Hamiltonian with the nonrelativistic wave function and we now allow the nuclear mass to go to infinity, as the relativistic recoil corrections are not significant at the aimed level of accuracy. The non vanishing terms of Breit-Pauli Hamiltonian [19] are

$$\begin{aligned} H_{\mathrm{REL}} \;=\; & \sum_i\left[-\frac{\boldsymbol{\nabla}_i^4}{8} + \frac{Z\pi}{2}\,\delta(\boldsymbol{r}_i)\right] \\ & -\sum_{i>j}\left(1 + \frac{8}{3}\boldsymbol{s}_i\cdot\boldsymbol{s}_j\right)\,\pi\,\delta(\boldsymbol{r}_{ij}) \\ & +\sum_{i>j}\frac{1}{2}\left(\frac{\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j}{r_{ij}} + \frac{\boldsymbol{r}_{ij}\cdot(\boldsymbol{r}_{ij}\cdot\boldsymbol{\nabla}_i)\,\boldsymbol{\nabla}_j}{r_{ij}^3}\right), \end{aligned} \qquad (3)$$

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where $\boldsymbol{s}_i$ is a spin operator for a particle i. In general, additional spin-orbit and spin-spin terms are present, but they vanish for S states. Also the $\boldsymbol{s}_i\cdot\boldsymbol{s}_j\delta(\boldsymbol{r}_{ij})$ term reduces to $-3/4\,\delta(\boldsymbol{r}_{ij})$. The QED (radiative) corrections can be expressed as an expectation value of some effective operators and the Bethe logarithm $\ln k_0$ [20, 21]

$$\begin{aligned} E_{\rm QED} &= \sum_{i>j}\left\{\left[\frac{164}{15}+\frac{14}{3}\ln\alpha\right]\langle\Psi\left|\delta(\boldsymbol{r}_{ij})\right|\Psi\rangle\right.\\ &\quad\left.-\frac{14}{3}\left\langle\Psi\left|\frac{1}{4\pi}P\left(\frac{1}{r_{ij}^3}\right)\right|\Psi\right\rangle\right\} \qquad (4)\\ &\quad+\sum_i\left[\frac{19}{30}+\ln(\alpha^{-2})-\ln k_0\right]\frac{4Z}{3}\langle\Psi\left|\delta(\boldsymbol{r}_i)\right|\Psi\rangle\,. \end{aligned}$$

Here, Z is the atomic number, m the electron mass and δ means the Dirac delta function. The distribution P is defined as the limit

$$\left\langle\phi\left|P\left(\frac{1}{r^3}\right)\right|\psi\right\rangle\equiv \qquad (5)$$

$$\lim_{a\to0}\int d\boldsymbol{r}\,\phi^*(\boldsymbol{r})\,\psi(\boldsymbol{r})\left[\frac{1}{r^3}\Theta(r-a)+4\,\pi\,\delta(\boldsymbol{r})\,(\gamma+\ln a)\right],$$

with Θ and γ being the step function and the Euler constant, respectively. The n-electron Bethe logarithm, $\ln k_0$, is defined by

$$\ln k_0 = -\frac{1}{D}\langle\Psi|\boldsymbol{\nabla}\,(H_0-E_0)\,\ln\big[2\,(H_0-E_0)\big]\,\boldsymbol{\nabla}\,|\Psi\rangle, \qquad (6)$$

$$\boldsymbol{\nabla} = \sum_i\boldsymbol{\nabla}_i, \qquad (7)$$

$$D = 2\,\pi\,Z\left\langle\Psi\left|\sum_i\delta(\boldsymbol{r}_i)\right|\Psi\right\rangle. \qquad (8)$$

The nonrelativistic energies, as well as relativistic and radiative corrections are calculated with exponentially correlated Gaussian (ECG) functions [22]. The wave function Ψ is expressed in the form of K-term linear combination of the multielectron basis functions $\psi_l(\mathbf{r})$

$$\Psi(\mathbf{r},\boldsymbol{\sigma})=\hat{\mathcal{A}}\left(\Xi_{S,M_S}(\boldsymbol{\sigma})\sum_{l=1}^{K}c_l\,\psi_l(\mathbf{r})\right). \qquad (9)$$

The operator $\hat{\mathcal{A}}$ ensures the antisymmetry of the total wave function with respect to the exchange of the electrons. The $\Xi_{S,M_S}(\boldsymbol{\sigma})$ is an n-electron spin eigenfunction with the quantum numbers S and M_S, and $\boldsymbol{\sigma}$ and $\mathbf{r}$ are the n-electron vectors in spin and coordinate space. The spatial basis functions are the n-electron atomic Singer functions [23] of S and P symmetry, respectively:

$$\psi_l(\mathbf{r})=\exp\left[-\mathbf{r}\,\mathbf{A}_l\,\mathbf{r}^T\right], \qquad (10)$$

$$\tilde{\psi}_l(\mathbf{r})=\boldsymbol{r}_i\exp\left[-\mathbf{r}\,\tilde{\mathbf{A}}_l\,\mathbf{r}^T\right], \qquad (11)$$

with $\boldsymbol{r}_i$ being the coordinate of the i-th electron. The linear parameters c_l are obtained by the standard inverse iteration method. The nonlinear parameters collected in the positive definite matrices $\mathbf{A}_l$ are determined variationally in an extensive optimization process. The minimization functional is the expectation value of H_0 if the wave function of a state is to be obtained, or the other functional, given in Eq. (21), for the calculation of Bethe logarithm. The final results of the optimization are shown in Table I. It is worth noting that the ground state energy of Be presented in this table is the most accurate nonrelativistic value to date.

TABLE I: Expectation values of various operators with nonrelativistic wave function of beryllium atom ($K=3600$) and its positive ion ($K=2000$) in atomic units. Implicit summation over i and over pairs $i>j$, respectively, is assumed.

	Be	Be^+
$\langle H_0\rangle$	$-14.667\,355\,627$	$-14.324\,763\,152$
$\langle\boldsymbol{\nabla}^2\rangle$	$-30.255\,167(4)$	$-29.555\,364$
$\langle\delta(r_i)\rangle$	$35.368\,90(2)$	$35.105\,022$
$\langle\delta(r_{ij})\rangle$	$1.605\,303(1)$	$1.580\,538$
$\langle\boldsymbol{p}_i\cdot\boldsymbol{p}_j\rangle$	$0.460\,228(2)$	$0.452\,919$
$\langle p_i^4\rangle/8$	$270.704\,68(25)$	$268.316\,415$
$\langle r_{ij}^{-1}\boldsymbol{p}_i\cdot\boldsymbol{p}_j+$ $r_{ij}^{-3}\boldsymbol{r}_{ij}\,(\boldsymbol{r}_{ij}\cdot\boldsymbol{p}_i)\,\boldsymbol{p}_j)\rangle$	$1.783\,65(2)$	$1.819\,811$
$\langle P(1/r_{ij}^3)\rangle/4\pi$	$-0.583\,03(5)$	$-0.597\,973$
$\ln k_0$	$5.750\,34(3)$	$5.751\,67(3)$

We recall here that with the ECG functions the cusp condition at the nucleus can never be fulfilled. This results in slow convergence of the expectation value of the relativistic operators appearing in Eq. (3). One way to overcome this problem is to transform these matrix elements to an equivalent, but more regular form, which has much better numerical convergence. An example of such regularization for the Dirac δ-function was given by Drachman [24]. He expressed the expectation value of $\delta(\boldsymbol{r}_{jk})$ in an equivalent form containing global operators, namely

$$\begin{aligned} 4\pi\langle\Psi\left|\delta(\boldsymbol{r}_{jk})\right|\Psi\rangle &= 2\left\langle\Psi\left|\frac{1}{r_{jk}}(E_\Psi-\hat{V})\right|\Psi\right\rangle\\ &\quad+\sum_i\frac{1}{m}\left\langle\boldsymbol{\nabla}_i\Psi\left|\frac{1}{r_{jk}}\right|\boldsymbol{\nabla}_i\Psi\right\rangle, \qquad (12) \end{aligned}$$

where $\hat{V}=\sum_{i>j}1/r_{ij}-\sum_i Z/r_i$. In a similar way, the relativistic kinetic energy term can be expressed by

$$\left\langle\Psi\left|\nabla_i^4\right|\Psi\right\rangle=4\left\langle\Psi\left|(E_\Psi-\hat{V})^2\right|\Psi\right\rangle-2\sum_{i>j}\left\langle\nabla_i^2\Psi\right|\nabla_j^2\Psi\big\rangle\,. \qquad (13)$$

The expectation values of various components of $H_{\rm REL}$ are shown in Table I. Their contribution to the uncertainty of the total energy is much below that of E_0, see Table II.

The calculation of the radiative correction is more subtle and it is the main subject of this work. The expectation value of $P(1/r_{ij}^3)$ in the ECG basis computed directly has a very slow numerical convergence. For this reason, we transform it to a much more regular form, in a similar way as for $\delta(\boldsymbol{r}_{ij})$. One finds a function, for which ∇^2 gives $P(1/r_{ij}^3)$,

$$\nabla_j^2\left(\frac{1+\gamma+\ln r_{jk}}{r_{jk}}\right) = -P\left(\frac{1}{r_{jk}^3}\right), \tag{14}$$

and for the matrix elements obtains the identity

$$\begin{aligned}\left\langle\Psi\middle|P\left(\frac{1}{r_{jk}^3}\right)\middle|\Psi\right\rangle &= \sum_i \frac{1}{m}\left\langle\boldsymbol{\nabla}_i\Psi\middle|\frac{\ln r_{jk}}{r_{jk}}\middle|\boldsymbol{\nabla}_i\Psi\right\rangle \qquad (15)\\ &+\left\langle\Psi\middle|4\pi(1+\gamma)\,\delta(\boldsymbol{r}_{jk})+2\,(E_\Psi-\hat{V})\,\frac{\ln r_{jk}}{r_{jk}}\middle|\Psi\right\rangle.\end{aligned}$$

The singular operators are no longer present, and the δ function is handled according to Eq. (12). The numerical convergence is improved by 3 orders of magnitude, well under the aimed precision (see Table I). The price one pays is more complicated integrals, which however can be performed analytically in terms of elementary and Clausen Cl_2 functions, for example

$$\begin{aligned}\int d\mathbf{r}\, e^{-a_1\,r_1^2-a_2\,r_2^2-a_3\,r_{12}^2}\,\frac{\ln(r_1)}{r_1\,r_2} &= \\ -\frac{2\,\pi^2}{a\,a_3}\,[\mathrm{Cl}_2(\pi+2\,b)+b\,c] \qquad (16)\end{aligned}$$

where

$$\begin{aligned} a &= \sqrt{a_1\,a_2+a_1\,a_3+a_2\,a_3}\\ b &= \arctan\left(\frac{a_3}{a}\right)\\ c &= \gamma+\ln\left(\frac{4\,a^2}{a_2+a_3}\right). \end{aligned} \tag{17}$$

The calculation of the Bethe logarithms [25] is the most numerically intensive part of this work. Details of such calculations with the ECG functions have been presented in the former work devoted to lithium atom [12]. Here we emphasize three most important elements. The first one is the use of the following compact integral representation of Bethe logarithm

$$\ln k_0 = \frac{1}{D}\int_0^1 dt\,\frac{f(t)-f_0\,-f_2\,t^2}{t^3}, \tag{18}$$

where

$$f(t) = -\left\langle\boldsymbol{\nabla}\,\frac{\omega}{H_0-E_0+\omega}\boldsymbol{\nabla}\right\rangle, \tag{19}$$

$$t = 1/\sqrt{1+2\,\omega}, \tag{20}$$

and D is defined in Eq. (8). This integral representation exhibits better numerical convergence than former ones [25], and we found that the integration over 200 equally spaced points allows for relative accuracy of the order of 10^{-6}. The second important element is the optimization of nonlinear parameters in ECG functions, Eq. (11), for several values of ω. It is achieved by the minimization the Hylleraas functional

$$\mathcal{J}_k[\tilde{\boldsymbol{\Psi}}] = \langle\tilde{\boldsymbol{\Psi}}|H_0-E_0+\omega|\tilde{\boldsymbol{\Psi}}\rangle+2\langle\tilde{\boldsymbol{\Psi}}|\boldsymbol{\nabla}|\Psi\rangle. \tag{21}$$

This optimization ensures that the integrand in Eq. (18) is calculated with sufficient accuracy. The exceptions are points at very low t. Here, following Schwartz [25], we perform a small t expansion

$$f(t) = f_0+f_2\,t^2+f_3\,t^3+f_4\,t^4\,\ln(t)+o(t^4)\,, \tag{22}$$

where

$$\begin{aligned} f_0 &= -\langle\boldsymbol{\nabla}^2\rangle\\ f_2 &= -2\,D\\ f_3 &= 8\,Z\,D\\ f_4 &= 16\,Z^2\,D \end{aligned} \tag{23}$$

and fit higher order coefficients to the calculated $f(t)$. This was the third important element in the calculation of the Bethe logarithm. The overall accuracy for $\ln k_0$ is of the order 10^{-5}, see Table I, and the limiting factor is the fitting procedure.

While we obtain the complete radiative correction of order α^3 Ry, higher order terms become the source of uncertainty of theoretical predictions. We calculate them on the basis of the known result for the binding one-loop correction to the hydrogen Lamb shift [1],

$$\delta E_{\mathrm{QED}} = 4\,\pi\,Z^2\left(\frac{139}{128}+\frac{5}{192}-\frac{\ln(2)}{2}\right)\langle\Psi|\sum_i\delta(\boldsymbol{r}_i)|\Psi\rangle \tag{24}$$

and estimate uncertainty for remaining terms to be 20% of δE_{QED}.

TABLE II: Components of the total binding energy for ^{9}Be atom and ion, and ionization energy in cm^{-1}. SMS and NMS subscripts designate specific and normal mass shift, respectively, and remaining energy components are defined by Eqs. (1)-(4) and (24). Physical constants are from [26].

	Be	Be$^+$	IP
E_0	−3219112.469(70)	−3143922.112(6)	75190.357(70)
E_{NMS}	195.986	191.408	−4.578
E_{SMS}	6.150	6.052	−0.098
$\alpha^2 E_{\mathrm{REL}}$	−518.028(5)	−510.614	7.414(5)
$\alpha^3 E_{\mathrm{QED}}$	74.576	74.020	−0.557
$\alpha^4\delta E_{\mathrm{QED}}$	3.388	3.362	−0.025(5)
total E	−3219350.398	−3144157.884	75192.514(80)
$E-E_0$	−237.928	−235.772	2.157(10)

We have repeated the whole calculations for Be$^+$ in order to compute the ionization energy. Results are summarized in Tables I and II. Final theoretical predictions for the ground state ionization energy of ^{9}Be are now accurate up to 0.08 cm^{-1}. The uncertainty comes almost exclusively from the nonrelativistic binding energy of Be. We have estimated the uncertainty of E_0 by a reanalysis of the former data in [27] and obtained it from the K^{-2} fit to energies calculated with optimized basis sets of length K.

Let us now turn to the physical consequences of the obtained result. First of all, we have demonstrated the availability of high precision theoretical predictions for energy levels of beryllium atom and light beryllium-like ions. Two experimental results for the ionization energy

$$\Delta E_{\rm exp1} = 75\,192.50(10)\,{\rm cm}^{-1}\ [28]\,, \tag{25}$$

$$\Delta E_{\rm exp2} = 75\,192.64(6)\,{\rm cm}^{-1}\ [29]\,, \tag{26}$$

agree well with equally accurate theoretical predictions, see Table II. This precision of the theoretical result can be still improved by having more accurate nonrelativistic binding energies. The relativistic and QED parts are calculated with much higher precision of 0.005 cm^{-1}. While ECG functions can be further optimized, the challenge is the use of a more effective correlated basis set. It is interesting to note, that in spite of increase of computer power, no significant advances in the precise calculation of nonrelativistic energies of four and more electron atoms have been observed. Some steps in this directions have been achieved by Sims and and Hagstrom [30] with a variant of exponential basis sets. We are pursuing ECG functions with linear in r_{ij} factors, and several promising results have already been obtained for the helium atom [31]. In a similar approach the nuclear recoil effects or the hyperfine splitting of excited states can be obtained with comparable precision, opening the window for the high precision determination of nuclear size, magnetic dipole, and electric quadrupole moments for various isotopes of beryllium.

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