

Calculation of Zeeman and hyperfine splitting using a finite Gaussian basis set

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The application of a finite basis set of Gaussians to calculating the Zeeman and hyperfine splitting in hydrogen-like ions is considered. The g -factor and relativistic factor for the hyperfine splitting are calculated. Calculations are also performed for second-order effects in the magnetic interaction, namely, the quadratic Zeeman effect and nuclear magnetic shielding. The results are compared with similar calculations using a B-spline basis set for finite-size nuclear models and with analytical formulas for the point model.

Keywords: Zeeman splitting, hyperfine splitting, finite basis set, highly charged ions.

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Introduction

The study of various physical effects in highly charged ions is an active area in atomic physics and quantum electrodynamics. This is due to the fact that in such systems the electric field of the nucleus is strong enough that it becomes essential to take into account contributions from higher orders of interaction with the nuclear field. On the other hand, the small number (one for hydrogen-like ions) of electrons in such ions allows calculations to be made for such systems with very high accuracy. At the same time, experiments with such ions allow us to obtain precise results [1–3], e.g., experiments to determine the g -factor in highly charged ions offer an accurate way to determine physical quantities and constants [4], such as the electron mass [5]. In addition to measuring g factor, existing experiments also make it possible to observe nonlinear effects related to magnetic interaction, such as the quadratic and third-order Zeeman effect [6]. In terms of theory these effects are considered, for instance, in [7]. On the other hand, the study of hyperfine splitting is of interest, since this effect strongly depends on the nuclear charge distribution. The study of this effect makes it possible to refine the models of nuclear potentials. The effect of nuclear magnetic shielding in highly charged ions is considered in detail, for example, in studies [8–10].

For the accurate calculation of the g -factor and the quadratic Zeeman effect, as is well known, it is necessary to take into account loop quantum electrodynamic (QED) corrections [11–15]. In [5], for the case of highly charged ions, QED contributions are compared with other physical contributions to the value of g -factor. For hydrogen-like ions, various corrections to the g -factor and the quadratic Zeeman effect were discussed in detail in [15]. For accurate calculation of hyperfine splitting and nuclear magnetic

shielding, taking into account such contributions also turns out to be important [16–18]. Although the finite basis of B-splines [19,20] is successfully used for many atomic and QED calculations, there is interest in using other basis sets. In particular, B-splines have not been successfully used to calculate the many-potential contribution from vacuum polarization. In recent studies, from the Gaussian basis has been used to calculate QED corrections. In papers [21,22], using this basis, the vacuum polarization correction was calculated in all orders in the interaction with the nuclear field, and in paper [23] the correction from the electron self-energy was calculated.

Recent advances in applying the Gaussian basis to calculate QED corrections, especially vacuum polarization, pave the way for using this basis to calculate more complex QED diagrams involving magnetic interaction. Thus, when calculating diagrams for QED corrections of g -factor, matrix elements arise similar to those that arise when calculating g -factor itself, therefore, it is of interest to study the applicability of the Gaussian basis to finding the latter. In [21–23] the interest in the Gaussian basis, rather than the related Slater functions, is due to the fact that major focus was made on heavy ions where the finite size of the nucleus shall be considered. For such systems, the Gaussian basis is well suited [24]. Apart from the atomic QED calculations, this basis is convenient in molecular calculations, where its further application to quasi-molecules may be of particular interest. The Gaussian basis is also widely used in quantum chemistry, where the influence of external fields may also be taken into account.

One of the difficulties associated with using the Gaussian basis (and in general bases of this kind, such as Slater functions) is the so-called numerical linear dependence, which imposes an upper limit on the functions number in a finite basic set for a given arithmetic precision of

calculations. Nevertheless, modern PCs make it possible to obviate this problem by using an arbitrary precision arithmetic. For example, in [21,22], this approach was applied to calculate the vacuum polarization, and in [25], the Dirac equation for a diatomic molecule was solved with high precision.

In this paper, we consider the calculation of the g -factor and quadratic Zeeman effect, hyperfine splitting, and the nuclear magnetic shielding constant. We compare the obtained results with the corresponding analytical expressions in case of a point nucleus and with calculations using the B-spline basis with the applied dual kinetic balance [26] in case of finite-size nucleus models.

We use the relativistic system of units $\hbar = c = m_e = 1$. The fine structure constant is defined as $\alpha = e^2/(4\pi)$, $e < 0$.

Basis set

In this study, the effects in hydrogen-like ions are considered. Such an ion can be considered a centrally symmetric relativistic system, which is described by the Dirac equation:

$$h_D \phi_n(x) = E_n \phi_n(x),$$

where

$$\begin{aligned} h_D &= -i\boldsymbol{\alpha}\nabla + \beta + V(x), \\ \beta &= \gamma^0, \\ \boldsymbol{\alpha} &= \gamma^0\boldsymbol{\gamma} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \end{aligned}$$

and $\boldsymbol{\gamma}$ and $\boldsymbol{\sigma}$ are Dirac and Pauli matrices, respectively. In case of central symmetry, the electron wave function is factorized as follows:

$$\phi_{n,\kappa,m_J}(x) = \frac{1}{r} \begin{bmatrix} P_{n,\kappa}(r)\Omega_{\kappa,m_J}(\theta, \varphi) \\ iQ_{n,\kappa}(r)\Omega_{-\kappa,m_J}(\theta, \varphi) \end{bmatrix},$$

where P, Q are large and small components of the electron wave function, $\Omega_{\kappa,m_J}(\theta, \varphi)$ is a spherical spinor, κ is the relativistic quantum number associated with the orbital angular momentum by $l = |\kappa + \frac{1}{2}| - \frac{1}{2}$, m_J is a projection of the total angular momentum. A separate equation is obtained for the radial components of the wave function, which is sometimes called the radial Dirac equation:

$$\begin{bmatrix} 1 + V & -\frac{d}{dr} + \frac{\kappa}{r} \\ \frac{d}{dr} + \frac{\kappa}{r} & -1 + V \end{bmatrix} \begin{bmatrix} P_{n,\kappa} \\ Q_{n,\kappa} \end{bmatrix} = E_{n,\kappa} \begin{bmatrix} P_{n,\kappa} \\ Q_{n,\kappa} \end{bmatrix}.$$

The finite basis set method for solving equation (1) is based on the approximation of the radial components of the wave function by a finite sum of functions from a certain given set:

$$P_{n,\kappa}(r) = \sum_{i=1}^n p_{n\kappa,i} \pi_i^L(r),$$

$$Q_{n,\kappa}(r) = \sum_{i=1}^n q_{n\kappa,i} \pi_i^S(r),$$

where $p_{n\kappa,i}, q_{n\kappa,i}$ are unknown coefficients. The finite basis set method for solving atomic problems has been described in many papers, e.g., the application to the Schrödinger equation is shown in [20], for the Dirac equation — in [19] (see also the review [24] and our work [22]).

The Gaussian basis is formed from a set of exponentials with a set of coefficients ξ_i generating this basis set. a common asymptotic behavior is introduced in each basis function for $r \rightarrow 0$. For the problem with a point nucleus with a charge number Z , the basis functions are defined as

$$\pi_i^\tau = N r^\gamma e^{-\xi_i r^2}, \quad (2)$$

where symbolic designation $\tau = L, S$ is introduced for the large and small components of the electron wave function, respectively, $\gamma = \sqrt{\kappa^2 - (Z\alpha)^2}$, N is a normalization factor. In the case of a finite nucleus, the asymptotic behavior at $r \rightarrow 0$ takes a different form [27] and for basis functions, the following expression is obtained for the Gaussians:

$$\pi_i^\tau = N r^{l_\tau} e^{-\xi_i r^2}, \quad (3)$$

where the following notations are introduced

$$l_L = \left| \kappa + \frac{1}{2} \right| + \frac{1}{2}, \quad l_S = \left| \kappa - \frac{1}{2} \right| + \frac{1}{2}.$$

Magnetic interaction

Let us consider the interaction of a relativistic electron located in the nucleus field with an external uniform magnetic field according to perturbation theory:

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

The energy of an electron in the ion nucleus field in the absence of a magnetic field corresponds to a zero order. For the case of point (Coulomb) potential of the nucleus, we have the following formula:

$$E_{n,\kappa} = \frac{1}{\sqrt{1 + \left(\frac{Z\alpha}{n - |\kappa| + \gamma} \right)^2}}. \quad (4)$$

For the first order of interaction with a magnetic field, we obtain

$$E^{(1)} = \frac{|e|}{2} B \langle a | U | a \rangle,$$

where B — is the magnetic field strength and

$$U = (\mathbf{r} \times \boldsymbol{\alpha})_z$$

is the operator of interaction with the magnetic field. For the g -factor the following definition is introduced:

$$E^{(1)} = \frac{|e|}{2} B g^{(1)} m_J. \quad (5)$$

Table 1. Energy $E_{n\kappa}$ of an electron in hydrogen-like tin and the correction due to the finite size of the nucleus E_{fns} , $Z = 50$, $r_n = 4.6519$ fm

Level	$E_{n\kappa}$, point nucleus		$E_{\text{fns}} \cdot 10^6$, shell nucleus		$E_{\text{fns}} \cdot 10^6$, sphere nucleus	
	Eq. (4)	Gaussian	DKB BS	Gaussian	DKB BS	Gaussian
$1s_{1/2}$	0.931 059 404 06	0.931 059 404 06	3.838 54	3.838 61	3.831 52	3.831 59
$2s_{1/2}$	0.982 613 709 46	0.982 613 709 46	0.540 40	0.540 42	0.539 41	0.539 43
$2p_{1/2}$	0.982 613 709 46	0.982 613 709 46	0.014 62	0.014 64	0.014 59	0.014 61
$2p_{3/2}$	0.983 218 136 26	0.983 218 136 26	0.0	0.0	0.0	0.0
$3s_{1/2}$	0.992 340 868 29	0.992 340 868 29	0.161 12	0.161 13	0.160 82	0.160 83
$3p_{1/2}$	0.992 340 868 29	0.992 340 868 29	0.005 15	0.005 16	0.005 14	0.005 15
$3p_{3/2}$	0.992 520 428 00	0.992 520 428 00	0.0	0.0	0.0	0.0
$3d_{3/2}$	0.992 520 428 00	0.992 520 428 00	0.0	0.0	0.0	0.0
$3d_{5/2}$	0.992 576 423 81	0.992 576 423 81	0.0	0.0	0.0	0.0

Table 2. Values of the g -factor, $g^{(1)}$ obtained for the ground state $1s_{1/2}$ of the electron for various hydrogen-like ions

Z	Shell nucleus			Sphere nucleus		Point nucleus	
	r_n (fm)	DKB BS	Gaussian	DKB BS	Gaussian	Eq. (6)	Gaussian
1	0.8783	1.999 964 499	1.999 964 499	1.999 964 499	1.999 964 499	1.999 964 499	1.999 964 499
6	2.4702	1.998 721 355	1.998 721 355	1.998 721 355	1.998 721 355	1.998 721 354	1.998 721 354
14	3.1224	1.993 023 592	1.993 023 592	1.993 023 592	1.993 023 592	1.993 023 572	1.993 023 572
20	3.4776	1.985 723 317	1.985 723 317	1.985 723 317	1.985 723 317	1.985 723 204	1.985 723 204
32	4.0742	1.963 138 744	1.963 138 744	1.963 138 743	1.963 138 743	1.963 137 509	1.963 137 509
50	4.6519	1.908 093 815	1.908 093 815	1.908 093 787	1.908 093 787	1.908 079 205	1.908 079 205
54	4.7859	1.892 138 210	1.892 138 210	1.892 138 159	1.892 138 159	1.892 114 649	1.892 114 649
82	5.5012	1.735 402 718	1.735 402 718	1.735 400 822	1.735 400 822	1.734 947 023	1.734 947 023
92	5.8571	1.656 128 812	1.656 128 812	1.656 122 675	1.656 122 675	1.654 846 170	1.654 846 170

In the case of a point nucleus, there is an analytical expression for $g^{(1)}$:

$$g^{(1)} = \frac{\kappa}{\kappa^2 - 1/4} \left(\kappa E_{n,\kappa} - \frac{1}{2} \right). \quad (6)$$

For the second-order interaction with a magnetic field (quadratic Zeeman effect), we have

$$E^{(2)} = \left(\frac{|e|}{2} B \right)^2 g^{(2)}(m_J),$$

where

$$g^{(2)} = \sum_{n \neq a} \frac{\langle a|U|n \rangle \langle n|U|a \rangle}{\varepsilon_a - \varepsilon_n}. \quad (7)$$

Corrections of the following orders are introduced similarly. Expressions for third-order corrections can be found, for example, in [7].

Another operator often considered in atomic calculations is the hyperfine interaction operator [9], which corresponds to the electron-nucleus interaction in the dipole approximation:

$$V_{\text{hfs}} = \frac{(\mathbf{r} \times \boldsymbol{\alpha})_z}{r^3}.$$

The expression for the hyperfine splitting of levels includes the relativistic factor $A(Z\alpha)$, which is defined in the case of the ground state of the electron as [28]

$$2(Z\alpha)^3 A(Z\alpha) = \langle 1, -1|V_{\text{hfs}}|1, -1 \rangle. \quad (8)$$

In the case of the point model of the nucleus, there is an analytical expression for the factor $A(Z\alpha)$:

$$A(Z\alpha) = \frac{n^3(2l+1)\kappa(2\kappa(\gamma+n_r) - N_{n,\kappa})}{N_{n,\kappa}^4 \gamma(4\gamma^2 - 1)}, \quad (9)$$

where $n_r = n - |\kappa|$ is the radial quantum number, and

$$N_{n,\kappa} = \sqrt{n_r^2 + 2n_r\gamma + \kappa^2}.$$

Next, we consider the correction from hyperfine splitting to the g -factor. The nucleus magnetic shielding associated with this effect is found as follows [9,29]:

$$\sigma_0 = \alpha \sum_{n \neq a} \frac{\langle a|U|n \rangle \langle n|V_{\text{hfs}}|a \rangle}{\varepsilon_a - \varepsilon_n}. \quad (10)$$

It is convenient to introduce the following definition: $\sigma_0 = \alpha(Z\alpha)S(Z\alpha)/3$ [9]; for the point potential of a hydrogen-like ion and the ground state of an electron, the value $S(Z\alpha)$ can be written as

$$S(Z\alpha) = \frac{2}{3} \left[\frac{2 + \gamma_1}{3(1 + \gamma_1)} + \frac{2}{\gamma_1(2\gamma_1 - 1)} \left(1 - \frac{\gamma_1}{2} + (Z\alpha)^2 \right) \right], \quad (11)$$

where $\gamma_1 = \sqrt{1 - (Z\alpha)^2}$.

Table 3. Calculations of the quadratic Zeeman effect expressed in terms of $g^{(2)}$ obtained for the ground state $1s_{1/2}$ electron for various hydrogen-like ions

Z	Shell nucleus		Sphere nucleus		Point nucleus
	DKB BS	Gaussian	DKB BS	Gaussian	Gaussian
1	18 777.532	18 777.532	18 777.532	18 777.532	18 777.532
6	520.302 27	520.302 27	520.302 27	520.302 27	520.302 17
14	94.479 364	94.479 364	94.479 364	94.479 364	94.479 193
20	45.618 125	45.618 125	45.618 125	45.618 125	45.617 898
32	17.016 251	17.016 251	17.016 251	17.016 251	17.015 875
50	6.204 866	6.204 866	6.204 865	6.204 865	6.204 132
54	5.137 824	5.137 824	5.137 822	5.137 822	5.136 959
82	1.535 204	1.535 204	1.535 192	1.535 192	1.532 279
92	0.983 797	0.983 797	0.983 773	0.983 773	0.978 853

Results

We used the Gaussian basis (Gaussian, expressions (2) and (3)) with an arbitrary precision arithmetic (50 digits). We compare the results with analytical formulas and with the results obtained using B-splines with dual kinetic balance (DKB BS) [26]. The number of basic functions in both basis sets is taken 100. The Gaussian basis set is selected such that parameters ξ_i form a geometric progression. To calculate the energy spectrum, g -factor and quadratic Zeeman effect, the following parameters were selected (the first and last coefficients ξ_1 and ξ_n in a series) of the basis set: $\xi_1 = (Z\alpha)^2 \cdot 10^{-7}$, $\xi_n = (Z\alpha)^2 \cdot 10^6$, for calculation of hyperfine splitting and nucleus magnetic shielding — $\xi_1 = (Z\alpha)^2 \cdot 10^{-4}$, $\xi_n = (Z\alpha)^2 \cdot 10^{11}$. As the nucleus potential models $V(r)$ the point nucleus, shell nucleus and uniformly charged sphere was defined. The fine structure constant was determined to be $\alpha = 1/137.035 999 177$.

Table 1 shows the energy levels of an electron in a hydrogen-like ion. For a point nucleus, the total energy value is given, while for the finite models, a correction to the energy due to the finite size of the nucleus is given. Tables 2 and 3 show the results of calculating the g factor $g^{(1)}$, formula (6), and the quadratic Zeeman effect expressed in terms of $g^{(2)}$, formula (7), for the electron ground state $1s_{1/2}$ ($\kappa = -1$, $n = 1$, $m_J = 1/2$). Table 2 shows the root-mean-square values of the radius r_n for the nuclear charge density distribution. The following tables 2–5 use the same values r_n for the corresponding ions. For all ions and nucleus models, there is a full consistency between calculations using a finite basic set of Gaussians and B-splines or formula (6).

Table 4 provides the values of relativistic factor $A(Z\alpha)$ for the correction of the hyperfine splitting for the electron ground state, (8). Similar to the g -factor, the presented values show a good agreement between the results of calculations with Gaussians and calculations with B-splines and the formula (9). The calculated nuclear magnetic

Table 4. The relativistic factor A for hyperfine splitting, calculated for $1s_{1/2}$ electron state for various hydrogen-like ions

Z	Shell nucleus		Sphere nucleus		Point nucleus	
	DKB BS	Gaussian	DKB BS	Gaussian	Eq. (9)	Gaussian
1	1.000 047	1.000 047	1.000 048	1.000 048	1.000 080	1.000 080
6	1.002 312	1.002 312	1.002 330	1.002 330	1.002 883	1.002 883
14	1.014 076	1.014 076	1.014 132	1.014 132	1.015 891	1.015 891
20	1.029 796	1.029 796	1.029 892	1.029 892	1.032 944	1.032 944
32	1.081 077	1.081 077	1.081 299	1.081 299	1.088 627	1.088 627
50	1.222 451	1.222 452	1.223 062	1.223 062	1.245 821	1.245 821
54	1.267 875	1.267 876	1.268 639	1.268 639	1.298 108	1.298 108
82	1.849 871	1.849 873	1.853 661	1.853 661	2.071 828	2.071 828
92	2.256 284	2.256 283	2.263 448	2.263 448	2.797 778	2.797 778

Table 5. The nuclear magnetic shielding constant expressed in terms of S and calculated for $1s_{1/2}$ electrons for various hydrogen-like ions

Z	Shell nucleus		Sphere nucleus		Point nucleus	
	DKB BS	Gaussian	DKB BS	Gaussian	Eq. (9)	Gaussian
1	1.000 143	1.000 143	1.000 143	1.000 143	1.000 143	1.000 143
6	1.005 176	1.005 176	1.005 176	1.005 176	1.005 180	1.005 180
14	1.028 489	1.028 489	1.028 492	1.028 492	1.028 566	1.028 566
20	1.059 000	1.059 000	1.059 008	1.059 008	1.059 271	1.059 271
32	1.158 220	1.158 220	1.158 267	1.158 267	1.159 857	1.159 857
50	1.434 254	1.434 255	1.434 564	1.434 564	1.446 244	1.446 244
54	1.524 274	1.524 274	1.524 722	1.524 722	1.542 208	1.542 208
82	2.712 993	2.712 996	2.717 672	2.717 672	2.990 511	2.990 511
92	3.567 861	3.567 859	3.578 440	3.578 440	4.379 221	4.379 221

shielding constant, formula (10), in terms of $S(Z\alpha)$, is presented in Table 5.

Conclusion

We considered the use of a finite Gaussian basis set to calculate corrections to the spectrum of hydrogen-like ions from Zeeman and hyperfine splitting. The results were obtained up to the second order in magnetic interaction. Calculations of the g -factor, the quadratic Zeeman effect, the relativistic factor for hyperfine splitting, and the magnitude of nuclear magnetic shielding were carried out. The energy spectrum of an electron in a hydrogen-like ion was also calculated. Calculations were made for a point nucleus and for two finite-size nucleus models. The tables in this study demonstrate an excellent agreement between the results obtained using Gaussian basis and the results obtained using B-splines or corresponding analytical formulas. In particular, the given accuracy allows us to see the degree of sensitivity of the considered effects to the choice of the nucleus model, especially for heavy ions. Thus, it was shown that the Gaussian basis set can be successfully used to calculate corrections from the magnetic interaction. This allows, in

particular, to apply this basis to verify the results obtained using B-splines.

We considered both first-order magnetic interaction matrix elements, $g^{(1)}$ and A , and second-order ones, $g^{(2)}$ and S . In the latter, the finite basis set is used to calculate intermediate states. Since the results obtained show excellent agreement with the finite basis method of B-splines, the applicability of the Gaussian basis for calculating intermediate states has been demonstrated.

For the finite Gaussian basis set, it was found that the results depend little on the choice of the basis parameters. This allows the considered corrections to be embedded in more sophisticated diagrams, which in turn may be sensitive to these parameters.

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Conflict of interest

The authors declare no conflict of interest.

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