Perturbation of Bound States of a Dirac Equation for an Electron in a Central-Symmetry Field

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The correction to the wave function in the problem of perturbation of bound states of a Dirac electron in a Coulomb field by an arbitrary central-symmetry potential is represented as an expansion in the complete set of eigenfunctions of a Sturm-Liouville operator which possesses only a discrete spectrum. This approach circumvents summation over continuous energy states with both negative or positive energies. Hence in a number of cases infinite sums of perturbation theory can be represented in a closed form. Finite expressions for first-order corrections to the electron Dirac wave function in the field of a screened Coulomb potential are obtained explicitly. The second and third order energies are expressed in terms of one of the components of the first order wave function.

1. Perturbation theory in the Rayleigh-Schrödinger formulation is finding ever increasing use in the calculation of atomic structures, since it makes it possible in principle to go outside the framework of the single-electron approximation[1]. Inasmuch as the wave equation can be solved exactly in the case of a Coulomb field, hydrogen-like functions are used most frequently as the single-electron basis functions for the zeroth approximation in such calculations. In the nonrelativistic theory, corrections of any order to the wave functions and energies of the states of the discrete spectrum can be determined on this basis in final form with the aid of a closed expression for the generalized Coulomb Green's function[2]. With increasing nuclear charge, allowance for the relativistic effects become essential, but in view of the difficulty of the problem a sufficiently complete relativistic calculation can be carried through to conclusion only in the simplest cases[3]. For systems with many electrons, even the nonrelativistic calculation entails considerable difficulties, pointing to the need for developing approximate methods.

Let us consider the motion of a Dirac particle in a centrally-symmetrical field of the atomic remainder. By separating in suitable fashion the Coulomb part of the effective potential, we regard the remaining part as a perturbation. Although the exact solution of the Dirac equation for the Coulomb field is well known[4], no closed expression in general form has been found as yet for the relativistic Coulomb Green's function; it is therefore customary to represent these functions by various infinite expansions[5]. We show in the present paper that in the relativistic theory the sums over the intermediate states, can be reduced in the case of a Coulomb field to final expressions without using the Green's function formalism, by reducing the problem to the equivalent problem of the perturbation of a Sturm-Liouville type of operator having only a discrete spectrum of eigenvalues. Such an approach avoids summation over continuous-spectrum states with both positive and negative energy. A concrete analysis is carried out for the class of analytic potentials that are most frequently encountered in atomic theory.

2. We seek the wave function (in the standard representation) in the form

$$\psi = \frac{1}{r}\begin{pmatrix} f_1(r)\,\Omega_{jlm} \\ i^{l-l'-1} f_2(r)\,\Omega_{jl'm} \end{pmatrix}, \tag{1}$$

where l and j are the values of the orbital and total angular momenta, m is the projection of the total angular momentum, $l' = 2j - l$, Ω_{jlm} is a spherical spinor[4], $f_1(r) = rf(r)$, $f_2(r) = -rg(r)$ are radial functions multiplied by r and defined by the equations

$$\begin{aligned} \frac{df_1}{dr} + \frac{\varkappa}{r} f_1 &= \frac{1}{\hbar c}[-mc^2 - E + U(r)]f_2, \\ \frac{df_2}{dr} - \frac{\varkappa}{r} f_2 &= \frac{1}{\hbar c}[-mc^2 + E - U(r)]f_1, \end{aligned} \tag{2}$$

where E is the total energy of the electron, U(r) is the potential-energy operator, and $\kappa = (l - j)(4j - 2l + 1) + \frac{1}{2}$.

Let

$$U(r) = -Ze^2/r + V(r), \qquad E = E_0 + E_1 + E_2 + \ldots, \tag{3}$$

where V(r) is a perturbation, E_0 is the energy of the electron in the Coulomb field, and $E_1, E_2, \ldots$, are the corrections to the energy. We assume further, following Fock[6], $E_0 = mc^2 \cos\epsilon$ and introduce as a new independent variable the quantity $x = 2\gamma r$, where $\gamma = mc \sin\epsilon/\hbar$. We seek the functions f_1 and f_2 in the form

$$f_1(x) = \frac{F(x) - G(x)}{2\sin(\varepsilon/2)}, \qquad f_2(x) = \frac{F(x) + G(x)}{2\cos(\varepsilon/2)}. \tag{4}$$

After simple transformations we obtain

$$\frac{dF}{dx} - \frac{\varkappa}{x} G = \left(-\frac{1}{2} + \frac{\alpha Z}{x}\operatorname{ctg}\varepsilon + w\operatorname{ctg}\varepsilon\right)F - \frac{1}{\sin\varepsilon}\left(\frac{\alpha Z}{x} + w\right)G, \tag{5a}$$

$$\frac{dG}{dx} - \frac{\varkappa}{x} F = \left(\frac{1}{2} - \frac{\alpha Z}{x}\operatorname{ctg}\varepsilon - w\operatorname{ctg}\varepsilon\right)G + \frac{1}{\sin\varepsilon}\left(\frac{\alpha Z}{x} + w\right)F, \tag{5b}$$

where α is the fine-structure constant and

$$w(x) = \frac{E - E_0 - V(x)}{2mc^2 \sin\varepsilon} \tag{6}$$

is a term connected with the presence of the perturbation. Eliminating from (5) one of the functions, F or G, we arrive at second-order equations. Thus, for the function F we obtain

$$\begin{aligned} &\frac{d^2F}{dx^2} + \frac{1}{x}\frac{\mu - x^2w'}{\mu + xw}\frac{dF}{dx} \\ &= \frac{1}{x}\left(\frac{\alpha Z}{x}\operatorname{ctg}\varepsilon - \frac{1}{2} + w\operatorname{ctg}\varepsilon\right)\frac{\mu - x^2w'}{\mu + xw}F \end{aligned} \tag{7}$$

$$+\left[\frac{k^2}{x^2}-\frac{\alpha Z}{x^2}(x+1)\operatorname{ctg}\varepsilon+\frac{1}{4}+(w'-w)\operatorname{ctg}\varepsilon-\left(\frac{\alpha Z}{x}+w\right)^2\right]F;$$

$$w'=dw/dx,\quad \mu=\alpha Z-\varkappa\sin\varepsilon,\quad k=|\varkappa|.$$

A similar equation can be obtained for the function G. Equation (7) will henceforth be regarded as the starting point for the subsequent calculation by perturbation theory, and the terms containing the function w(x) will be regarded as small. The relativistic effects are nowhere regarded as small.

Expanding the denominators in (7) in powers of the correction term w up to the third term inclusive and grouping terms of like order, we arrive at the equation

$$\begin{aligned}
&-\frac{d}{dx}\left(x\frac{dF}{dx}\right)+\left(\frac{x}{4}+\frac{k^2-\alpha^2Z^2}{x}-N\right)F\\
&=-\frac{x}{\mu}\frac{d}{dx}\left[xw-\frac{1}{2\mu}(xw)^2+\frac{1}{3\mu^2}(xw)^3\right]\frac{dF}{dx}\\
&+\left[2\alpha Zw+xw\operatorname{ctg}\varepsilon+\frac{1}{\mu}(xw)'\left(\varkappa\cos\varepsilon-\frac{x}{2}\right)\right]F\\
&+\left[xw^2-\frac{1}{2\mu^2}\left(\varkappa\cos\varepsilon-\frac{x}{2}\right)\frac{d}{dx}(xw)^2\right]F\\
&+\frac{1}{3\mu^2}\left(\varkappa\cos\varepsilon-\frac{x}{2}\right)\frac{d(xw)^3}{dx}F,
\end{aligned}\tag{8}$$

where $N=\alpha Z\cot\epsilon+\frac{1}{2}$. The operator in the left-hand side of (8)

$$L=-\frac{d}{dx}x\frac{d}{dx}+\frac{s^2}{4x}+\frac{x}{4},\qquad s=2[k^2-(\alpha Z)^2]^{1/2}$$

corresponds to the case of a pure Coulomb field with the charge of the nucleus Z. The system of eigenfunctions of such an operator is well known[6]. It has only a discrete spectrum of non-negative and equidistant eigenvalues

$$N=p+s/2+{}^1/_2,\tag{9}$$

where p = 0, 1, 2, ..., or, in accordance with the definition of N

$$\alpha Z\operatorname{ctg}\varepsilon=p+[k^2-(\alpha Z)^2]^{1/2}.\tag{10}$$

The use of the operator L as the unperturbed operator makes it possible to avoid summation over the intermediate states of the continuous spectrum and over the states with negative energy, for at $Z<137$ there are no negative energy levels belonging to the discrete spectrum in the case of attraction. We thus arrive at a convenient formulation of our problem in the form of the problem of the perturbation of a Sturm-Liouville operator having only a discrete spectrum. A list of several pertinent perturbation-theory formulas is given in[7], where the similarity with the problem of perturbation of the spectrum of a one-dimensional harmonic oscillator is noted.

Starting from (8), we can determine the perturbation-theory corrections up to third order inclusive. The direct use of this equation is, however, difficult because the operator in the right-hand side, which contains the derivative of the sought function, is not Hermitian. We transform the sought function in such a way that the operator acting on it contains only Hermitian terms. To this end, we put

$$F(x)=Z(x)y(x),$$

$$Z(x)=C\exp\left\{\frac{1}{2\mu}\left[xw-\frac{1}{2\mu}(xw)^2+\frac{1}{3\mu^2}(xw)^3\right]\right\}.\tag{11}$$

Substituting (11) in (8) we obtain the equation

$$\begin{aligned}
(L-N)y=&\left[2\alpha Zw+xw\operatorname{ctg}\varepsilon+\frac{x}{2\mu}(xw)''\right.\\
&\left.+\frac{(xw)'}{\mu}\left(\varkappa\cos\varepsilon+\frac{1}{2}-\frac{x}{2}\right)\right]y+\left\{xw^2-\frac{3x}{4\mu^2}[(xw)']^2\right.\\
&\left.+\frac{[(xw)^2]'}{2\mu^2}\left(\frac{x}{2}-\varkappa\cos\varepsilon-\frac{1}{2}\right)-\frac{x}{2\mu^2}(xw)(xw)''\right\}y\\
&+\frac{1}{\mu^3}\left\{\frac{1}{3}\left(\varkappa\cos\varepsilon+\frac{1}{2}-\frac{x}{2}\right)[(xw)^3]'\right.\\
&\left.+\frac{3}{2}x(xw)[(xw)']^2+\frac{x}{2}(xw)^2(xw)''\right\}y,
\end{aligned}\tag{12}$$

which does not include non-Hermitian operators.

We seek the eigenfunction of (12) in the form

$$y(x)=y^{(0)}(x)+y^{(1)}(x)+\ldots\tag{13}$$

where $y^{(0)}(x)$ is the eigenfunction of the operator L. At a fixed s, the total orthonormal system of functions of this operator takes the form[6]

$$y_p(x)=\left[\frac{p!}{\Gamma(s+p+1)}\right]^{1/2}x^{s/2}e^{-x/2}L_p^s(x),\tag{14}$$

where $p=0,1,2,\ldots$, $L_p^s(x)$ are Laguerre polynomials. We have used here the definition customarily used in the mathematical literature for these polynomials[6]. Confining ourselves to first-order terms in (12) and taking (6) into account, we obtain after multiplying by $y^{(0)}$ and integrating with respect to x

$$\begin{aligned}
E_1=&\frac{\alpha Z}{2\mu(p^2+k^2+ps)}\left\{2\alpha Z\mu V_{pp}+\mu\operatorname{ctg}\varepsilon(xV)_{pp}\right.\\
&\left.+\left(\varkappa\cos\varepsilon+\frac{1}{2}\right)(xV)_{pp}'-\frac{1}{2}[x(xV)']_{pp}+\frac{1}{2}[x(xV)'']_{pp}\right\},
\end{aligned}\tag{15}$$

where

$$W_{pq}=\int_0^\infty y_p(x)W(x)y_q(x)\,dx.$$

The exact expressions for the second- and third-order corrections to the energy are given in the appendix. To find them it is necessary to determine the first-order wave function. Putting

$$y_p^{(1)}(x)=\sum_{q\neq p}C_qy_q(x)\tag{16}$$

and determining from (16) the explicit form of the coefficients C_q, we obtain

$$\begin{aligned}
y_p^{(1)}(x)=&\frac{E_1}{\lambda\mu}\left(\mu\operatorname{ctg}\varepsilon-\frac{1}{2}\right)\{[p(p+s)]^{1/2}y_{p-1}(x)\\
&-[(p+1)(p+s+1)]^{1/2}y_{p+1}(x)\}-\frac{1}{\lambda\mu}\sum_{q\neq p}\frac{y_q(x)}{q-p}\cdot\\
&\times\{2\alpha Z\mu V_{qp}+\mu\operatorname{ctg}\varepsilon(xV)_{qp}+({}^1/_2+\varkappa\cos\varepsilon)\cdot\\
&\times[(xV)']_{qp}-{}^1/_2[x(xV)']_{qp}+{}^1/_2[x(xV)'']_{qp}\}.
\end{aligned}\tag{17}$$

where $\lambda=2mc^2\sin\epsilon$. Taking (11) into account, we obtain directly

$$\begin{aligned}
F_0(x)&=Cy^{(0)}(x),\\
F_1(x)&=Cx(E_1-V)y^{(0)}(x)/2\lambda\mu+Cy^{(1)}(x).
\end{aligned}\tag{18}$$

Further, knowing the function F, we can determine G with the aid of (5a). With first-order accuracy we have

$$G_0(x)=C(\delta+\kappa)y_{p-1}(x),\tag{19}$$

$$G_1(x)=x\frac{E_1-V}{\lambda\mu}(F_0\cos\varepsilon-G_0)+\frac{1}{\delta-\varkappa}\left[\left(p+\frac{s}{2}-\frac{x}{2}\right)F_1-x\frac{dF_1}{dx}\right]$$

where $\delta = [p(p+s)+\kappa^2]^{1/2}$.

The same results are obtained by starting from the equation for the function G. We note, however, that in the practical calculations, in the case when $\kappa < 0$ ($\kappa = -l-1$), it is more convenient to start from Eq. (7), as was done above. If $\kappa > 0$ ($\kappa = l$), it is more convenient to use the equation for G. In this case $p = n_r + 1$ ($p = 1, 2, \ldots$), where n_r is the radial quantum number.

We determine the constant C from the normalization condition

$$\int_0^\infty (f_1^2 + f_2^2)\,dr = 1. \tag{20}$$

3. We shall show that the expansion (16) makes it possible to obtain finite expressions for the first-order wave function, and consequently, in accordance with (A.1) and (A.3), also for the second- and third-order energies. We consider the class of analytically specified potentials in the form

$$V(x) = Ax^{m-1}e^{-\beta x} \quad (m = 0, 1, 2, \ldots). \tag{21}$$

The non-Coulomb part of the effective potential of the closed electron shells, described by the screened hydrogen-like functions, is a linear combination of expressions of the type (21)[7]. In order not to clutter up the calculation with technical details, let us consider an unperturbed state with radial quantum number $n_r = 0$. There are two possibilities, $\kappa < 0$, $p = 0$ ($j = l + 1/2$) and $\kappa > 0$, $p = 1$ ($j = l - 1/2$). For the first-order energy we have: at $j = l + 1/2$

$$E_1 = A\frac{\Gamma(s+m)}{\Gamma(s+1)}\frac{1}{(1+\beta)^{s+m}}, \tag{22}$$

at $j = l - 1/2$

$$E_1 = A\frac{\Gamma(s+m)(a_0\beta^2 + a_1\beta + a_2)}{\Gamma(s+1)(s+k^2+1)(1+\beta)^{s+m+2}} \tag{23}$$

$$a_0 = (s+1)[\varkappa^2 - \varkappa/2(\delta-\varkappa)],$$

$$a_1 = m\left(1+\frac{1}{s}\right)\left(2\varkappa^2 - \frac{\varkappa}{\delta-\varkappa}\right) - \frac{2}{s}(s+m)(\alpha Z)^2,$$

$$a_2 = (s+m)(s+m+1)\left(\frac{\varkappa^2}{s} - \frac{1}{2}\right) - \frac{2(\alpha Z)^2}{s}m(s+m) \tag{24}$$

$$+ m(m-1)(s+1)\left[\frac{\varkappa^2}{s} - \frac{\varkappa}{2(\delta-\varkappa)}\right],$$

where $\delta = (s + k^2 + 1)^{1/2}$.

Formulas (22) and (23) admit of an analytic continuation to the case of arbitrary $\mathrm{Re}\, m > -1$. In the derivation of these formulas we took relation (10) into account. From now on we use atomic units.

Let us determine the corrections to the wave functions for the case of a perturbed potential of the Yukawa type ($m = 0$). The generalization to the case of arbitrary positive m is effected by m-fold differentiation of the obtained expressions with respect to the parameter β. At $j = l + 2$, we determine the wave function by putting $p = 0$ in (17) and using formula (14) for the function $y_q(x)$. The infinite sums over the intermediate states, which enter in (17), can be represented in this case in close form with the aid of the generating function for Laguerre polymials[8]. In accordance with (18), we obtain ultimately

$$F_1(x) = \frac{A\varkappa}{4Z^2}\frac{F_0(x)}{(1+\beta)^s}\left\{s+1-x+\frac{\beta}{2(1+\beta)}\right.$$

$$-\frac{4k^2}{s}\int_0^\beta [1-(1+t)^s e^{-tx}]\frac{dt}{t} - \frac{4(\alpha Z)^2}{s}$$

$$\left.\times(1+\beta)^s\left[\int_\beta^\infty \frac{dt}{t(1+t)^s} + \mathrm{Ei}(-\beta x)\right]\right\}, \tag{25}$$

where $\mathrm{Ei}(-\beta x)$ is the integral exponential function and

$$F_0(x) = [\Gamma(s+1)]^{-1/2}x^{s/2}e^{-x/2}.$$

The integral in the last term of (25) can be expressed in terms of the incomplete B function

$$\int_\beta^\infty \frac{dt}{t(1+t)^s} = (-1)^s B_{-1/\beta}(s, 1-s).$$

The terms independent of x in the curly brackets of the right-hand side of (25) are chosen on the basis of the orthogonality conditions of the functions $F_0(x)$ and $F_1(x)$.

Knowing the function $F_1(x)$, we determine $J_1(x)$ from formula (19)

$$G_1(x) = -F_0(x)\frac{Ak^2}{2sZ^2}\left\{e^{-\beta x} + \frac{e^x}{x^s(1+\beta)^s}\right.$$

$$\left.\times[\Gamma(s+1,x) - \Gamma(s+1,(1+\beta)x)]\right\}, \tag{26}$$

where $\Gamma(s+1, x)$ is the incomplete Gamma function[8]. At $p = 0$ we have $\kappa = -\delta$ and, in accordance with (19), $G_0(x) \equiv 0$. Determining the normalization constant from the condition (20) with allowance for the relation (4), we obtain, accurate to first order in A

$$f_1^{(1)}(x) = \frac{\alpha Z}{k}\left[\frac{Z}{k-s/2}\right]^{1/2}\left\{F_1(x) - G_1(x)\right.$$

$$\left.-\frac{AkF_0(x)}{4Z^2(1+\beta)^{s+1}}[1+(s+1)\beta]\right\}$$

$$f_2^{(1)}(x) = \frac{\alpha Z}{k}\left[\frac{Z}{k+s/2}\right]^{1/2}\left\{F_1(x) + G_1(x)\right.$$

$$\left.-\frac{AkF_0(x)}{4Z^2(1+\beta)^{s+1}}[1+(s+1)\beta]\right\}. \tag{27}$$

Formulas (27) give both components of the radial wave function for the states $1s_{1/2}$, $2p_{3/2}$, $3d_{5/2}$, $4f_{7/2}$, etc.

At $\kappa > 0$ ($j = l - 1/2$) it is more convenient to start from the equation for the function G. Going over, in analogy with formula (11), to the function y(x), we have

$$\tilde{G}_0(x) = (\delta+\varkappa)\tilde{y}^{(0)}(x),$$

$$\tilde{G}_1(x) = x(E_1 - V)\tilde{G}_0(x)/2\lambda\mu' + (\delta+\varkappa)\tilde{y}^{(1)}(x);$$

$$\mu' = \alpha Z(1+\varkappa/\delta), \quad \tilde{y}^{(0)}(x) = y_{p-1}(x). \tag{28}$$

A formula analogous to (17) holds for the function $\tilde{y}^{(1)}(x)$. Further, assuming $p = 1$, we obtain in this case, too, a finite expression for the function $\tilde{G}_1(x)$ which is orthogonal to the function $g_0(x)$

$$\tilde{G}_1(x) = \tilde{y}^{(0)}(x)\frac{A\delta}{4Z^2}\left\{E_1(s+2)(\delta+\varkappa)(x-s-1)\right.$$

$$+E_1(2x-s-1)\delta + \delta\frac{1-\beta}{(1+\beta)^{s+1}} - \frac{2\delta}{1+\beta}e^{-\beta x}$$

$$+\frac{4(\alpha Z)^2}{s}(\delta+\varkappa)\left[\int_\beta^\infty \frac{dt}{t(1+t)^s} + \mathrm{Ei}(-\beta x)\right]$$

$$+\frac{2}{(1+\beta)^s}\left[(\delta+\varkappa)\left(1+\frac{2\varkappa^2}{s}\right) - \frac{\beta(\beta+s+2)}{(1+\beta)^2}\delta\right]$$

$$\left.\times\int_0^\beta [1-(1+t)^s e^{-tx}]\frac{dt}{t}\right\}, \tag{29}$$

where E_1 is determined by formula (23) at $m = 0$. From the well known function $\tilde{G}(x)$ we determine the function $\tilde{F}(x)$ with the aid of (5b):

$$\bar{F}_1(x)=\tilde{y}^{(0)}(x)\frac{A\delta}{4Z^2}\Big\{-E_1(s+2)[x^2-2x(s+2)+(s+1)^2]+E_1\omega[(s+1)^2-(s+3)x]+e^{-\beta x}\times\Big[\frac{4(\alpha Z)^2}{s}+\frac{2\beta}{1+\beta}(s+1)\omega-(s+2)\Big]+\omega\frac{1-\beta}{(1+\beta)^{s+1}}(s+1-x)+\frac{4(\alpha Z)^2}{s}(s+1-x)\cdot\times\Big[\int_\beta^\infty\frac{dt}{t(1+t)^s}+\mathrm{Ei}(-\beta x)\Big]+\frac{2}{(1+\beta)^s}\Big[\Big(1+\frac{2k^2}{s}\Big)-\omega\frac{\beta(\beta+s+2)}{(1+\beta)^2}\Big]\Big[\frac{e^x}{x^s}\Gamma(s+1,x)-\frac{e^x}{x^s}\Gamma(s+1,(1+\beta)x)+(s+1-x)\int_0^\beta[1-(1+t)^s e^{-tx}]\frac{dt}{t}\Big]\Big\},\quad(30)$$

where $\omega=\delta/(\delta+\kappa)$.

The functions $\tilde{G}$ and $\tilde{F}$ must be multiplied by a constant D chosen to satisfy the normalization condition. Accurate to first order, we have $D=D_0+AD_1$. In accord with formula (4)

$$f_1^{(1)}(x)=\Big[\frac{2}{\delta}\Big(\delta-\frac{s}{2}-1\Big)\Big]^{-1/2}[D_0(\bar{F}_1-\bar{G}_1)+AD_1(\tilde{F}_0-\tilde{G}_0)],$$

$$f_2^{(1)}(x)=\Big[\frac{2}{\delta}\Big(\delta+\frac{s}{2}+1\Big)\Big]^{-1/2}[D_0(\bar{F}_1+\bar{G}_1)+AD_1(\tilde{F}_0+\tilde{G}_0)].\quad(31)$$

Formulas (31) determine the correction to the wave function of the states $2p_{1/2}$, $3d_{3/2}$, $4f_{5/2}$, etc. Applying the operator $(-\partial/\partial\beta)^m$ to the functions $f_i^{(1)}$, we obtain the corresponding functions for the potentials of type (21) at $m>0$. There are grounds for assuming that the proposed method is effective also for a larger class of perturbing operators. Thus, the second-order correction to the energy of the exchange interaction can also be represented in closed form[9].

In the nonrelativistic limit ($\alpha Z\to 0$), the function $f_2(x)\to 0$, and the functions $f_1^{(1)}(x)$, given by formulas (27) and (31) go over into the corresponding nonrelativistic functions obtained by Pavinskiĭ and the author[9].

In conclusion, the author is deeply grateful to P. P. Pavinskiĭ for support and interest in the work.

APPENDIX

Substituting in (12) the expression (6) for w and separating the terms of second and third order with respect to the perturbation V, we obtain after integration the following expressions for the energies E_2 and E_3:

$$E_2=\frac{1}{2\delta(\delta-\kappa)}\Big\{E_1\Big(\mu\,\mathrm{ctg}\,\varepsilon-\frac{1}{2}\Big)([(p+1)(s+p+1)]^{1/2}C_{p+1}+[p(s+p)]^{1/2}C_{p-1})-\frac{E_1^2}{\lambda\mu}\Big[3p^2+3p(s+1)+\frac{1}{2}(s+1)(s+2)+(2p+s+1)\Big(\mu^2-\kappa\cos\varepsilon-\frac{5}{4}\Big)\Big]+\frac{E_1}{\lambda\mu}\Big\langle 2\mu^2xV-\Big(\kappa\cos\varepsilon+\frac{1}{2}-\frac{x}{2}\Big)(x^2V)'-\frac{3}{2}x(xV)'-\frac{x^2}{2}(xV)''\Big\rangle_{00}+\frac{1}{\lambda\mu}\Big\langle\frac{1}{2}(\kappa\cos\varepsilon+\frac{1}{2}-\frac{x}{2})[(xV)^2]'+\frac{3}{4}[(xV)']^2-x\mu^2V^2+\frac{x^2}{2}V(xV)''\Big\rangle_{00}+\Big\langle 2\alpha Z\mu V+\mu\,\mathrm{ctg}\,\varepsilon xV+\Big(\kappa\cos\varepsilon+\frac{1}{2}-\frac{x}{2}\Big)(xV)'+\frac{x}{2}(xV)''\Big\rangle_{01}\Big\}.\quad(A.1)$$

We have introduced here the notation (i, j = 0, 1):

$$\langle f(x)\rangle_{ij}=\int_0^\infty y^{(i)}(x)f(x)y^{(j)}(x)\,dx,\quad(A.2)$$

C_q are the expansion coefficients.

Knowing the first-order wave function we can, as is well known, obtain also the third-order correction to the energy. In our case we have

$$E_3=\frac{1}{2\delta(\delta-\kappa)}\Big\{\frac{E_1E_2}{\lambda\mu}\Big[\Big(p+\frac{s+1}{2}\Big)(5+4\kappa\cos\varepsilon-4\mu^2)-6p^2-6p(s+1)-(s+1)(s+2)\Big]+\frac{E_2}{\lambda\mu}\Big\langle 2\mu^2xV-\Big(\kappa\cos\varepsilon+\frac{1}{2}-\frac{x}{2}\Big)(x^2V)'-\frac{3}{2}x(xV)'-\frac{x^2}{2}(xV)''\Big\rangle_{00}+\frac{1}{2\lambda^2\mu^2}\times\Big\langle x^2(E_1-V)^2\Big[(x-2\kappa\cos\varepsilon-1)(E_1-(xV)')-\frac{3(E_1-(xV)')^2}{E_1-V}+x(xV)''\Big]\Big\rangle_{00}+\frac{1}{\lambda\mu}\Big\langle x(E_1-V)\Big[-2\mu^2(E_1-V)+(2\kappa\cos\varepsilon+1-x)\times(E_1-(xV)')+\frac{3}{2}\frac{(E_1-(xV)')^2}{E_1-V}-x(xV)''\Big]\Big\rangle_{01}-E_1\Big(\mu\,\mathrm{ctg}\,\varepsilon-\frac{1}{2}\Big)\langle x\rangle_{11}-E_1\Big(2\alpha Z\mu+\kappa\cos\varepsilon+\frac{1}{2}\Big)\langle 1\rangle_{11}+\Big\langle 2\alpha Z\mu V+\mu\,\mathrm{ctg}\,\varepsilon xV+\Big(\kappa\cos\varepsilon+\frac{1}{2}-\frac{x}{2}\Big)(xV)'-\frac{x}{2}(xV)''\Big\rangle_{11}\Big\}\quad(A.3)$$

As seen from (A.1) and (A.3), to calculate the corrections to the energy it suffices to know one of the components of the radial wave function. Substituting here relations (25) or (29) for $y^{(1)}(x)$ we obtain for E_2 and E_3 finite expressions containing only elementary functions[9].

Using (15) and (A.1) we have calculated the corrections E_1 and E_2 to the energies of the $3d_{3/2}$ and $3d_{5/2}$ states of the valence electron of the iso-electronic series of sodium-like ions. The calculation of the third-order correction is justified only when the exchange interaction is taken into account in second order. When Z is varied from 23 to 95, the relative correction E_1 changes from 1.88 to 0.76% of the unperturbed energy. The correction E_2 decreases from 0.31 to 0.12%. The relative values of the corrections to the doublet splitting decrease from 35 and 4.2% at Z = 23 to 14 and 1.5% at Z = 95 in the first and second orders, respectively.

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