

Anapole moments and magnetic fields in alkali-metal atoms from Stark mixing

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Toroidal dipole (anapole) moments and magnetic fields due to inversion symmetry breaking by an external electric field are studied for the alkali-metal atoms from Li to Rb. It is demonstrated that a hydrogenic atomic model is inadequate for this purpose, while a nonhydrogenic model based on the quantum-defect method yields numbers for the anapole moments in excellent agreement with those predicted by a semiempirical product rule.

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Consideration of parity (P) and time-reversal (T) invariance restricts the multipole moments of nondegenerate quantum-mechanical systems. For example, if P and T are both conserved an atom can have charge, magnetic dipole, electric quadrupole, etc. Contrarily, there occur electric dipole, magnetic quadrupole, etc., if both P and T are violated. The most general expansion of the static magnetic field due to a localized current distribution consists of two terms that have opposite parity for the same multipole order l [1]. One of the terms, say T_1 , is the source of conventional multipole expansion of the field outside the source region (charge and current) and satisfies P and T invariance for odd l , but requires both P and T violation for even l . It is important to note that in T_1 we do not have any multipole moment that violates P but not T invariance. On the other hand, the expansion in the second term T_2 , having opposite P properties as compared to T_1 , is restricted to the source volume and for odd l it requires P but not T violation and for even l , T but not P violation. The odd l terms are called the toroidal magnetic multipole moments because in classical electrodynamics this third family of moments could arise from the expansion of vector potential associated with poloidal current distribution of toroidal magnets. Historically, it was Zeldovich [2] who discovered this type of multipole moment and coined the term ‘‘anapole’’ to denote the toroidal dipole moment (TDM). Obviously, the anapole is a wrong-parity magnetic dipole moment. The TDM occurs together with the magnetic quadrupole moment having the same dimensions and identical signature under space inversion [3].

The anapole moment is defined as either a second moment of the poloidal current density \vec{j} or a first moment of the toroidal magnetic field \vec{B} of this current and we have [4]

$$\vec{t} = -\frac{\pi}{c} \int d^3r r^2 \vec{j} = \frac{1}{2} \int d^3r \vec{r} \times \vec{B}. \quad (1)$$

The TDM has been extensively studied in the context of P -violating charge- and neutral-current interactions. The nuclear anapoles have been found to be of particular interest [5] because via electromagnetic interaction with a penetrating atomic electron, these could produce nuclear-spin-dependent parity-nonconserving atomic interactions [6]. The analysis of anapole moments for both chiral and achiral molecules with an unpaired spin is also a subject of considerable

current interest [7,8]. In the recent past Lewis and Blinder [9] considered the breaking of inversion symmetry in atoms by an electric field and found that the Stark mixing of opposite parity states induces anapole fields in paramagnetic atoms. They presented a detailed calculation of the field and associated moment for the hydrogenic ground state and emphasized that it will require a major effort to carry out a similar analysis for the alkali-metal atoms. The present paper is an effort to substantiate the conjecture of Lewis and Blinder. In the following we briefly review their work and shed light upon additional considerations that will be needed for our study.

Classically, the toroidal magnetic field [10]

$$\vec{B} = \frac{4\pi}{c} f(r) \vec{r} \times \vec{m} \quad (2)$$

arises from poloidal current density given by

$$\vec{j} = \frac{1}{r} \frac{df}{dr} (\vec{r}(\vec{r} \cdot \vec{m}) - r^2 \vec{m}) - 2f\vec{m}, \quad (3)$$

where \vec{m} is a fixed vector giving the orientation of \vec{t} . The radial function $f(r)$ can be obtained by evaluating the radial component of \vec{j} such that

$$\hat{r} \cdot \vec{j} = -2f\vec{m} \cdot \hat{r}. \quad (4)$$

From Eqs. (1) and (2), we get \vec{t} as the fourth moment of $f(r)$ in the direction of \vec{m} and write

$$\vec{t} = -\frac{16\pi^2}{3c} \vec{m} \int_0^\infty dr r^4 f(r). \quad (5)$$

Conversion of the above classical relations to quantum theory is rather straightforward. For example, current density \vec{j} of the Schrödinger equation can be decomposed into orbital and spin parts as

$$\vec{j} = \vec{j}_L + \vec{j}_S. \quad (6)$$

For the unperturbed ground state

$$\phi_{1s} = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr} \chi \quad (7)$$

of a hydrogenic atom, the toroidal spin current density

$$\vec{j}_s = \frac{2Z^4}{\pi} \hat{r} \times \vec{S} e^{-2Zr} \quad (8)$$

with $\vec{S} = \langle \vec{\sigma} \rangle / 2$ generates the ordinary magnetic dipole field of the electron. Because of T invariance the orbital current in this state is zero. Here χ stands for the Pauli spin function, \vec{S} for the atomic spin in units of \hbar , and \hat{r} is a unit vector. When an electric field \vec{E} is applied the ground state is perturbed and the current density \vec{j}_s acquires an additional poloidal component \vec{j}'_s , which manifests itself in producing the toroidal field and anapole moment.

The first-order perturbation correction ϕ'_{1s} to ϕ_{1s} can in principle be obtained from the Rayleigh-Schrödinger perturbation theory [11]. But it is easier to work with a simple variant [12] of this traditional perturbation technique in which ϕ'_{1s} is calculated from the solution of an inhomogeneous differential equation

$$(H_{\text{Sch}} - \varepsilon_{1s}) \phi'_{1s} = -(\vec{E} \cdot \vec{r}) \phi_{1s}, \quad (9)$$

where H_{Sch} is the Schrödinger-Coulomb Hamiltonian and ε_{1s} is the ground-state energy. Equation (9) is analytically solvable and we have

$$\phi'_{1s} = -\frac{\vec{E} \cdot \vec{r}}{Z^2} \left(1 + \frac{Zr}{2} \right) \phi_{1s}. \quad (10)$$

The first-order wave function $\phi_{1s} + \phi'_{1s}$ can now be used to get the additional poloidal component in the form

$$\vec{j}'_s = \frac{2Z}{\pi} \left[\left(1 + \frac{Zr}{2} \right) \vec{E} \times \vec{S} - Z \left(\frac{3}{2} + Zr \right) (\vec{E} \cdot \vec{r}) \hat{r} \times \vec{S} \right] e^{-2Zr}. \quad (11)$$

From Eqs. (2), (4), and (11) we can write

$$f(r) = -\frac{Z}{\pi} \left(1 + \frac{Zr}{2} \right) e^{-2Zr} \quad (12)$$

and

$$\vec{B} = 4\alpha Z \left(1 + \frac{Zr}{2} \right) e^{-2Zr} [(\vec{E} \times \vec{S}) \times \vec{r}], \quad (13)$$

where \vec{m} has been identified with $\vec{E} \times \vec{S}$. In rational relativistic units the fine-structure constant $\alpha = 1/c$. The TDM can be computed by using Eq. (12) in Eq. (5).

The valence electron of an alkali-metal atom may be assumed to move in a potential due to the nucleus and to the core electrons and to spend much of its time in the outer region where the nucleus is screened by the core electrons and where the potential is of Coulomb form and some fraction of its time penetrating the region of the core. In this region there is a stronger attractive potential that causes the orbit to precess. To a first approximation the electron may be assumed to move in a pure Coulomb field with an effective

nuclear charge such that the orbit precession could be neglected. Then the alkali spectra are described by a hydrogenic model in which the energy levels of the valence electrons are degenerate.

To be more realistic the orbit precession arising due to interaction of the valence electron with the ionic core should be taken into account. In this case the l degeneracy is removed and the so-called quantum-defect method [13] can be used to provide an accurate description for the energy spectra. An interesting aspect of this method is that the value of the quantum defect (change in the principal quantum number) determines not only the energy of the state but also spatial character of the wave function. For example, the hydrogenic wave functions are expressed in terms of the confluent hypergeometric or regular Whittaker functions. As opposed to this the nonhydrogenic wave functions resulting from the removal of l degeneracy require the irregular Whittaker functions for their description.

In this work we shall use both hydrogenic and nonhydrogenic wave functions to study the Stark-induced anapole moment of alkali-metal atoms and examine their relative merits and demerits. We shall see that in the hydrogenic model it is possible to derive an analytical approach to the problem by a straightforward generalization of the work of Lewis and Blinder [9] and thereby derive an order-of-magnitude estimate for the anapole moment. The nonhydrogenic wave functions of the quantum-defect method being characterized by irregular Whittaker functions do not permit one to proceed analytically but can predict accurate numerical results.

A. Hydrogenic approach

In this approach the energy levels of the valence electrons are degenerate. In the presence of degeneracy the solutions of equations like Eq. (9) are obstructed by the solvability condition [14]. Thus the analysis of anapole fields and toroidal moments for alkali-metal atoms needs a separate consideration. Fortunately, an appropriate inhomogeneous equation satisfying the solvability condition can also be written to obtain the first-order correction to a wave function belonging to a degenerate energy level [15]. We shall take recourse to this equation for the present study. The appropriate general inhomogeneous equation is given by

$$\begin{aligned} & [\varepsilon_{nl} - H_{\text{Sch}}(\vec{r})] \phi'_{nlm}(\vec{r}) \\ &= (\vec{E} \cdot \vec{r}) \phi_{nlm}(\vec{r}) - \sum_{\gamma} \phi_{\gamma}(\vec{r}) \int \phi_{\gamma}(\vec{r}') \\ & \times (\vec{E} \cdot \vec{r}') \phi_{nlm}(\vec{r}') d^3r', \end{aligned} \quad (14)$$

where the γ sum extends over the whole degenerate subspace of $\phi_{nlm}(\vec{r})$. The unperturbed wave function $\phi_{nlm}(\vec{r})$ is given by

$$\phi_{nlm}(\vec{r}) = R_{nl}(\vec{r}) Y_l^m(\theta, \phi). \quad (15)$$

Here $Y_l^m(\theta, \phi)$ stands for the scalar spherical harmonic and $R_{nl}(r)$ for the bound state radial solution of the Coulomb problem given by

$$R_{nl}(r) = N_{nl} \rho^l e^{-\rho/2} L_{n-l-1}^{2l+1}(\rho) \quad (16)$$

with

$$N_{nl} = \left[\frac{4Z^3(n-l-1)!}{n^4(n+l)!} \right]^{1/2}. \quad (17)$$

In Eq. (16) $L_s^k(\cdot)$ denotes the associated Laguerre polynomial of order s and $\rho = 2Zr/n$. Since $H' = \vec{E} \cdot \vec{r}$ can connect only the states of opposite parity, the solution of Eq. (14) can be chosen in the form

$$\phi'_{nlm}(\vec{r}) = F_{n,l}(r) Y_{l-1}^m(\theta, \phi) + G_{n,l}(r) Y_{l+1}^m(\theta, \phi). \quad (18)$$

The valence electrons of alkali-metal atoms are s electrons ($l=0, m=0$). In this case the first term in Eq. (18) becomes irrelevant. Thus from Eqs. (14) and (18) we get,

$$\left[\rho \frac{d^2}{d\rho^2} + 2 \frac{d}{d\rho} - \frac{\rho}{4} + n - \frac{2}{\rho} \right] \times G_{n,0}(\rho) = \frac{En^2\rho}{2\sqrt{3}Z^2} \left[rR_{n,0} + \frac{3n\sqrt{n^2-1}}{2Z} R_{n,1} \right]. \quad (19)$$

We now change the dependent variable in Eq. (19) by substituting

$$G_{n,0}(\rho) = \rho e^{-\rho/2} Q(\rho), \quad (20)$$

where $Q(\rho)$ is a polynomial in ρ . For the sake of brevity we omit the subscript n and $l(=0)$ on the right-hand side of Eq. (20). From Eqs. (19) and (20) we get

$$\begin{aligned} \rho Q'' + (4-\rho)Q' + (n-2)Q \\ = E \left(\frac{n}{12Z^3} \right)^{1/2} \sum_{j=0}^{n-1} \left[(-1)^j \right. \\ \left. \times \left\{ 1 + \frac{3(n+1)(n-3)}{(j+2)(j+3)} \right\} \frac{n! \rho^{j+1}}{j!(n-1-j)!(j+1)!} \right]. \end{aligned} \quad (21)$$

Since the right-hand side of Eq. (21) involves a finite sum, the solution to it can be related to the solution of the nonhomogeneous confluent hypergeometric equation [16]

$$x \frac{d^2 y}{dx^2} + (c-x) \frac{dy}{dx} - ay = x^{\sigma-1}, \quad (22)$$

where σ is a constant. Thus the complete primitive of Eq. (21) can be written as

$$\begin{aligned} Q(\rho) = C_1 F_1(2-n, 4; \rho) + E \left(\frac{n}{12Z^3} \right)^{1/2} \sum_{j=0}^{n-1} (-1)^j \\ \times \left[1 + \frac{3(n+1)(n-1-j)}{(j+2)(j+3)} \right] \\ \times \frac{n!}{j!(n-1-j)!(j+1)!} \theta_{j+2}(2-n, 4; \rho). \end{aligned} \quad (23)$$

Equation (18) in conjunction with Eqs. (20) and (23) gives the first-order correction $\phi'_{n00}(\vec{r})$ of the valence electrons of alkali-metal atoms due to the applied electric field \vec{E} . The constant of integration C in Eq. (23) can be obtained by using the constraint [15,17]

$$\langle \phi | \phi' \rangle = 0. \quad (24)$$

The quantity $\theta_j(\cdot)$ is expressed in terms of a generalized hypergeometric function as

$$\theta_\sigma(a, c; x) = \frac{x^\sigma}{\sigma(\sigma+c-1)} {}_2F_2(1, \sigma+a; \sigma+1, \sigma+c; x). \quad (25)$$

The wave function as obtained above will give a general expression of the additional poloidal current \vec{j}'_s , which in turn will determine the corresponding results for $f(r)$, B ($=|\vec{B}|$), and t ($=|\vec{t}|$). For Li the expression for $f(r)$ and B are given by

$$f_{\text{Li}}(r) = \frac{Z}{32\pi} e^{-Zr} (2-Zr)(Z^2 r^2 - 30), \quad (26)$$

and

$$B_{\text{Li}} = \frac{1}{8} Zr e^{-Zr} (2-Zr)(Z^2 r^2 - 30). \quad (27)$$

Although somewhat lengthy, algebraic expressions similar to those in Eqs. (26) and (27) can also be constructed for Na, K, and Rb. Interestingly, we could find simple expressions (in units of a_0^4)

$$t_{\text{Li}} = \frac{2.752}{Z^4}, \quad t_{\text{Na}} = \frac{23.218}{Z^4}, \quad t_{\text{K}} = \frac{114.473}{Z^4}, \quad t_{\text{Rb}} = \frac{408.464}{Z^4} \quad (28)$$

for the magnitudes of the anapole moment or TDM of these atoms. The toroidal magnetic fields are given in units of $\alpha(\vec{E} \times \vec{S}) \sin \theta$, where θ is the angle between \vec{m} and \vec{r} .

B. Nonhydrogenic approach

Here the wave function of our interest is provided by the quantum-defect method, and Seaton [13] derived the general solution

$$\begin{aligned} P_{vnl}(\vec{r}) = [v_n^2 \Gamma(v_n + l + 1) \Gamma(v_n - l)]^{-1/2} \\ \times W_{v_n, l+1/2} \left(\frac{2r}{v_n} \right) Y_l^m(\hat{r}) \chi, \end{aligned} \quad (29)$$

where the effective quantum number $v_n = n - \mu$ with μ , the so-called quantum defect. The nonhydrogenic states (29) are solutions of the Schrödinger equation for a potential $V(r)$ that approaches $-2/r$ only asymptotically and v_n is a noninteger dependent on the value of the principal quantum number n although the quantum defect μ is a slowly varying function of n . In writing Eq. (29) we have assumed that the variation of μ with energy is negligibly small. It is of interest

to note that although Seaton's wave function is of approximate nature for small r , it has been used successfully for the entire range of r in studies of alkali-metal and alkaline-earth-metal atoms [13]. Further, the wave functions $P_{\nu_n l}(\vec{r})$ for different values of l belong to nondegenerate energy levels. Physically, this implies that interaction of the valence electron with the ionic core results in the removal of l degeneracy. In view of this, one would like to calculate the perturbative correction to $P_{\nu_n l}(\vec{r})$ by using an equation similar to that in Eq. (9). Unfortunately, due to the appearance of the irregular Whittaker function in Eq. (29), it is not possible to solve the associated inhomogeneous differential equation by using analytic techniques. Therefore, implementing the standard Rayleigh-Schrödinger perturbation theory we write the first-order correction $P'_{\nu_n 0}(\vec{r})$ to the valence-electron wave function of the alkali-metal atoms in the form

$$P'_{\nu_n 0}(\vec{r}) = \frac{E}{[3\nu_n^2\Gamma(\nu_n+1)\Gamma(\nu_n)]^{1/2}} \times \sum_k \left[\frac{R_{kn}}{[\nu_k^2\Gamma(\nu_k+2)\Gamma(\nu_k-1)]^{1/2}} \frac{1}{(\varepsilon_{\nu_n 0} - \varepsilon_{\nu_k 1})} \right] \times P_{\nu_k 1}(\vec{r}) \quad (30)$$

with

$$R_{kn} = \int_0^\infty r W_{\nu_k, 3/2}(r) W_{\nu_n, 1/2}(r) dr. \quad (31)$$

In the above the summation over k includes the value of principal quantum number n since in the nonhydrogenic model the l degeneracy has already been removed. As in the hydrogenic case we have

$$f(r) = \frac{1}{4\pi} \frac{1}{[\nu_n^2\Gamma(\nu_n+1)\Gamma(\nu_n)]} \times \sum_k \left[\frac{R_{kn}}{[\nu_k^2\Gamma(\nu_k+2)\Gamma(\nu_k-1)]} \frac{1}{(\varepsilon_{\nu_n 0} - \varepsilon_{\nu_k 1})} \right] \times \frac{1}{r} W_{\nu_k, 3/2}(r) W_{\nu_n, 1/2}(r) \quad (32)$$

to study the nonhydrogenic behavior of the toroidal magnetic field and anapole moments by the use of Eqs. (2) and (5).

Before computing the numbers for t or analyzing the behavior of B by using the present formalism it may be of some interest to investigate how the values of the polarizability implied by Eqs. (20) and (30) do compare with experiments. Admittedly, such a comparison is expected to provide an indication for the atomic model to be used for the present purpose, since in the semiempirical product rule [9] $\vec{t} = (2\pi/e)\vec{\mu} \times \vec{d}$ with $\vec{\mu} = -\alpha e a_0 \vec{S}$ and $\vec{d} = \alpha_E \vec{E}$ is directly proportional to the values of dipole polarizability α_E . Moreover, this rule is an exact result in the one-particle nonrelativistic theory used in this paper.

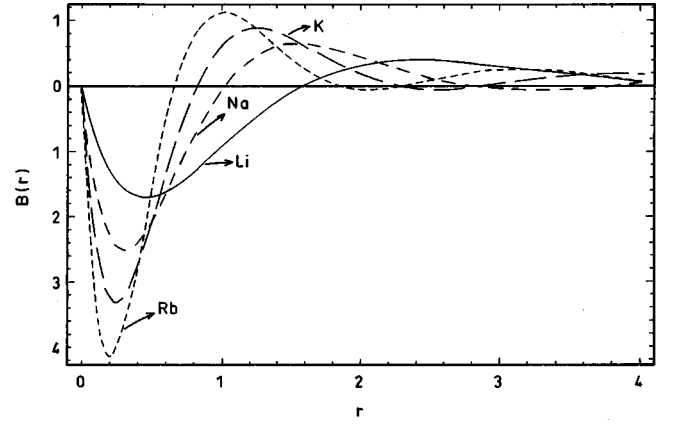


FIG. 1. Toroidal magnetic field of the valence electron in units of $\alpha(\vec{E} \times \vec{S}) \sin \theta$ as a function of r in a.u.

For the hydrogenic case the expression for polarizability is given by [15]

$$\alpha_h(n, 0, 0) = -\frac{2}{\sqrt{3}} \int_0^\infty R_{n,0}(r) r^3 G_{n,0}(r) dr. \quad (33)$$

We have used the subscript h on α to indicate that Eq. (33) represents the polarizability calculated on the basis of hydrogenic wave functions in which energy levels have l degeneracy. From Eqs. (16), (20), (23), and (33) we have obtained $\alpha_h(\text{Li}) = 120/Z_{\text{Li}}^4$, $\alpha_h(\text{Na}) = 1012.5/Z_{\text{Na}}^4$, $\alpha_h(\text{K}) = 4992/Z_{\text{K}}^4$, and $\alpha_h(\text{Rb}) = 17\,812.5/Z_{\text{Rb}}^4$. For the nonhydrogenic (nh) case it is not possible to construct a simple expression for $\alpha_{\text{nh}}(\nu_n)$. By using Eq. (30) we have, however, derived an infinite series representation for it to write

$$\alpha_{\text{nh}}(\nu_n) = \frac{2}{3[\nu_n^2\Gamma(\nu_n+1)\Gamma(\nu_n)]} \times \sum_k \left[\frac{1}{[\nu_k^2\Gamma(\nu_k+2)\Gamma(\nu_k-1)]} \frac{R_{kn}^2}{(\varepsilon_{\nu_n 0} - \varepsilon_{\nu_k 1})} \right]. \quad (34)$$

It is of interest to note that by using the values of α_h in the product rule we recover the results for t given in Eq. (28). This agreement clearly explains the reason for the $1/Z^4$ dependence of the anapole moment.

For the hydrogenic model we shall require the values of the effective nuclear charges as seen by the valence electron. We have determined the values of Z by a fit to binding energies through the use of the hydrogenic formula $E_n = -Z^2/2n^2$. An approach similar to ours has been used earlier in different physical contexts [18]. To work with the nonhydrogenic model we shall require, in addition to the ground-state energy, the numbers for binding energies and quantum defects for excited p states. We have taken the relevant data from the classic work of Ham [19]. Ham has given values of energy levels and quantum defects for the p electrons up to $k=6, 7, 8,$ and 9 for Li, Na, K, and Rb, respectively. Thus in calculating $\alpha_{\text{nh}}(\nu_n)$ we could include

TABLE I. Results for Z_{eff} , α_h , α_{nh} , t_h , and t_{nh} .

Element	Z_{eff} of the valence electrons	Polarizabilities (units of a_0^3)		Toroidal or anapole moments (units of a_0^4)	
		α_h	α_{nh}	t_h	t_{nh}
Li	1.259	47.762	163.500 (163.700)	1.094	3.744 (3.749)
Na	1.844	87.569		2.005	
K	2.259	191.695	289.521 (295.600)	4.389	6.630 (6.769)
Rb	2.770	302.556	318.517 (330.000)	6.929	7.294 (7.557)

only five terms in the sum present in Eq. (34). Fortunately, we have found that the finite truncation of the sum gives well-converged results.

In Table I we present our results for effective nuclear charges (Z_{eff}), polarizabilities (α_h and α_{nh}), and corresponding toroidal dipole moments (t_h and t_{nh}) for the elements Li, Na, K, and Rb. We have calculated the results for the dipole moments by using the product rule [9]. We have given in parenthesis in the column for α_{nh} the experimental values of dipole polarizabilities. The corresponding values of t are given similarly in the column for t_{nh} . From our data for α_h and α_{nh} it is clear that the nonhydrogenic model for alkali-metal atoms is far more realistic than the hydrogenic one. For example, in the case of Li the value of α_h is only 29% of the experimental value, while the value for α_{nh} is almost in exact agreement with the experimental result. For higher alkali metals, however, our results for α_{nh} exhibit some deviation from the corresponding experimental data. Interestingly, the hydrogenic model gets better as we go to high- Z alkali metals and this model recovers 92% of the experimental polarizability for Rb. Since the values of the anapole moment have been calculated by using the product rule the numbers for t_h and t_{nh} show similar behavior as observed for the polarizabilities.

We have analytically demonstrated that the expressions for hydrogenic toroidal dipole moments in Eq. (28) found from the *ab initio* calculations agree with those obtained from the product rule by using values of the appropriate polarizabilities. Such a clear demonstration was not, however, possible for the nonhydrogenic case. Thus we recalculated the results for t_{nh} from Eqs. (5) and (32) and found a similar agreement for the numbers for t_{nh} given in Table I. This indicates that in this work we derived a perfectly valid approach to study the Stark-induced anapole moment from the first principle. A hydrogenic model could account only for the qualitative behavior of t while the nonhydrogenic nature of the valence electrons of alkali-metal atoms provided some additional insight for the effect under study.

In Fig. 1 we display the radial dependence of the toroidal magnetic field of the hydrogenic valence electrons. The variation of B for Li, Na, K, and Rb are denoted by solid, dashed, dashed with dots, and dotted lines, respectively. An important feature of our results is that both maxima and minima of the curves for higher alkali metals are more pronounced and closer to the origin than the corresponding results for lower ones. This may be attributed to the fact that the valence electrons of high- Z alkali metals have greater probability of residing in the immediate vicinity of the nucleus and also producing a more intense toroidal magnetic field. We have verified that the radial dependence of the toroidal magnetic field of the nonhydrogenic electrons is identical to that of the hydrogenic electrons except that the respective curves are pushed a little away from the origin. We have not separately displayed the nonhydrogenic B fields because they do not give any new insight into additional physical realization. From our point of view the hydrogenic calculation also appears to be quite instructive although somewhat pedagogic.

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