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LETTER TO THE EDITOR

On the αZ expansion for the Dirac energy of a one-electron atom

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Abstract. A procedure for directly prescribing a term of arbitrary order in an αZ expansion of the Dirac energy of a one-electron atom is presented, and utilised to obtain higher-order corrections to the Dirac fine-structure formula. These can then be combined with terms not included in the Dirac formalism and applied, for example, to semi-empirical charge-screening parametrisations of multi-electron atoms.

Although the energy eigenvalues of the Dirac equation for a one-electron atom are given by an elementary analytic expression, the exact formula involves nested powers and roots of quantities close to unity, and is inconvenient for precise numerical evaluation. Thus an expansion is usually made in powers of αZ, where α is the fine-structure constant and Z is the nuclear charge. This expansion was first formulated in the context of the Bohr atom, and an interesting interpretation of the correspondence principle suggested that the unexpanded expression is an approximation and an appropriately truncated expansion correctly describes the atom. For a truly one-electron atom extensive numerical tabulations of energy levels are available (Garcia and Mack 1965) and such classical models are of only historical interest. However, this single-electron Dirac-energy expansion has also been utilised for multi-electron atoms in studies which account for core electrons through an effective screened charge (Edlén 1964). Here the test of the model lies not in the rigor of its theoretical formulation, but in the regularity of its parametrisation of measured data and its effectiveness for reliable isoelectronic interpolation and extrapolation. In testing the usefulness of these classical models in parametrising a number of isoelectronic data collections it became necessary to generate higher terms in the Sommerfeld–Dirac expansion. To facilitate this, an explicit expression has been developed by which an arbitrary term can be obtained directly as a function of the various quantum numbers. For terms up to $(\alpha Z)^{18}$ a tabulated set of determining coefficients is provided herein.

The relativistic energy of a one-electron atom was first obtained and expanded to order $(\alpha Z)^8$ by Sommerfeld (1919). This formula was then immediately applied to a multi-electron system, to deduce an effective screened charge from x-ray L-doublet separations (Sommerfeld 1919). In this context arguments were presented that data should be reduced using a truncated form of the series expansion rather than the exact expression (Sommerfeld and Heisenberg 1922, Green 1923). These arguments were based upon the correspondence principle, which held that terms smaller than the energy which would be radiated per orbital revolution according to the classical theory should not be retained. Guidelines for the truncation of the expansion as

a function of charge and quantum numbers were proposed. Green (1923) extended Sommerfeld's expansion to order $(\alpha Z)^{10}$, and compared the regularity of empirical screening parameters for various orders of truncation, finding some evidence for higher regularity with truncation of the expansion according to these guidelines. When the Dirac theory was developed, Sommerfeld's expansion required only a restatement in modern symbols. The series is still seldom carried beyond order $(\alpha Z)^8$, but this is due to the realisation that the Dirac equation is itself an approximation, and does not contain effects such as the interaction of the electron with its radiation field, the finite extent and finite mass of the nucleus, etc, which can also contribute terms of this order in αZ. In the simplest case of an $l = 1$ doublet, the radiative correction to the fine-structure splitting is proportional to $\alpha(\alpha Z)^2 \ln(\alpha Z)^2$. It is interesting that this quantity is negative, and thus has a tendency to nullify the effects of higher terms in the expansion of the Dirac energy, which are always positive, and could explain the apparent success of the correspondence principle truncation of the classical model. Expressions which describe the various corrections not included in the Dirac energy as a function of α, Z and the various quantum numbers are available (Garcia and Mack 1965, Sobel'man 1972) which can be combined with the Dirac energy, expanded to various orders as described herein, and used to construct empirical models for the parametrisation of data.

The Dirac energy of a one-electron atom is given by

$$\frac{E(n,j,Z)}{mc^2} = \left(1 + \frac{(\alpha Z)^2}{[n - j - \frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - (\alpha Z)^2}]^2}\right)^{-1/2} \tag{1}$$

where E is the relativistic energy, which includes the rest energy mc^2, n is the principal quantum number and j is the total angular-momentum quantum number. The number of parameters in equation (1) can be reduced to two through the substitutions

$$x \equiv (\alpha Z/n)^2 \tag{2}$$

$$b \equiv n/(j + \tfrac{1}{2}) \tag{3}$$

in terms of which equation (1) becomes

$$E/mc^2 = [1 + x/[1 - (1 - \sqrt{1 - b^2 x})/b]^2]^{-1/2}. \tag{4}$$

Equation (4) is a nesting of four binomial quantities

$$E/mc^2 = (1 + xv)^{-1/2} \tag{5}$$

$$v \equiv (1 - u/b)^{-2} \tag{6}$$

$$u \equiv (1 - t) \tag{7}$$

$$t \equiv (1 - b^2 x)^{1/2} \tag{8}$$

which can each be subsequently expanded by the binomial theorem

$$E/mc^2 = \sum_{p=0}^{\infty} \binom{-1/2}{p} (xv)^p \tag{9}$$

$$v^p = \sum_{q=0}^{\gamma} \binom{-2p}{q} (-u/b)^q \tag{10}$$

$$u^q = \sum_{r=0}^{q} \binom{q}{r} (-t)^r \tag{11}$$

$$t^r = \sum_{s=0}^{\infty} \binom{r/2}{s} (-b^2 x)^s \tag{12}$$

where the binomial coefficients have their standard definition

$$\binom{A}{B} \equiv \frac{A!}{B!\,(A-B)!}. \tag{13}$$

If equations (9)–(12) are combined, powers of x and b collected, and the orders of summation over q and r are interchanged with that over s, they form

$$\frac{E}{mc^2} = \sum_{p=0}^{\infty}\sum_{s=0}^{\infty} x^{p+s} \sum_{q=0}^{\infty} b^{2s-q}\binom{-1/2}{p}\binom{-2p}{q} \sum_{r=0}^{q} \binom{q}{r}\binom{r/2}{s}(-1)^{q+r+s}. \tag{14}$$

To obtain the numerical coefficients for specific powers of x and b we shift the p sum to $P = p + s$, interchange the orders of s and q summations, and shift the q sum to $Q = 2s - q$. After repaying the substitutions of equation (2) and (3) this yields

$$\frac{E(n, j, Z)}{mc^2} = \sum_{P=0}^{\infty} \left(\frac{\alpha Z}{n}\right)^{2P} \sum_{Q=0}^{2P} \left(\frac{n}{j+\frac{1}{2}}\right)^{Q} C_{PQ} \tag{15}$$

where

$$C_{PQ} = \sum_{s=s_{\min}}^{Q} \binom{-1/2}{P-s}\binom{-2P+2s}{2s-Q} \sum_{r=0}^{2s-Q} \binom{2s-Q}{r}\binom{r/2}{s}(-1)^{r-s-Q} \tag{16}$$

with $s_{\min} = Q/2$ for Q even and $s_{\min} = (Q+1)/2$ for Q odd. Notice that the C_{PQ} involve only finite sums (which in practice contain a very limited number of non-vanishing terms) and correspond to a single set of rational numbers, independent of n, j or Z. Values for C_{PQ} for P and Q from 0 to 9 are listed in table 1. Notice that $C_{0Q} = \delta_{0Q}$, so that the $P = 0$ term yields simply the rest energy, and that $C_{1Q} = -\delta_{0Q}/2$, so that the $P = 1$ term yields the Balmer energy. Terms with $P \geqslant 2$

Table 1. Columns correspond to a given value of P in $(\alpha Z/n)^{2P}$. Rows correspond to a given value of Q in $[n/(j+\frac{1}{2})]^{Q}$. Entries are presented as rational fractions, with the common denominator for each column denoted as 'Norm'.

C_{PQ}	$P=0$	1	2	3	4	5	6	7	8	9
$Q=$ 0	1	−1	3	−5	35	−63	231	−429	6435	−12155
1			−4	12	−120	280	−1260	2772	−48048	102960
2				−6	120	−420	2520	−6930	144144	−360360
3				−2	−8	180	−1960	7770	−210672	648648
4					−24	80	0	−2520	129360	−576576
5					−8	−24	504	−1736	15120	121968
6						−30	140	518	−39312	152460
7						−10	−84	690	−11664	−33660
8							−84	140	9072	−58608
9							−28	−140	7920	−8624
10								−126	1200	16632
11								−42	−1872	11880
12									−1584	1320
13									−528	−3168
14										−2574
15										−858
Norm	1	2	8	16	128	256	1024	2048	32768	65536

have non-vanishing C_{PQ} for $Q > 0$, thus involving j, and therefore constitute the fine structure.

The fine-structure separation $\Delta\sigma$ of a multiplet of orbital angular momentum l is given by

$$\Delta\sigma(n, l, Z) \equiv [E(n, l + \tfrac{1}{2}, Z) - E(n, l - \tfrac{1}{2}, Z)]. \tag{17}$$

Since they do not involve j, the rest energy, the Balmer energy, and all terms containing C_{P0} cancel, and the first terms in equation (15) which contribute to equation (17) have $P = 2$ and $Q = 1$. From table 1 we can also see that for $P > 1$ the C_{PQ} vanish for $Q \geqslant 2P - 2$. Thus the sums in equation (15) can be shifted to $\beta = P - 2$ and $\gamma = Q - 1$ when inserted in equation (17), which becomes

$$\frac{\Delta\sigma(n, l, Z)}{mc^2} = \sum_{\beta=0}^{\infty} \left(\frac{\alpha Z}{n}\right)^{2\beta+4} \sum_{\gamma=0}^{2\beta} \left(\frac{n^{\gamma+1}}{(l+1)^{\gamma+1}} - \frac{n^{\gamma+1}}{l^{\gamma+1}}\right) C_{\beta+2,\gamma+1}. \tag{18}$$

If we factor out the lead term and denote $R \equiv -\alpha^2 mc^2 C_{21}$, where R is the Rydberg constant (which may include the standard 'reduced mass' correction, but has an accompanying correction of order $(\alpha Z)^4$ for the relativistic non-separability of reduced masses) then the expression assumes the form

$$\Delta\sigma(n, l, Z) = \frac{R\alpha^2 Z^4}{n^3 l(l+1)} \sum_{\beta=0}^{\infty} (\alpha Z)^{2\beta} A_\beta(n, l) \tag{19}$$

where

$$A_\beta(n, l) = \sum_{\gamma=0}^{2\beta} \frac{n^\gamma}{n^{2\beta}} \frac{(l+1)^{\gamma+1} - (l)^{\gamma+1}}{[l(l+1)]^\gamma} \frac{C_{\beta+2,\gamma+1}}{C_{21}}. \tag{20}$$

Clearly $A_0(n, l) = 1$. Equation (20) can be used together with table 1 to obtain $A_\beta(n, l)$ for arbitrary values of β, n and l. These can be compared with published expressions

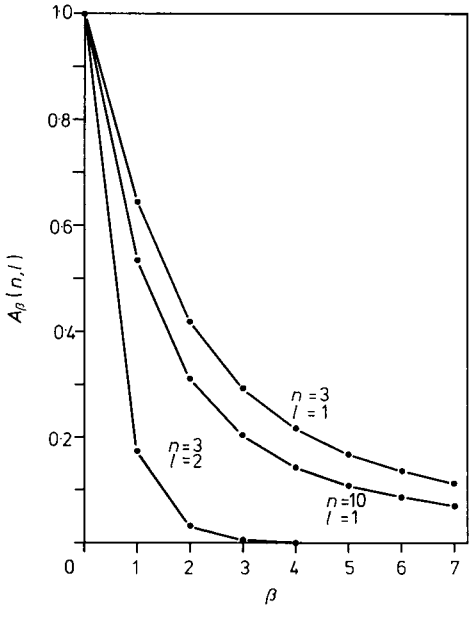

Figure 1. Plot of the fine-structure correction coefficients A_β against β, the order of the correction in $(\alpha Z)^{2\beta}$ for the 3p, 10p and 3d levels.

for $A_1(n, l)$ and $A_2(n, l)$ (Edlén 1964) and for $A_1(n, 1)$, $A_2(n, 1)$ and $A_3(n, 1)$ (Curtis 1977). Figure 1 shows $A_\beta(n, l)$ plotted against β for various values of n and l. The diminution of A_β with increasing β is rather gradual, particularly in the case of p states ($l = 1$) and the rapid convergence of equation (19) relies heavily upon the smallness of $(\alpha Z)^2$.

Although terms arising in this expression of order higher than $(\alpha Z)^8$ are probably negligible in most cases, this procedure provides a convenient means of testing this, and, if desired, of including these terms in an analysis.

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