LETTER TO THE EDITOR

On the \( \alpha Z \) expansion for the Dirac energy of a one-electron atom

L J Curtis
Department of Physics, University of Lund, S-223 62 Lund, Sweden

Received 14 September 1977

Abstract. A procedure for directly prescribing a term of arbitrary order in an \( \alpha Z \) 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 \( \alpha Z \), where \( \alpha \) 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 (Edlen 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 \( (\alpha Z)^8 \) a tabulated set of determining coefficients is provided herein.

The relativistic energy of a one-electron atom was first obtained and expanded to order \( (\alpha Z)^6 \) 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 \( (zZ)^8 \), 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 \( (zZ)^8 \), 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 \( zZ \). In the simplest case of an \( l = 1 \) doublet, the radiative
correction to the fine-structure splitting is proportional to \( \pi (zZ)^6 \ln(zZ)^2 \). 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 \( z, Z \) 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 constuct
empirical models for the parametrisation of data.

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

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

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

\[
x = (sZ/n)^2
\]
\[
b = n(j + \frac{1}{2})
\]
in terms of which equation (1) becomes

\[
E/me^2 = \left[ 1 + x/[1 - (1 - b^2 x)/b]^2 \right]^{-1/2}
\]

Equation (4) is a nesting of four binomial quantities

\[
E/me^2 = (1 + x)^{-1/2}
\]
\[
v = (1 - u/b)^{-2}
\]
\[
u = (1 - t)
\]
\[
t = (1 - b^2 x)^{1/2}
\]

which can each be subsequently expanded by the binomial theorem

\[
E/me^2 = \sum_{p=0}^{\infty} (-1/2)(xe)^p
\]
\[
v^p = \sum_{k=0}^{\infty} (-2)^p(-u/b)^p
\]
\[
u^p = \sum_{t=0}^{\infty} (2)(-t)^p
\]
\[
t^p = \sum_{b=0}^{\infty} (b^2)(-b^2 x)^p
\]
where the binomial coefficients have their standard definition

\[ \binom{n}{k} = \frac{n!}{k!(n-k)!} \]  

(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

\[ \frac{E}{m^2c^2} = \sum_{p=0}^{\infty} \sum_{s=0}^{\infty} x^{s+p} b^{s} q^{-p} r^{-s} \sum_{n=0}^{\infty} \binom{n}{p} \binom{n}{s} \binom{n}{q} \binom{n}{r} (-1)^{s+r+p}. \]  

(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

\[ \frac{E(n,j,Z)}{m^2c^2} = \sum_{P=0}^{\infty} \binom{nZ}{n} \binom{2P}{2n} \sum_{Q=0}^{\infty} \binom{n}{j+\frac{1}{2}}^Q \frac{1}{Q!} C_{PQ}, \]  

(15)

where

\[ C_{PQ} = \sum_{s=0}^{s_{\text{max}}} \binom{P}{s} \binom{Q}{s} \binom{Z}{s} \binom{Z}{s} \sum_{r=0}^{s_{\text{max}}} \binom{Q}{r} \binom{Q}{r} (-1)^{r-s} \]  

(16)

with \( s_{\text{max}} = Q/2 \) for \( Q \) even and \( s_{\text{max}} = (Q+1)/2 \) 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 \( C_{PQ} = \delta_{PQ} \) so that the \( P = 0 \) term yields simply the rest energy, and that \( C_{1Q} = -\delta_{1Q}^2 \), so that the \( P = 1 \) term yields the Balmer energy. Terms with \( P \geq 2 \)

| \( C_{PQ} \) | \( P = 0 \) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| \( Q = 0 \) | 0 | 1 | -1 | 3 | -5 | 35 | -63 | 231 | -429 | 6435 | -12155 |
| 1 | -4 | 12 | -120 | 280 | -1260 | 2772 | -48084 | 102960 |
| 2 | -6 | 120 | -1260 | 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 | |

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

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

(17)

Since they do not involve \( j \), the rest energy, the Balmer energy, and all terms containing \( C_{pq} \) 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 \( Q \leq 2P - 2 \). Thus the sums in equation (15) can be shifted to \( \beta = P - 2 \) and \( \gamma = Q - 1 \) when inserted in equation (17), which becomes

\[
\frac{\Delta \sigma(n, l, Z)}{mc^2} = \sum_{\beta \geq 0} \left( \frac{az}{n} \right)^{2\beta+4} \sum_{\gamma \geq 0} \left( \frac{n^{\beta+1}}{(l+1)^{\beta+1}} - \frac{n^{\gamma+1}}{l^{\gamma+1}} \right) C_{\beta+2,\gamma+1}.
\]

(18)

If we factor out the lead term and denote \( R = -z^2mc^2C_{31} \), where \( R \) is the Rydberg constant (which may include the standard ‘reduced mass’ correction, but has an accompanying correction of order \( (zZ)^4 \) for the relativistic non-separability of reduced masses) then the expression assumes the form

\[
\Delta \sigma(n, l, Z) = \frac{Rz^2Z^4}{n^3(l+1)} \sum_{\beta \geq 0} (zZ)^{2\beta} A_\beta(n, l)
\]

(19)

where

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

(20)

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

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Plot of the fine-structure correction coefficients \( A_\beta \) against \( \beta \), the order of the correction in \((zZ)^{2\beta}\) for the 3p, 10p and 3d levels.}
\end{figure}
for $A_1(n, l)$ and $A_2(n, l)$ (Edlén 1964) and for $A_3(n, 1)$, $A_4(n, 1)$ and $A_5(n, 1)$ (Curtis 1977). Figure 1 shows $A_6(n, l)$ plotted against $\beta$ for various values of $n$ and $l$. The diminution of $A_6$ with increasing $\beta$ 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 $(\alpha Z)^n$ 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.

References

Edlén B 1964 Handb. Phys. 27/167 (Berlin: Springer)
Green J B 1923 Phys. Rev. 21 397-401
Sommerfeld A 1919 Atombau und Spektrallinien (Braunschweig: Vieweg)
Sommerfeld A and Heisenberg W 1922 Z. Phys. 10 393-8