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Dirac eigenvalues for screened Coulomb potentials

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Abstract. We consider a single fermion moving in a screened Coulomb potential having the form $V(r) = g(-1/r)$, where g is monotone increasing and concave. The method of potential envelopes is applied to this problem and it is shown that close approximations for the relativistic eigenvalues are given by the simple expression

$$E_{nj}^{P} = \min_{u\in(0,1)} \{D(u) - uD'(u) + V[-1/D'(u)]\}$$

where $D(u) = D_{nj}^{P}(u)$ are the known exact eigenvalues for the hydrogenic atom with potential $-u/r$. Specific results for the first four eigenvalues of the atoms $Z = 14(5)84$ are compared to corresponding accurate values found numerically by the use of Dirac spinor orbits.

1. Introduction

In this paper we apply the potential envelope method to the problem of a single electron moving in a screened Coulomb potential and obeying Dirac's equation. The goal is to obtain a simple analytical approximation for the discrete part of the energy spectrum.

In an earlier paper some results were obtained for relativistic problems in which the potential is a convex transformation of the Coulomb potential (Hall 1985a). Here the quality of the method is tested on the relativistic screened Coulomb problem which is important in atomic physics. The potential is a concave transformation $V(r) = g(-1/r)$ of the pure Coulomb potential and the corresponding non-relativistic theory leads to upper bounds on the energy eigenvalues (Hall 1985b).

A very brief summary of the potential envelope method will be given here in § 3. It is perhaps remarkable that the method which was originally introduced for non-relativistic problems can be applied with equal ease in the relativistic domain which usually presents greater difficulties for eigenvalue methods. The only substantial difference encountered is that the approximation is not known to yield energy *bounds* for relativistic problems. Since the results we have found so far all follow the same pattern as for the Schrödinger case it is certainly tempting to ignore this qualitative change in the logical situation. However, the Dirac Hamiltonian operator is not bounded below and we therefore do not have the usual variational characterisation of the eigenvalues at our disposal. Consequently, at this time we are unable to claim *a priori* inequalities between the envelope approximations and the corresponding exact eigenvalues.

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The potential we shall use for illustration is the screened Coulomb potential of Mehta and Patil (1978) which is given by

$$V(r) = -(v/r)[1 - r\lambda(1-1/Z)/(1+r\lambda)] \tag{1.1}$$

with

$$v = \alpha Z \qquad \lambda = 0.98\alpha Z^{1/3} \tag{1.2}$$

where α is the fine structure constant and Z is the atomic number. We shall examine the first four energy eigenvalues for the atoms $Z = 14(5)84$ and compare the results of our geometrical theory with accurate numerical values obtained by using Dirac spinor orbits. A spinor orbit is the graph $\{\psi_1(r), \psi_2(r)\}$, $r \in (0, \infty)$, generated by the radial factors in the large and small components of the Dirac spinor. The form of these orbits is very sensitive to the trial value of the energy.

2. Dirac eigenvalues

The central potential $V(r)$ which we are considering in this paper is the time component of a Lorentz 4-vector, just like the potential $-1/r$ in the hydrogenic atom. However, the Dirac eigenvalues for a particle in a screened Coulomb potential do not have the same degeneracies as those of the corresponding non-relativistic problem nor those of the relativistic hydrogenic atom. We must therefore adopt a labelling scheme that is sufficiently general. The total angular momentum j and the parity P are good quantum numbers for the general central-field problem: we introduce a third (radial) quantum number $n = 1, 2, 3, \ldots$, which counts the eigenvalues in a jP subspace with a given fixed and allowed value for the z component m_j of the angular momentum. The eigenvalues E^P_{nj} labelled in this way and ordered according to $E^P_{n'j} \geqslant E^P_{nj}$, $n' > n$ all have degeneracy exactly $(2j+1)$. We measure energies in units of mc^2, where m is the mass of the electron, and lengths in terms of the associated Compton wavelength $\hbar/mc$. We follow essentially the notation of the book by Messiah (1961) and, in terms of the above variables, we write the coupled radial equations for the central field problem as follows:

$$\begin{aligned}(-\mathrm{d}/\mathrm{d}r + \tau k/r)\psi_2(r) &= (E - m - V(r))\psi_1(r) \\ (\mathrm{d}/\mathrm{d}r + \tau k/r)\psi_1(r) &= (E + m - V(r))\psi_2(r).\end{aligned} \tag{2.1}$$

The parity of the spinor $\Psi^P_{jm_j}$ constructed from the large and small radial factors $r^{-1}\psi_1(r)$ and $r^{-1}\psi_2(r)$ is given by

$$P = (-1)^{j+\tau/2} = (-1)^l \tag{2.2}$$

where $\tau = \pm 1$ and $l = j + \frac{1}{2}\tau$ is the lower index of the spherical harmonic factor associated with the 'large' radial function $\psi_1(r)$. As we have chosen to write the radial factors in the spinor Ψ in the form $r^{-1}\psi_1(r)$ and $r^{-1}\psi_2(r)$, we must impose boundary conditions and normalisation as follows:

$$\psi_1(0) = \psi_2(0) = 0 \qquad \int_0^\infty (\psi_1^2(r) + \psi_2^2(r))\,\mathrm{d}r < \infty. \tag{2.3}$$

The pure hydrogenic spectrum is a key ingredient in the present application of the envelope method. In the notation of this paper these well known eigenvalues for the

potential $V(r) = -u/r$ and mass $m = 1$ have the form

$$D(u) = D^P_{nj}(u) = \{1 + u^2[\nu - k + (k^2 - u^2)^{1/2}]^{-2}\}^{-1/2}$$
$$k = j + \tfrac{1}{2} \qquad \nu = n + k - \tfrac{1}{2}(1 - \tau) \tag{2.4}$$

where the symbol ν represents the principal quantum number and the Coulomb coupling u satisfies $u < 1$ (the '$Z < 137$' limit for relativistic hydrogenic atoms). In terms of our labelling scheme the special Coulomb degeneracies become

$$\begin{aligned} &k \text{ odd:} \qquad E^+_{n+1j} = E^-_{nj} \\ &k \text{ even:} \qquad E^+_{nj} = E^-_{n+1j}. \end{aligned} \tag{2.5}$$

Meanwhile the derivative of $D(u)$ has the form

$$D'(u) = -u[\nu - k + k^2(k^2 - u^2)^{-1/2}]\{u^2 + [(\nu - k + (k^2 - u^2)^{1/2}]^2\}^{-3/2} < 0. \tag{2.6}$$

We note that it follows from (2.6) that $D''(u) < 0$ for $u \in (0, k)$. In summary, then, $D(u)$ is a positive, monotone decreasing and concave function of $u \in (0, k)$; $D(u)$ is physically meaningful only for $u < 1$. In the non-relativistic limit $D(u)$ becomes

$$D^P_{nj}(u) \to \mathscr{E}_{nl}(u) = 1 - u^2/2\nu^2 = 1 - u^2/2(n + l)^2 \qquad l = j - \tfrac{1}{2}(1 - \tau). \tag{2.7}$$

Thus by substituting $\mathscr{E}_{nl}(u)$ for $D^P_{nj}(u)$ in the equations of this paper we recover the corresponding results of the Schrödinger theory (with the rest mass 1 added) which were discussed in Hall (1985b).

3. The potential envelope method

The potential envelope method is a very general technique for approximating the spectrum of an operator. We now outline the main steps leading to the specific result we use in this paper.

We suppose that the central potential $V(r)$ has the representation

$$V(r) = g(h(r)) \qquad h(r) = -1/r \tag{3.1}$$

where the transformation function $g(h)$ is monotone increasing and concave for $h \in (-\infty, 0)$. In the corresponding Schrödinger theory the concavity assumption leads to energy upper bounds, and similarly convexity leads to lower bounds. As we mentioned in the introduction, we are not yet able to claim *a priori* that the approximation leads to definite bounds in relativistic applications. However, a definite convexity is useful for technical reasons (we can divide by $g''(h) \neq 0$) and also the screened Coulomb potentials which have been used in atomic physics, like the Mehta–Patil potential which we adopt here, are indeed concave transformations of $h = -1/r$. Monotonicity is required so that the tangent lines to $g(h)$ are attractive (shifted) Coulomb potentials for which we have the known exact solutions at our disposal.

These tangential potentials have the form

$$V^{(t)}(r) = A + Bh(r) \tag{3.2}$$

where (by calculus) we have

$$A = g(h) - hg'(h) \qquad B = g'(h) \tag{3.3}$$

and $h = h(t) < 0$, $t \in (0, \infty)$, is the point of contact between $V(r)$ and its tangent $V^{(t)}(r)$. The potential inequality (implied by the concavity of g) which we are still unable to

exploit in the relativistic case is given by

$$V(r) \leqslant V^{(t)}(r). \tag{3.4}$$

If we now insert the tangential potential $V^{(t)}(r)$ in the radial equations (2.1) we obtain the tangential spectrum

$$E^{(t)} = g(h) - hg'(h) + D(g'(h)) \tag{3.5}$$

where $D(u) = D^P_{nj}(u)$ is the pure hydrogenic energy function given by (2.4) and we have chosen to use $h = -1/t$ as a new variable. The next step towards our result is to find the envelope of the family $\{E^{(t)}\}$ of tangential energy functions. We do this in the standard way by solving $\partial E^{(t)}/\partial h = 0$ simultaneously with (3.5). After cancellation of $g''(h) \neq 0$ the critical point is given by

$$h = D'(g'(h)). \tag{3.6}$$

In order to simplify the final formulae we now change variables again to $u = g'(h)$ and consider the following energy function which is obtained if (3.6) is substituted in (3.5):

$$E(u) = D(u) - uD'(u) + g(D'(u)) \tag{3.7}$$

and its derivatives

$$E'(u) = (g' - u)D'' \qquad E''(u) = (g''D'' - 1)D'' + (g' - u)D'''. \tag{3.8}$$

It follows from (3.7) and (3.8) that the critical point and the critical value of $E(u)$ are the same as those of the energy function in (3.5). Meanwhile, since $D'' < 0$ we see that if g is convex ($g'' > 0$) then the critical point is a minimum; whereas if g is concave (as in the present application) then the critical point is a minimum if $g''D'' < 1$ and a maximum if $g''D'' > 1$. We resolved this last question as we did in the Schrödinger case by simply plotting the function $E(u)$. Figure 1 shows the curve $E^+_{2\,1/2}(u)$ for gold

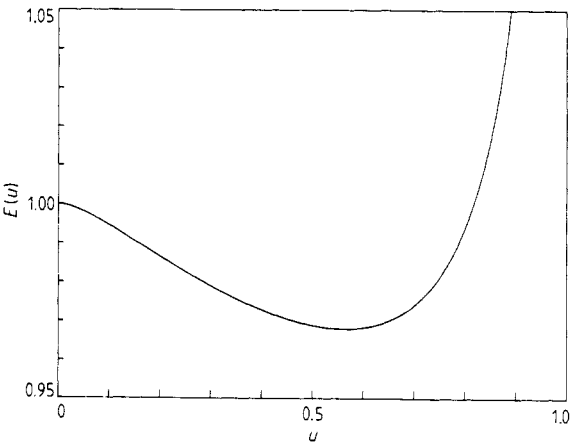

Figure 1. The $E(u)$ function for gold ($Z = 79$) whose minimum yields the envelope estimate for the eigenvalue $E^+_{2\,1/2}$. The minimum value $E = 0.968\,1262$ occurs at $u = 0.564\,2797$ and corresponds to an energy of -16.287 keV measured from the ionisation threshold: the accurate value is -16.898 keV.

($Z = 79$). Thus we can summarise our present envelope approximation by the simple compact formula

$$E_{nj}^{P} \simeq \min_{u\in(0,1)} [D(u) - uD'(u) + V(-1/D'(u))] \tag{3.9}$$

where $D(u) = D_{nj}^{P}(u)$ is the known exact trajectory function for the hydrogenic atom. We note that the transformation function $g(h)$ has now been replaced by the original potential $V(r) = g(-1/r)$: only the existence of g was required for the derivation of (3.9). The earlier non-relativistic result (Hall 1985b, equation (2.8)) is recovered (with the rest mass 1 added on) if the relativistic hydrogenic energies $D_{nj}^{P}(u)$ are replaced by the corresponding Schrödinger energies given here in (2.7).

The positive quantity $D(u) - uD'(u) = s$ represents the rest mass plus the kinetic energy. The whole theory can be reformulated in terms of the variable s and this leads to the concept of 'kinetic potentials' (Hall 1984, 1985a).

4. Results

We consider the collection of 15 atoms with $Z = 14(5)84$ which we studied earlier in the Schrödinger theory (Hall 1985b). There are four eigenvalues in the general (central-field) relativistic problem which correspond to $\nu = (n + l) \leqslant 2$ for the non-relativistic hydrogenic atom, namely

$$E_{nj}^{P} = E_{1\,1/2}^{+},\ E_{2\,1/2}^{+},\ E_{1\,1/2}^{-},\ E_{1\,3/2}^{-}.$$

The envelope approximations, which are based on the hydrogenic atom, faithfully follow the Coulomb degeneracies so that, in accordance with (2.5), we have $E_{2\,1/2}^{+} = E_{1\,1/2}^{-}$ for the approximations. The minimisation in the envelope formula (3.9) is very effectively and quickly carried out with the aid of Newton's method. The shape of the energy curve $E(u)$ illustrated for gold in figure 1 is ideally suited for this approach. The results for the 60 eigenvalues which we have considered are shown in table 1. The closely spaced Coulomb-like spectrum certainly offers a very demanding test for any kind of eigenvalue method.

In order to be quite sure how our simple approximation fared in this test we computed the 60 eigenvalues numerically and the results are shown in parentheses in table 1. It is customary in a theoretical paper not to report at length on the question of numerical technique. However, it may be of some interest to indicate briefly how we obtained the comparison data. Since the screened Coulomb potential has the Coulomb singularity $V(r) \sim -v/r$ at the origin we began the numerical integration of the radial equations (2.1) with the Coulomb ratio for $\psi_1(0+)/\psi_2(0+)$. Thereafter, we looked at what we call a Dirac spinor orbit which is the graph $\{\psi_1(r), \psi_2(r)\}$ for $r \in (0, \infty)$. The spinor orbit for the eigenvalue $E_{2\,1/2}^{+}$ of gold is shown in figure 2. If the energy is now reduced by just $\frac{1}{2}$ eV the orbit no longer closes and this is illustrated in figure 3. In this way very accurate eigenvalues can be obtained automatically with the aid of a microcomputer.

5. Conclusion

Once the abstract formulation of a physical problem has been established it is very hard today for an analytical technique to compete with a well written computer program.

Table 1. Envelope approximations (in keV) for the eigenvalues E^P_{nj} generated by the screened Coulomb potential $V(r)$. Corresponding accurate eigenvalues obtained numerically by the use of Dirac spinor orbits are shown in parentheses.

Z	$E^+_{1\,1/2}$	$E^+_{2\,1/2}$	$E^-_{1\,1/2}$	$E^-_{1\,3/2}$
14	−1.9591 (1.9998)	−0.1877 (0.2493)	−0.1877 (0.2157)	−0.1870 (0.2147)
19	−3.8090 (3.8646)	−0.4269 (0.5249)	0.4269 (0.4724)	−0.4237 (0.4685)
24	−6.3130 (6.3829)	−0.7904 (0.9268)	−0.7904 (0.8545)	−0.7810 (0.8438)
29	−9.491 (9.574)	−1.290 (1.466)	−1.290 (1.373)	−1.268 (1.349)
34	−13.363 (13.460)	−1.935 (2.151)	−1.935 (2.039)	−1.890 (1.989)
39	−17.954 (18.063)	−2.736 (2.993)	−2.736 (2.860)	−2.653 (2.771)
44	−23.288 (23.410)	−3.703 (4.001)	−3.703 (3.849)	−3.561 (3.698)
49	−29.398 (29.532)	−4.847 (5.188)	−4.847 (5.015)	−4.619 (4.773)
54	−36.320 (36.465)	−6.181 (6.564)	−6.181 (6.371)	−5.829 (6.002)
59	−44.095 (44.251)	−7.718 (8.145)	−7.718 (7.931)	−7.195 (7.386)
64	−52.774 (52.942)	−9.476 (9.947)	−9.476 (9.713)	−8.721 (8.930)
69	−62.418 (62.597)	−11.473 (11.991)	−11.473 (11.736)	−10.411 (10.638)
74	−73.098 (73.287)	−13.734 (14.298)	−13.734 (14.023)	−12.267 (12.512)
79	−84.901 (85.101)	−16.287 (16.898)	−16.287 (16.603)	−14.294 (14.557)
84	−97.934 (98.145)	−19.165 (19.826)	−19.165 (19.510)	−16.496 (16.776)

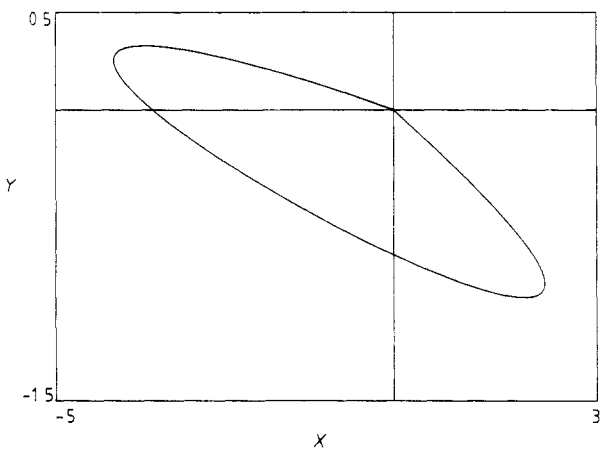

Figure 2. The Dirac spinor orbit corresponding to the energy $E = E^+_{2\,1/2}$ for gold ($Z = 79$). The variables $X = \psi_1(r)$ and $Y = \psi_2(r)$ are the large and small radial factors in the Dirac spinor.

The main advantage of the analytical method is that it reveals how various aspects of the problem are related: we can more easily investigate the effect of changes in parameters. However, if the analytical results are very complicated, then the qualitative information we seek may still be intractably embedded in the properties of certain special functions.

The geometrical approximation method which we have applied to the screened Coulomb problem in this paper is important mainly because of its simplicity. Although in the final stages of any serious applications the eigenvalues will have to be known extremely accurately, for the purposes of initial exploration it is very useful to have a simple approximate recipe like (3.9) in which the original potential $V(r)$ appears explicitly along with all its various parameters.

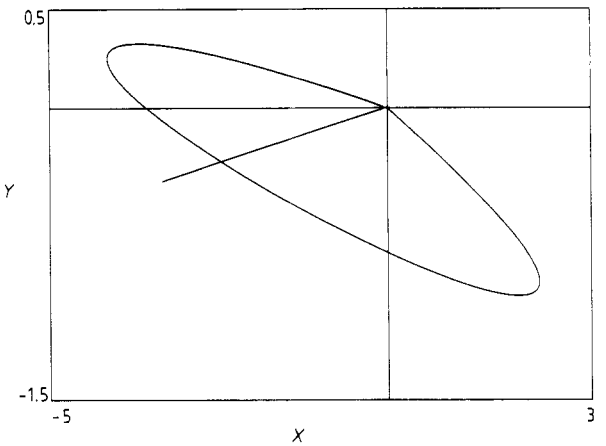

Figure 3. The Dirac spinor orbit corresponding to the energy $E = E^{+}_{21/2} - \frac{1}{2}$ eV for gold ($Z = 79$). The dramatic change in the orbit (compared with figure 2) is produced by an energy change of only $\frac{1}{2}$ eV in 16 898 eV and this indicates the accuracy which can be obtained when spinor orbits are used to determine the eigenvalues. The variables $X = \psi_1(r)$ and $Y = \psi_2(r)$ are the large and small radial factors in the Dirac spinor.

If $V_1(r)$ and $V_2(r)$ are attractive central potentials of the type we have discussed in this paper (time components of Lorentz 4-vectors) and $V_1(r) \leqslant V_2(r)$ for $r \in (0, \infty)$, we have not yet found a counterexample to the conjecture that the corresponding Dirac eigenvalues are necessarily ordered in the same way, as indeed they are in the Schrödinger theory. It is true that variations in the mass (the 'scalar' potential) produce a non-monotonic expanding effect on the relativistic spectrum, but we are keeping the rest mass constant. If a relativistic comparison theorem could be established with sufficient generality to include the potentials we have used in this paper, then the simple eigenvalue formula (3.9) could immediately be strengthened to the inequality

$$E^{P}_{nj} \leqslant \min_{u \in (0,1)} \{D(u) - uD'(u) + V[-1/D'(u)]\} \tag{5.1}$$

along with a similar result, with the inequality reversed, in the case where the transformation function g is convex. The ordering conjecture is certainly satisfied for the family of Coulombic potentials $V(r) = \alpha - \beta/r$ with $\beta > 0$. Moreover, in the context of atomic physics a counterexample to the conjecture would seem physically very bizarre. In view of the recent advances in the variational theory of Dirac eigenvalues (e.g. Goldman 1985, Franklin and Intemann 1985) it may eventually be possible either to prove (5.1) under suitable conditions or to reformulate the envelope method for relativistic problems so that eigenvalue bounds are obtained.

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References

Franklin J and Intemann R L 1985 *Phys. Rev. Lett.* **54** 2068
Goldman S P 1985 *Phys. Rev.* A **31** 3541
Hall R L 1984 *J. Math. Phys.* **25** 2708
—— 1985a *J. Math. Phys.* **26** 1779
—— 1985b *Phys. Rev.* A **32** 14
Mehta C H and Patil S H 1978 *Phys. Rev.* A **17** 34
Messiah A 1961 *Quantum Mechanics* vol II (Amsterdam: North-Holland) p 924