Pramana – J. Phys., Vol. 38, No. 5, May 1992, pp. 521–530. © Printed in India.

Examples of the minimax technique in relativistic atomic one-electron calculations

SHIBNATH DATTA* and S N DATTA†

*Department of Physics, Raja Rammohan Roy College, Radhanagar, Hooghly, West Bengal, India

†Department of Chemistry, Indian Institute of Technology, Bombay 400 076, India

MS received 20 November 1991; revised 3 February 1992

Abstract. Several examples of the application of the minimax technique to relativistic calculations on one-electron atoms are given here. Normalizable eigenfunctions corresponding to the ground states of one-electron atoms with various angular momenta are derived analytically.

Keywords. Minimax technique; Dirac atoms; bound states; eigenfunctions.

PACS Nos 11·10; 31·15

1. Introduction

It is known that the minimax theorem guarantees the occurrence of an upper bound to the ground state energy of a relativistic one-electron system when the trial wave function used has well-behaved properties. The state of a one-electron system is described by a four-component spinor that can be written as

$$\psi = N\begin{pmatrix} u \\ l \end{pmatrix} \tag{1}$$

where the upper component u and the lower component l are two-component spinors and N is the normalization constant. The lower component l is formally obtained from the application of an operator Ω on u: $l = \Omega u$. Variation of $\langle H_D \rangle$, the expectation value of the Dirac Hamiltonian H_D, as a functional of Ω leads to a stationary point. The optimum coupling operator is given by

$$\Omega^0 = c(E^0 + c^2 - V_{\text{ext}})^{-1}\sigma\cdot\mathbf{p} \tag{2}$$

where V_{ext} is the external potential, $\mathbf{p}$ the linear momentum and σ_x, σ_y and σ_z the spin matrices due to Pauli. We adopt the system of units: $m = 1$, $|e| = 1$ and $\hbar = 1$; c is the speed of light. The optimized energy E^0 must be determined from the equation (Rosicky and Mark 1975)

$$(u, [E^0 - c^2 - V_{\text{ext}}]u) = c^2(u, \sigma\cdot\mathbf{p}[E^0 + c^0 - V_{\text{ext}}]^{-1}\sigma\cdot\mathbf{p}u). \tag{3}$$

One can easily show that E^0 is a maximum (Datta and Devaiah 1988). One can also show that when $-2c^2 < \langle V_{\text{ext}} \rangle_u < 0$, that is, when the expectation value of the

potential represents a realistic bound state, a well-behaved upper component function u gives one and only one real solution E^0 such that

$$E^0 > c^2 + \langle V_{\text{ext}} \rangle_u. \tag{4}$$

A subsequent variation of E^0 as functional of u generates an upper bound (Datta and Devaiah 1988).

Sometimes it becomes advantageous to use, in stead of (3), the analogous equation in terms of the lower component l:

$$(l, [E^0 + c^2 - V_{\text{ext}}]l) = c^2(l, \sigma\cdot\mathbf{p}[E^0 - c^2 - V_{\text{ext}}]^{-1}\sigma\cdot\mathbf{p}l). \tag{5}$$

This result is obtained by writing $u = \omega l$ and then maximizing $\langle H_D \rangle$ by varying ω. The optimum operator ω^0 is given by

$$\omega^0 = c[E^0 - c^2 - V_{\text{ext}}]^{-1}\sigma\cdot\mathbf{p}. \tag{6}$$

In this paper we provide several examples of the minimax calculation on Dirac one-electron atoms where $V_{\text{ext}} = -Zr^{-1}$. Our starting point is necessarily the central equation (3) or (5). The objective is to derive, from the application of the standard variation method, a few low-lying eigenvalues of the discrete spectrum and the associated eigenfunctions of H_D. These illustrations do not contribute any new theory. Their importance lies in that they are new analytical calculations for the derivation of standard atomic results.

2. Simple cases

It would be worthwhile to discuss a few simple cases before the general treatment is presented. Though simple, these treatments point out the possible pitfalls and fallacies one encounters while carrying out a general variational analysis.

Example 1. Spinors of s symmetry from STO bases

The simplest possible form of the upper component is

$$u = N_n r^{n-1}\exp(-\zeta r)\begin{pmatrix} Y_{00}(\theta, \phi) \\ 0 \end{pmatrix} \tag{7}$$

where N_n is the normalization constant of the upper radial component. The parameter n can vary continuously, that is, n can be a fraction. Use of this upper component in (3) yields

$$E^0 - c^2 + n^{-1}\zeta Z = c^2 N_n^2 \int_0^\infty \mathrm{d}r[(E^0 + c^2) + Zr^{-1}]^{-1} \times [(1-n) + \zeta r]^2 r^{2n-2}\exp(-2\zeta r). \tag{8}$$

When $E^0 < -c^2$, the integrand on the right hand side has a simple pole at $r = -(E^0 + c^2)^{-1}Z$. The principal value of the integral is in general complex as

discussed in the appendix. If one wants to keep up a real solution $E^0 < -c^2$ one must avoid the simple pole by writing

$$n = 1 - (E^0 + c^2)^{-1}\zeta Z. \tag{9}$$

This substitution immediately leads to the results

$$E^0 = \pm c^2[1 + \alpha^2(\zeta^2 - 2\zeta Z)]^{1/2} \tag{10}$$

where α is the fine structure constant, and

$$n_\pm = 1 + (\zeta - 2Z)^{-1}(1 - \varepsilon)Z \tag{11}$$

where ε is the ratio of energy E^0 and rest energy mc^2,

$$\varepsilon = c^{-2}E^0. \tag{12}$$

The point $\zeta = 2Z$ in a singular point of n_-. That the negative solutions of E are at all possible does not contradict our earlier assertion (Datta and Devaiah 1988) that, for a well-behaved upper component function, no solution $E^0 < (c^2 + \langle V_{ext}\rangle_u)$ is possible for a realistic expectation value of the external potential. When $0 \leqslant \zeta < 2Z$, one finds that $n_- \leqslant 0$ and the expectation value, $\langle V_{ext}\rangle_u = -n^{-1}Z$, is actually positive. For $\langle V_{ext}\rangle_u > 0$ real solutions of negative energy are indeed possible, but the wave functions are non-normalizable. The plot of n_- as a function of ζ is shown in figure 1. For $\zeta > 2Z$, the parameter n_- is positive and $\langle V_{ext}\rangle_u$ decreases monotonically from

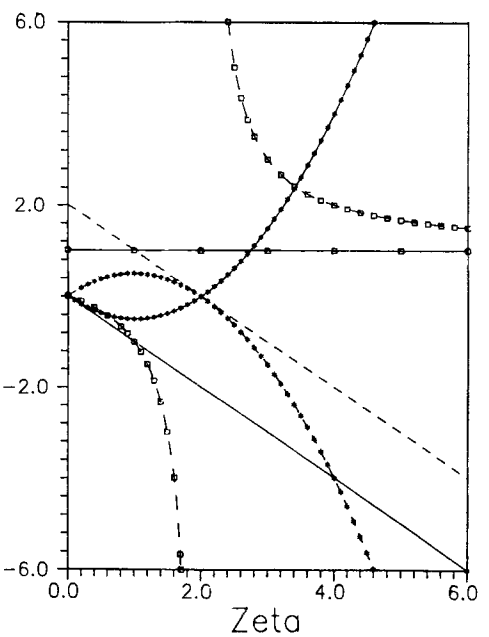

Figure 1. Calculated $(E_\pm \mp c^2)$, $\langle V_{ext}\rangle_\pm$ and $n_\pm$ as functions of exponent ζ for $l = 0$ and $Z = 1$. Solid and dashed lines correspond to the positive-energy solutions and the negative-energy ones respectively. Symbols are used as follows: (i) * stands for $(E_\pm \mp c^2)$ in atomic unit and (ii) □ for $n_\pm$, and (iii) lines without symbols are plots of $\langle V_{ext}\rangle_\pm$ in atomic unit.

zero as ζ increases (from $2Z$). A real solution $E^0 < -c^2$ exists but the wave function is again unrealistic since the expectation value of 'kinetic energy', $\langle c\alpha\cdot\mathbf{p}\rangle$, is negative [as can be seen from the difference of curves in figure 1], and a sensible function is not obtained from the variation of energy with ζ.

Variation of E^0 with ζ gives the optimized exponent $\zeta = Z$ and hence the following:

(i) A minimum, E^0_+, for the positive E^0 values,

$$E^0_+ = c^2\gamma_1 \equiv E_{1s} \tag{13}$$

with $n_+ = (1-\alpha^2Z^2)^{-1/2} \equiv \gamma_1$. In this case the optimized s spinor is identical with the $1s$ eigenfunction of H_D with eigenvalue E_{1s}.

(ii) A maximum, E^0_-, for the negative solutions of E^0,

$$E^0_- = -E^0_+ \tag{14}$$

with $n_- = -\gamma_1$. The state represented by the maximum is not a realistic bound state.

The minimum E^0_+ is generated here as a byproduct. The right way to obtain the minimum is to start from (5). If we write

$$l = N_n r^{n-1}\exp(-\zeta r)\begin{pmatrix} Y_{10}(\theta,\phi) \\ 2^{-1/2}\,Y_{11}(\theta,\phi)\end{pmatrix} \tag{15}$$

then (5) takes the shape

$$E^0 + c^2 + n^{-1}\zeta Z = c^2N_n^2\int_0^\infty \mathrm{d}r[(E^0-c^2)+Zr^{-1}]^{-1} \times[(1+n)-\zeta r]^2 r^{2n-2}\exp(-2\zeta r). \tag{16}$$

The integrand in the right hand side has a simple pole for $0 < E^0 < c^2$. In order to get rid of the complications arising from this pole we write

$$n = -1 + (c^2 - E^0)^{-1}\zeta Z \tag{17}$$

which immediately leads to (10) and subsequently to the minimum and maximum specified above [see (13) and (14)].

A very special case arises when a positive integer is chosen for n and the principal value of the integral in (8) becomes real. A solution $E < 0$ is then possible, but it must be viewed as a spurious solution. When $n = 1$, (8) yields the minimum

$$E_{\min} = c^2 - \frac{1}{2}Z^2 - \frac{1}{8}\alpha^2Z^4 + \frac{1}{16}\alpha^4Z^6 + \ldots \tag{18}$$

and the optimized exponent

$$\zeta = Z\left[1 + \frac{1}{2}\alpha^2Z^2 - \frac{1}{8}\alpha^4Z^4 + \ldots\right]. \tag{19}$$

The minimum is an upper bound to the ground state energy,

$$E_{\min} = E_{1s} + \frac{1}{8}\alpha^4Z^6 + \ldots. \tag{20}$$

Example 2. Continuum state solutions

If we choose the upper component given by (7) with ζr replaced by $i\mathbf{p}\cdot\mathbf{r}$ we get a trial function for the continuum states. We use (3) and after carrying out integration over a spherical volume of radius R, we obtain

$$E^0 = \pm(c^4 + c^2p^2)^{1/2} - \left(1 + \frac{1}{2n}\right)\frac{Z}{R} + O[(Z/R)^2 \text{ and higher}]. \tag{21}$$

Obviously, to order $R^{-1}Z$, there is no solution in the range

$$-c^2 + \langle V_{\text{ext}}\rangle_n < E^0 \leqslant c^2 + \langle V_{\text{ext}}\rangle_n. \tag{22}$$

If energy is to be negative, the integral obtained from (3) would have a simple pole; in the case the integral is substituted by its principal value as in the appendix, we see that a real solution $E < 0$ exists for a finite R only when n is a positive integer, so it must be spurious. As $R \to \infty$ one obtains the continuum state eigenvalues

$$E_p^0 = \pm[c^4 + c^2p^2]^{1/2} \tag{23}$$

The parameter n is not optimized here. It would be optimized only if one attempts to calculate the continuum state eigenfunctions and not merely the eigenvalues. Continuum state eigenfunctions of positive energy were calculated by Darwin (1928) and an algorithm for computing the negative-energy eigenfunctions has been recently discussed by Belifante (1991).

3. Lowest eigenvalues of the discrete spectrum

So far we have considered discrete states with $l = 0 (j = 1/2)$. We now derive eigenstates of the lowest eigenvalues for different combinations of l and j by a minimization procedure starting from (5). The cases $j = l + 1/2$ and $j = l - 1/2$ are treated separately for reasons which will be obvious later.

Example 3. $j = l + 1/2$

Following Bethe and Salpeter (1957) we write the lower component as

$$l = f(r)\begin{pmatrix} -i[(2l+3)^{-1}(l-m+3/2)]^{1/2}\, Y_{l+1,m-1/2}(\theta,\phi) \\ -i[(2l+3)^{-1}(l+m+3/2)]^{1/2}\, Y_{l+1,m+1/2}(\theta,\phi) \end{pmatrix}. \tag{24}$$

The trial small component must have as few radial nodes as possible such that the energy is maximally lowered. Hence it is written as

$$f(r) = Nr^{n-1}\exp(-\zeta r). \tag{25}$$

Use of this expression in (5) results in

$$E + c^2 + n^{-1}\zeta Z = c^2N^2\int_0^\infty \mathrm{d}r[(E-c^2)r + Z]^{-1} \times [(n+l+1) - \zeta r]^2 r^{2n-1}\exp(-2\zeta r). \tag{26}$$

In order to avoid the simple pole for $0 < E < c^2$ one demands

$$\zeta = (n + l + 1)(c^2 - E)Z^{-1} \tag{27}$$

which gives the energy E as

$$E = 1 - 2n\alpha^2 Z^2 (1 + l)^{-1}[(n + l + 1)^2 - \alpha^2 Z^2]^{-1}. \tag{28}$$

If E is minimized by varying n one gets

$$n_{\min} = [(1 + l)^2 - \alpha^2 Z^2]^{1/2} \equiv \gamma_{l+1}, \tag{29}$$

and

$$\varepsilon = c^{-2} E_{\min} = (l + 1)^{-1} \gamma_{l+1}. \tag{30}$$

Further, using (27) one calculates the exponent

$$\zeta = (l + 1)^{-1} Z \tag{31}$$

such that the optimized large and small radial components are

$$g(r) = N'[(1 + \varepsilon)/2]^{1/2} r^{\gamma_{l+1} - 1} \exp[-Zr/(l + 1)], \tag{32}$$

and

$$f(r) = -[(1 - \varepsilon)/(1 + \varepsilon)]^{1/2} g(r) \tag{33}$$

respectively. By putting $l = 0, 1, 2$, etc. in these equations one obtains the eigenfunctions $1s_{j=1/2}$, $2p_{j=3/2}$, $3d_{j=5/2}$ etc.

Example 4. $J = l - 1/2$

The trial lower component is written as (Bethe and Salpeter 1957)

$$l = f(r) \begin{pmatrix} -i[(2l-1)^{-1}(l + m - 1/2)]^{1/2}\, Y_{l-1,m-1/2}(\theta, \phi) \\ i[(2l-1)^{-1}(l - m - 1/2)]^{1/2}\, Y_{l-1,m+1/2}(\theta, \phi) \end{pmatrix} \tag{34}$$

such that

$$\alpha \cdot \mathbf{p} l = -[\mathrm{d}f/\mathrm{d}r - (l-1)r^{-1} f] \begin{pmatrix} [(2l+1)^{-1}(l - m + 1/2)]^{1/2}\, Y_{l,m-1/2} \\ [(2l+1)^{-1}(l + m + 1/2)]^{1/2}\, Y_{l,m+1/2} \end{pmatrix}. \tag{35}$$

If one chooses the small radial component as in (25) one obtains

$$\mathrm{d}f/\mathrm{d}r - (l-1)r^{-1} f = [(n-l)r^{-1} - \zeta] \tag{36}$$

and for $n < l$ the pole arising out of $(E - c^2 + r^{-1}Z)$ in the denominator in (5) is not eliminated. Therefore, the best lower-energy choice for f is

$$f(r) = (c_1 + c_2 r) r^{n-1} \exp[-\zeta r]. \tag{37}$$

When this expression is used in (5), the denominator is found to be cancelled by a factor in the numerator of the integrand if one writes

$$(E - c^2)[\zeta Z + (n - l)(E - c^2)]c_1 - Z[\zeta Z + (n - l + 1)(E - c^2)]c_2 = 0. \tag{38}$$

This leaves the equation

$$c_1^2[Z-c^2Z^{-1}(l^2-n^2)]I_{2n-1}+[c_1^2\{(c^2+E)+c^2\zeta Z^{-1}(l-n)\}$$
$$+c_1c_2\{2Z-c^2(l^2-n^2)Z^{-1}+c^2\zeta(n+l+1)(c^2-E)^{-1}\}]I_{2n}$$
$$+[c_1c_2\{2(c^2+E)-c^2\zeta^2(c^2-E)^{-1}+c^2\zeta Z^{-1}(l-n)\}$$
$$+c_2^2\{Z+c^2\zeta(n+l+1)(c^2-E)^{-1}\}]I_{2n+1}+c_2^2[(c^2+E)$$
$$-c^2\zeta^2(c^2-E)^{-1}]I_{2n+2}=0 \tag{39}$$

where the integrals I's are given by

$$I_i=\int_0^\infty \mathrm{d}r r^i\exp[-2\zeta r]=(2\zeta)^{-(i+1)}\Gamma(i+1). \tag{40}$$

Since this should be satisfied by all values of n for every ζ, the part that is explicity independent of n is equated to zero. This gives

$$\varepsilon=c^{-2}E=(1-\alpha^2\zeta^2)^{1/2} \tag{41}$$

and

$$c_1^2[Z-c^2Z^{-1}(l^2-n^2)]+[c_1^2\{(c^2+E)+c^2\zeta Z^{-1}(l-n)\}$$
$$+c_1c_2\{2Z-c^2(l^2-n^2)Z^{-1}-c^2\zeta(n+l+1)(c^2-E)^{-1}\}]\zeta^{-1}n$$
$$+[c_1c_2\{(c^2+E)+c^2\zeta Z^{-1}(l-n)\}+c_2^2\{Z+c^2\zeta$$
$$\times(n+l+1)(c^2-E)^{-1}\}]\zeta^{-2}n\left(n+\frac{1}{2}\right)=0. \tag{42}$$

Minimization of E by varying n as shown in figure 2 for different l gives

$$n=(l^2-\alpha^2Z^2)^{1/2}\equiv\gamma_l, \tag{43}$$

$$\varepsilon=(1+\gamma_l)N^{-1}, \tag{44}$$

and

$$\zeta=N^{-1}Z, \tag{45}$$

where

$$N=[(1+\gamma_l)^2+\alpha^2Z^2]^{1/2}. \tag{46}$$

The relationship (37) along with (43), (45) and (46) defines the small radial components of the ground state wavefunctions for various non-zero l, (functions $2p_{1/2}$, $3d_{3/2}$, $4f_{5/2}$, etc.). The lowest eigenvalues are given by (44).

4. Discussion

We have given here a few examples of the application of the minimax technique in relativistic atomic calculations. These examples clarify the advantage of the minimax procedure — that an upper bound to the ground state energy is always obtained from the use of a well-behaved trial function.

One important difficulty in relativistic quantum mechanical calculations is that

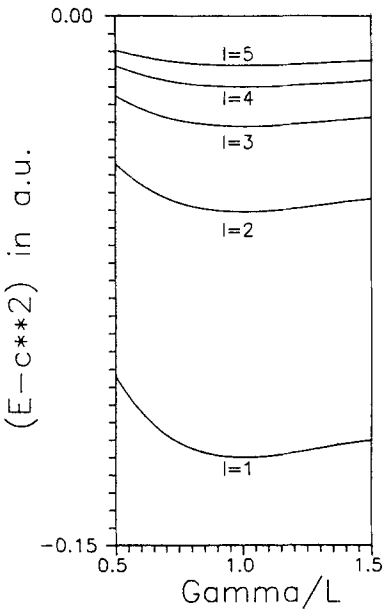

Figure 2. Numerical demonstration of the minimization of energy for $j = l - 1/2$. Energy E has been calculated from (42) subject to (38) and (41). We have taken $Z = 1$.

energies same as the ground state energy can be calculated with different spinors (Datta 1987). This difficulty does not arise in the energy minimization procedure starting from either (3) or (5).

For the sake of completeness we point out the $c \to \infty$ limit of the results calculated in this work. In this limit (3) changes into the purely nonrelativistic version

$$(u, [E + c^2 - Zr^{-1}]u) = \frac{1}{2}(u, p^2 u). \tag{47}$$

Solutions for $j = l + 1/2$ change since $n_{\min}$ in (29) changes to $(l + 1)$. Optimized parameters for $j = l - 1/2$ also change; the limiting values are $n_{\min} = l$, $N = l + 1$, and $\zeta = Z(l + 1)^{-1}$. In both the cases we find

$$\min E_l = c^2 - Z^2/2(l + 1)^2 \tag{48}$$

corresponding to wave functions with radial components

$$g_l(r) = N_l r^l \exp[-Zr/(l + 1)], \tag{49}$$
$$f_l(r) = 0.$$

These are precisely the nonrelativistic ground state energies and wavefunctions.

Acknowledgement

One of the authors (S N Datta) acknowledges support from the Department of Science and Technology for a research grant.

Appendix

Our objective is to evaluate the principal value $P(n)$ of the integral $\int_0^\infty dz\, f(z)$ where $f(z) = z^n(z-a)^{-1}\exp(-bz)$ with $a>0$, $b>0$ and $-1<n<1$.

We note that $|f(z)| \to 0$ as $z \to \infty$ for $-\pi/2 < \theta < \pi/2$ while $z = Re^{i\theta}$ such that $\int f(z)dz \to 0$ as $R \to \infty$, the integration being carried out over the right vertical semicircle. If $n>0$, there is no essential singularity of $f(z)$ at $z=0$. If n is not zero or an integer, positive or negative, then $(x=0, y=0)$ is the branch point with the x-axis as the branch cut.

For $n>0$ (but $n<1$) we draw the contour as shown in figure 3(a) and obtain

$$[\exp(2\pi in)-1]P(n) = i\pi[1-\exp(2\pi in)]a^n\exp(-ab) \tag{A.1}$$

where $P(n)$ is the principal value sought. Hence for $n \neq 0$ and $n \neq 1$,

$$P(n) = -i\pi a^n\exp(-ab) \tag{A.2}$$

For the positive integral values of n, as for the fractional values $-1<n<0$ and $n>1$, one may calculate the principal values by using the recurrence relationship

$$P(n+1) = b^{-(n+1)}\Gamma(n+1) + aP(n). \tag{A.3}$$

Thus for $-1<n<0$ we get

$$P(n) = -i\pi a^n\exp(-ab) - a^{-1}b^{-(n+1)}\Gamma(n+1). \tag{A.4}$$

$P(n)$ is obviously not continuous at $n=0$. The principal value at $n=0$ is evaluated by drawing the two contours in figure 3(b). Integration along the upper contour yields

$$P(0) = i\pi\exp(-ab) + \int_0^\infty dy(y+ia)^{-1}\exp(-iby) \tag{A.5}$$

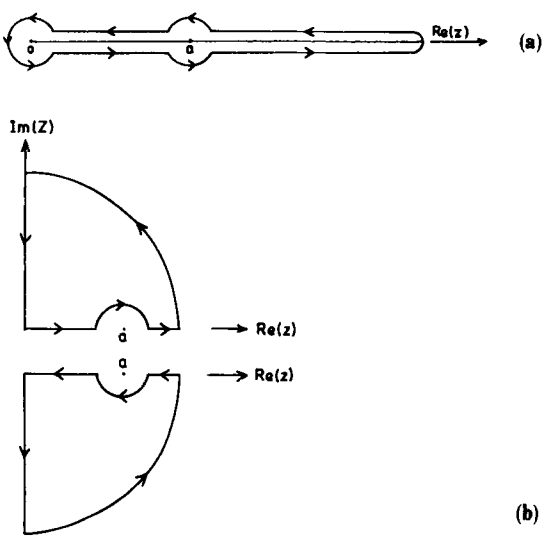

Figure 3. Contour for integration in the complex r plane: (a) $0<n<1$; (b) $n=0$. Two contours have been used in case (b).

and that along the lower contour gives the result

$$P(0) = -i\pi\exp(-ab) - \int_{-\infty}^{0} dy(y+ia)^{-1}\exp(-iby). \tag{A.6}$$

Combining these two expressions one obtains a real principal value

$$P(0) = \int_{0}^{\infty} dy(y^2+a^2)^{-1}(y\cos by - a\sin by). \tag{A.7}$$

Knowing $P(0)$, the value $P(i)$ where i is a positive integer can be easily calculated.

One notes that $P(n)$ is in general complex. It is purely imaginary in the range $0 < n < 1$, and purely real for $n = 0$ and for integral values of n.

References

Belifante F J 1991 *Comput. Phys.* **1** 319
Bethe H A and Salpeter E E 1957 *Quantum mechanics of one- and two-electron atoms* (Berlin: Springer-Verlag)
Darwin C G 1928 *Proc. R. Soc. London* **A118** 654
Datta S N 1987 *Pramana – J. Phys.* **28** 633
Datta S N and Devaiah G 1988 *Pramana – J. Phys.* **30** 387
Rosicky F and Mark F 1975 *J. Phys.* **B8** 2581