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Convergence of the non-relativistic and relativistic R-matrix expansions at the reaction volume boundary

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Abstract. The convergence of the non-relativistic and relativistic fixed-boundary-condition R-matrix expansions at the reaction volume boundary is discussed. It is shown that in the non-relativistic case the expansion of the wavefunction converges to this function at the boundary. In the relativistic case, however, the expansion does not generally converge to the wavefunction at the reaction surface because the set of relativistic basis functions spanning the interior of the reaction volume is incomplete on the surface. With one exception, this fact has not been recognized before and has been a source of errors in previous presentations of the relativistic R-matrix method. We present a corrected derivation of the R-matrix theory for the Dirac equation and generalize it to the multi-channel case. We also explain why, in spite of being based on an incorrect theory, the results of electron–atom and electron–ion scattering calculations performed so far within the framework of the relativistic R-matrix method were not afflicted by these errors.

1. Introduction

The original derivation of the non-relativistic R-matrix method presented by Wigner and Eisenbud [1] was shortly afterwards generalized by Goertzel [2] to systems described by the Dirac equation. Nearly thirty years later the relativistic generalization of the method was reinvestigated by Chang [3] in the context of electron scattering from atoms. A general presentation of the theory was followed by applications of the method to electron–atom and electron–ion scattering and atomic photoionization processes [4–19]. An alternative form of the relativistic R-matrix method, based on the Kohn variational principle, has been presented recently by Hamacher and Hinze [20] and a program implementing this alternative approach is now being written [21]. Such extensive work might suggest that the relativistic theory, like its non-relativistic counterpart, is well established. Therefore, it was astonishing that in rederiving the relativistic R-matrix formulae we found a fundamental expression relating the R-matrix to values of the large and small components of a wavefunction at the reaction volume boundary, as given in [2, 3], to be incorrect. The same false expression is contained in some of the other papers describing applications of the method [4–7, 9, 14]. The incorrectness of Goertzel's presentation of the relativistic R-matrix theory has been pointed out by Rosenthal [22]. However, his conclusion that the R-matrix theory for the Dirac equation could not be constructed is wrong [23]. The theory has been defended by Halderson [24] but his proof of existence of the theory has been non-rigourous and incomplete.

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Searching for an origin of the difficulty we realized that a crucial point was to answer the question: 'Does a fixed-boundary-condition R-matrix expansion of the wavefunction converge to this function at the reaction volume boundary?' This problem was in some sense sidestepped by Wigner and Eisenbud in the paper which originated the non-relativistic R-matrix theory [1]. They expressed the opinion that the expansion converged at the boundary and mentioned that, under some simplifying restrictions, they were able to prove this. However, a proof was not presented. Lane and Thomas [25] and Breit [26] discussed only non-uniform convergence of the derivative series while other well known reviews of the R-matrix theory [27–29] omitted the problem. In section 2 we give a simple proof that in the non-relativistic single-channel case the expansion is indeed convergent. In section 3 we consider the relativistic single-channel case and derive a somewhat unexpected result that generally the relativistic expansion does not converge to the wavefunction at the boundary. An immediate consequence of this result is that previous presentations of the relativistic R-matrix theory [2, 3] were erroneous. Generalization of the results obtained in section 3 to the relativistic multi-channel case is presented in section 4, where we correct Goertzel and Chang's errors. We also show that, in spite of being based on the incorrect theory, results of relativistic R-matrix calculations performed thus far fortuitously are not affected by these errors. The results obtained in section 3 are illustrated by an analytical example presented in appendix B.

2. The non-relativistic single-channel case

We want to find a solution to the radial Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + U(r) - E\right)P(r) = 0 \qquad 0 \leqslant r \leqslant a \tag{1}$$

augmented by an initial condition $P(0) = 0$, using the R-matrix method. Here $U(r)$ is an effective radial potential being a sum of a spherically symmetric scattering potential $V(r)$ and a centrifugal potential $\hbar^2 l(l+1)/2mr^2$. We generate an orthonormal basis set $\{P_i\}$ by solving the boundary value problem

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + U(r) - E_i\right)P_i(r) = 0 \qquad 0 \leqslant r \leqslant a \tag{2}$$

$$P_i(0) = 0 \qquad aP_i'(a) - b_{\mathrm{N}}P_i(a) = 0\,. \tag{3}$$

Here b_{N} is a fixed real constant and the subscript N refers to the non-relativistic case. Since eigensolutions to this Sturm–Liouville problem form a complete orthonormal set (they are assumed to be normalized to unity) on the interval $0 < r < a$ and $P(0) = P_i(0) = 0$, we can expand the function P in the basis $\{P_i\}$

$$P(r) = \sum_i C_i P_i(r) \qquad 0 \leqslant r < a \tag{4}$$

with

$$C_i = \int_0^a \mathrm{d}r\; P_i(r)P(r)\,. \tag{5}$$

To find the expansion coefficients $\{C_i\}$ we multiply equation (1) by $P_i(r)$, equation (2) by $P(r)$, subtract and integrate from $r = 0$ to $r = a$, obtaining

$$\int_0^a \mathrm{d}r \left(P_i(r)\frac{\mathrm{d}^2P(r)}{\mathrm{d}r^2} - P(r)\frac{\mathrm{d}^2P_i(r)}{\mathrm{d}r^2}\right) = \frac{2m}{\hbar^2}(E_i - E)\int_0^a \mathrm{d}r\; P_i(r)P(r)\,. \tag{6}$$

From the Green formula, the conditions satisfied by $P(r)$ and $P_i(r)$ at $r = 0$ and (5) we have

$$P_i(a)P'(a) - P(a)P_i'(a) = \frac{2m}{\hbar^2}(E_i - E)C_i \tag{7}$$

where a prime denotes differentiation with respect to the argument. Finally, employing (3) we obtain

$$P(r) = \frac{\hbar^2}{2ma}\left[aP'(a) - b_{\mathrm{N}}P(a)\right]\sum_i \frac{P_i(a)P_i(r)}{E_i - E} \qquad 0 \leqslant r < a\,. \tag{8}$$

Equation (8) is valid for r as close to a as we please and therefore for $r \to a^-$

$$P(a) = \frac{\hbar^2}{2ma}\left[aP'(a) - b_{\mathrm{N}}P(a)\right]\lim_{r\to a^-}\sum_i \frac{P_i(a)P_i(r)}{E_i - E} \tag{9}$$

since P is assumed to be a continuous function. Now we define the R-matrix for the case considered as

$$R(E) = \frac{\hbar^2}{2ma}\sum_i \frac{P_i(a)P_i(a)}{E_i - E}\,. \tag{10}$$

So defined the R-matrix satisfies the relation

$$P(a) = R(E)[aP'(a) - b_{\mathrm{N}}P(a)]\,. \tag{11}$$

This relation is by no means obvious, even though one might get this impression from some papers [26, 27, 30]. For equation (11) to be valid requires that one may interchange the operations $\lim_{r\to a^-}$ and $\sum_i$ in (9) while the question concerning the possibility of such an interchange is non-trivial. Below we show that in the non-relativistic case the interchange may be performed, i.e. (11) is indeed valid.

To this end we define an auxiliary function $\bar{P}$ as

$$\bar{P}(r) = \frac{\hbar^2}{2ma}\left[aP'(a) - b_{\mathrm{N}}P(a)\right]\sum_i \frac{P_i(a)P_i(r)}{E_i - E} \qquad 0 \leqslant r \leqslant a \tag{12}$$

i.e.

$$\bar{P}(r) = P(r) \qquad \text{for} \quad 0 \leqslant r < a \tag{13}$$

and

$$\bar{P}(a) = \frac{\hbar^2}{2ma}\left[aP'(a) - b_{\mathrm{N}}P(a)\right]\sum_i \frac{P_i(a)P_i(a)}{E_i - E} \qquad \text{for} \quad r = a\,. \tag{14}$$

It follows from the boundary condition satisfied by the basis functions $\{P_i\}$ that

$$a\bar{P}'(a) - b_{\mathrm{N}}\bar{P}(a) = 0\,. \tag{15}$$

The next step is to derive a differential equation satisfied by the function $\bar{P}$. Acting on both sides of (12) with an operator

$$\mathcal{H}_{\mathrm{N}} - E = \left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + U(r) - E\right) + \frac{\hbar^2}{2m}\delta(r-a)\left(\frac{d}{dr} - \frac{b_{\mathrm{N}}}{r}\right) \tag{16}$$

we obtain

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + U(r) - E\right)\bar{P}(r) = \frac{\hbar^2}{2ma}\left[aP'(a) - b_{\mathrm{N}}P(a)\right]\sum_i P_i(a)P_i(r) \qquad 0 \leqslant r \leqslant a\,. \tag{17}$$

The set $\{P_i\}$ is complete for $0 < r < a$ and a completeness relation for this open interval is

$$\sum_i P_i(r)P_i(r') = \delta(r - r') . \tag{18}$$

Here $0 < r < a$ and $0 < r' < a$. We cannot implicitly assume that this relation also holds for $r' = a$. For that reason we presume

$$\sum_i P_i(r)P_i(a) = A_{\mathrm{N}}\delta(r - a) \qquad 0 < r \leqslant a \tag{19}$$

where the constant A_{N} remains for the moment undetermined. Comparison of equations (15), (17) and (19) shows that the function $\bar{P}$ satisfies a singular inhomogeneous second-order differential equation

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + U(r) - E\right)\bar{P}(r) = A_{\mathrm{N}}\frac{\hbar^2}{2ma}\left[aP'(a) - b_{\mathrm{N}}P(a)\right]\delta(r - a) \qquad 0 \leqslant r \leqslant a . \tag{20}$$

We exclude for the moment the case $b_{\mathrm{N}} = \mp\infty$. Integrating both sides of equation (20) twice over an infinitesimal interval $a - \varepsilon \leqslant r \leqslant a$ ($\varepsilon \to 0^+$) we obtain

$$-\frac{\hbar^2}{2m}\left[\bar{P}'(a) - P'(a)\right] = A_{\mathrm{N}}\frac{\hbar^2}{2ma}\left[aP'(a) - b_{\mathrm{N}}P(a)\right] \tag{21}$$

$$-\frac{\hbar^2}{2m}\left[\bar{P}(a) - P(a)\right] = 0 . \tag{22}$$

Together with (15), equations (21) and (22) constitute a set of three algebraic equations for three unknowns A_{N}, $\bar{P}(a)$ and $\bar{P}'(a)$. The solution to this system is

$$A_{\mathrm{N}} = 1 \tag{23}$$

$$\bar{P}(a) = P(a) \tag{24}$$

$$\bar{P}'(a) = \frac{b_{\mathrm{N}}}{a}P(a) \tag{25}$$

provided $b_{\mathrm{N}} \neq \mp\infty$. For completeness of our discussion we observe that for $b_{\mathrm{N}} = \mp\infty$

$$A_{\mathrm{N}} = 0 \qquad \bar{P}(a) = 0 . \tag{26}$$

These considerations lead to the following important conclusions valid provided $b_{\mathrm{N}} \neq \mp\infty$. The set $\{P_i\}$ generated by the boundary value problem (2), (3) is complete on the interval $0 < r \leqslant a$. The expansion (12) defining the function $\bar{P}$ converges to P for any r belonging to this interval *including* the point $r = a$ (although in general the derivative series $\bar{P}'(a)$ does *not* converge to $P'(a)$ unless the ratio b_{N}/a coincides with the natural logarithmic derivative at the energy E [31]). Therefore the interchange of the operations $\lim_{r\to a^-}$ and $\sum_i$ in (9) is admissible and the R-matrix defined by (10) indeed satisfies the relation (11).

There are claims in the literature that the non-relativistic fixed-boundary-condition basis set $\{P_i\}$ is not complete at $r = a$ [32–34]. We have proved above (cf equations (19) and (23)) that as long as $b_{\mathrm{N}} \neq \mp\infty$ these claims are incorrect.

3. The relativistic single-channel case

In this section we apply the procedure outlined above to the relativistic case. We attempt to solve the radial Dirac equation

$$\begin{pmatrix} mc^2 - E + V(r) - c\hbar(\mathrm{d}/\mathrm{d}r - \kappa/r) \\ c\hbar(\mathrm{d}/\mathrm{d}r + \kappa/r) - mc^2 - E + V(r) \end{pmatrix}\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = 0 \qquad 0 \leqslant r \leqslant a \tag{27}$$

with an initial condition $P(0) = 0$. We generate an orthonormal basis set $\{(P_i, Q_i)^{\mathrm{T}}\}$ by solving the following boundary value problem

$$\begin{pmatrix} mc^2 - E_i + V(r) - c\hbar(\mathrm{d}/\mathrm{d}r - \kappa/r) \\ c\hbar(\mathrm{d}/\mathrm{d}r + \kappa/r) - mc^2 - E_i + V(r) \end{pmatrix} \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} = 0 \qquad 0 \leqslant r \leqslant a \tag{28}$$

$$P_i(0) = 0 \qquad (2mac/\hbar)Q_i(a) - b_{\mathrm{R}} P_i(a) = 0\,. \tag{29}$$

Here b_{R} is a fixed real constant and the subscript R refers to the relativistic case. To avoid a misunderstanding we observe that the constant b_{R} does not coincide with the constant b used by Norrington and Grant [6, 7] and Thumm and Norcross [14, 18]. The constants b_{R} and b are related by $b_{\mathrm{R}} = b + \kappa$. Next, we expand the function $(P, Q)^{\mathrm{T}}$ in this basis

$$\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = \sum_i C_i \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} \qquad 0 < r < a\,. \tag{30}$$

The coefficients $\{C_i\}$ are given by

$$C_i = \int_0^a \mathrm{d}r\ [P_i(r)P(r) + Q_i(r)Q(r)] \tag{31}$$

provided the functions $\{(P_i, Q_i)^{\mathrm{T}}\}$ have been normalized to unity. To find the coefficients $\{C_i\}$ we multiply (27) by $(P_i(r), Q_i(r))$, equation (28) by $(P(r), Q(r))$, subtract and get

$$(E_i - E)[P_i(r)P(r) + Q_i(r)Q(r)] + c\hbar\frac{\mathrm{d}}{\mathrm{d}r}[Q_i(r)P(r) - P_i(r)Q(r)] = 0\,. \tag{32}$$

Integrating equation (32) from $r = 0$ to $r = a$, using the boundary conditions satisfied by $P(r)$ and $P_i(r)$ at $r = 0$ and utilizing (31) we have

$$C_i = \frac{c\hbar}{E_i - E}[P_i(a)Q(a) - P(a)Q_i(a)]\,. \tag{33}$$

Finally, employing the boundary condition satisfied by $P_i(a)$ and $Q_i(a)$ we find

$$\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = \frac{\hbar^2}{2ma}\left[(2mac/\hbar)Q(a) - b_{\mathrm{R}}P(a)\right]\sum_i \frac{P_i(a)}{E_i - E}\begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} \qquad 0 < r < a \tag{34}$$

and for $r \to a^-$

$$\begin{pmatrix} P(a) \\ Q(a) \end{pmatrix} = \frac{\hbar^2}{2ma}\left[(2mac/\hbar)Q(a) - b_{\mathrm{R}}P(a)\right]\lim_{r\to a^-}\sum_i \frac{P_i(a)}{E_i - E}\begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix}. \tag{35}$$

Now, following Chang [3], we *define* the relativistic R-matrix for the case considered as

$$R(E) = \frac{\hbar^2}{2ma}\sum_i \frac{P_i(a)P_i(a)}{E_i - E}\,. \tag{36}$$

This author, followed by others [4–7, 9, 14, 18], asserts that so defined the R-matrix satisfies in the single-channel case a relation

$$P(a) \overset{?}{=} R(E)\left[(2mac/\hbar)Q(a) - b_{\mathrm{R}}P(a)\right] \tag{37}$$

analogous to the non-relativistic equation (11). Below we show that in general the relation (37) does *not* hold.

We define an auxiliary two-component function $(\bar{P}, \bar{Q})^{\mathrm{T}}$

$$\begin{pmatrix} \bar{P}(r) \\ \bar{Q}(r) \end{pmatrix} = \frac{\hbar^2}{2ma}\left[(2mac/\hbar)Q(a) - b_{\mathrm{R}}P(a)\right]\sum_i \frac{P_i(a)}{E_i - E}\begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} \qquad \text{for} \quad 0 \leqslant r \leqslant a \tag{38}$$

i.e.

$$\begin{pmatrix} \bar{P}(r) \\ \bar{Q}(r) \end{pmatrix} = \begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} \qquad \text{for} \quad 0 < r < a \tag{39}$$

and

$$\begin{pmatrix} \bar{P}(a) \\ \bar{Q}(a) \end{pmatrix} = \frac{\hbar^2}{2ma} \left[(2mac/\hbar) Q(a) - b_{\mathrm{R}} P(a) \right] \sum_i \frac{P_i(a)}{E_i - E} \begin{pmatrix} P_i(a) \\ Q_i(a) \end{pmatrix} \qquad \text{for} \quad r = a\,. \tag{40}$$

Obviously,

$$(2mac/\hbar)\bar{Q}(a) - b_{\mathrm{R}}\bar{P}(a) = 0 \tag{41}$$

because of the boundary condition satisfied by the basis functions $\left\{(P_i, Q_i)^{\mathrm{T}}\right\}$ at $r = a$. Note also that although the right-hand sides of equations (35) and (40) look similar, nevertheless, they may differ because the operations $\lim_{r\to a^-}$ and $\sum_i$ do not necessarily commute.

To find a relation between $(\bar{P}(a), \bar{Q}(a))^{\mathrm{T}}$ and $(P(a), Q(a))^{\mathrm{T}}$ we act on both sides of (38) with the operator

$$\begin{aligned} \mathcal{H}_{\mathrm{R}} - E = &\begin{pmatrix} mc^2 - E + V(r) - c\hbar(\mathrm{d}/\mathrm{d}r - \kappa/r) \\ c\hbar(\mathrm{d}/\mathrm{d}r + \kappa/r) - mc^2 - E + V(r) \end{pmatrix} \\ &+ \delta(r-a) \begin{pmatrix} -\eta\, b_{\mathrm{R}}(\hbar^2/2ma) & \eta\, c\hbar \\ -(1-\eta)\, c\hbar & (1-\eta)\,(2mac^2)/b_{\mathrm{R}} \end{pmatrix} \end{aligned} \tag{42}$$

where the singular term on the right-hand side of the above definition is the relativistic generalization of the Bloch surface operator with η being an arbitrary real number. We obtain

$$(\mathcal{H}_{\mathrm{R}} - E) \begin{pmatrix} \bar{P}(r) \\ \bar{Q}(r) \end{pmatrix} = \frac{\hbar^2}{2ma} \left[(2mac/\hbar) Q(a) - b_{\mathrm{R}} P(a) \right] \sum_i P_i(a) \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix}. \tag{43}$$

For $0 < r < a$ the right-hand side of (43) must vanish because of (27) and (39). Since the set $\left\{(P_i, Q_i)^{\mathrm{T}}\right\}$ is complete for $0 < r < a$, we have from the definition of completeness

$$\sum_i \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} \begin{pmatrix} P_i(r') & Q_i(r') \end{pmatrix} = \delta(r - r') \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{44}$$

for $0 < r < a$ and $0 < r' < a$. This completeness relation is not, however, satisfied for $r' = a$ because of the restrictive boundary conditions (29) which the functions $\left\{(P_i, Q_i)^{\mathrm{T}}\right\}$ must obey at $r = a$. The form of the conditions (29) suggests that for $r' = a$ instead of (44) we must have

$$\sum_i \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} \begin{pmatrix} P_i(a) & Q_i(a) \end{pmatrix} = A_{\mathrm{R}}\delta(r - a) \begin{pmatrix} 1 & b_{\mathrm{R}}(\hbar/2mac) \\ b_{\mathrm{R}}(\hbar/2mac) & b_{\mathrm{R}}^2(\hbar/2mac)^2 \end{pmatrix} \tag{45}$$

for $0 < r \leqslant a$. The constant A_{R} remains for the moment undetermined. Comparing (41), (43) and (45) we find that the function $(\bar{P}, \bar{Q})^{\mathrm{T}}$ satisfies a singular inhomogeneous differential equation

$$\begin{aligned} &\begin{pmatrix} mc^2 - E + V(r) - c\hbar(\mathrm{d}/\mathrm{d}r - \kappa/r) \\ c\hbar(\mathrm{d}/\mathrm{d}r + \kappa/r) - mc^2 - E + V(r) \end{pmatrix} \begin{pmatrix} \bar{P}(r) \\ \bar{Q}(r) \end{pmatrix} \\ &\qquad = A_{\mathrm{R}} \frac{\hbar^2}{2ma} \left[(2mac/\hbar) Q(a) - b_{\mathrm{R}} P(a) \right] \delta(r - a) \begin{pmatrix} 1 \\ b_{\mathrm{R}}(\hbar/2mac) \end{pmatrix}. \end{aligned} \tag{46}$$

Integrating both sides of this equation over an interval $a-\varepsilon \leqslant r \leqslant a$ ($\varepsilon \to 0^+$) we obtain

$$\begin{pmatrix} -c\hbar\left[\bar{Q}(a)-Q(a)\right] \\ c\hbar\left[\bar{P}(a)-P(a)\right] \end{pmatrix} = A_{\mathrm{R}}\frac{\hbar^2}{2ma}\left[(2mac/\hbar)Q(a)-b_{\mathrm{R}}P(a)\right]\begin{pmatrix} 1 \\ b_{\mathrm{R}}(\hbar/2mac) \end{pmatrix}. \tag{47}$$

Equations (41) and (47) constitute a set of three algebraic equations for three unknowns A_{R}, $\bar{P}(a)$ and $\bar{Q}(a)$. The solution to this system is

$$A_{\mathrm{R}} = \frac{(2mac/\hbar)^2}{b_{\mathrm{R}}^2+(2mac/\hbar)^2} \tag{48}$$

$$\bar{P}(a) = \frac{(2mac/\hbar)}{b_{\mathrm{R}}^2+(2mac/\hbar)^2}\left[(2mac/\hbar)P(a)+b_{\mathrm{R}}Q(a)\right] \tag{49}$$

$$\bar{Q}(a) = \frac{b_{\mathrm{R}}}{b_{\mathrm{R}}^2+(2mac/\hbar)^2}\left[(2mac/\hbar)P(a)+b_{\mathrm{R}}Q(a)\right]. \tag{50}$$

Notice that A_{R} is independent of $P(a)$ and $Q(a)$ as it should be.

These results have important consequences. Utilizing equation (48) the 'completeness' relation (45) is rewritten in the form

$$\sum_i \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix}\begin{pmatrix} P_i(a) & Q_i(a) \end{pmatrix} = \frac{\delta(r-a)}{b_{\mathrm{R}}^2+(2mac/\hbar)^2}\begin{pmatrix} (2mac/\hbar)^2 & b_{\mathrm{R}}(2mac/\hbar) \\ b_{\mathrm{R}}(2mac/\hbar) & b_{\mathrm{R}}^2 \end{pmatrix} \tag{51}$$

for $0<r\leqslant a$. An immediate observation is that it is impossible to find such a value of the constant b_{R} for which the right-hand side of equation (51) would be $\delta(r-a)\left(\begin{smallmatrix} 1 & 0 \\ 0 & 1 \end{smallmatrix}\right)$. This means that the set $\left\{(P_i, Q_i)^{\mathrm{T}}\right\}$ generated by the boundary value problem (28), (29) is *not* complete in the space of two-component functions $(P, Q)^{\mathrm{T}}$ at the end point $r=a$. We note, however, that for $b_{\mathrm{R}}=0$ the set of the upper components $\{P_i\}$ is complete at $r=a$ for P's while for $b_{\mathrm{R}}=\mp\infty$ the set of the lower components $\{Q_i\}$ is complete at $r=a$ for Q's. These general statements are excellently illustrated by (49) and (50). In general $\bar{P}(a)\neq P(a)$ and $\bar{Q}(a)\neq Q(a)$ but for $b_{\mathrm{R}}=0$ we have $\bar{P}(a)=P(a)$ and $\bar{Q}(a)=0$ while for $b_{\mathrm{R}}=\mp\infty$ we have $\bar{P}(a)=0$ and $\bar{Q}(a)=Q(a)$. We observe also that there is an exceptional case when the equalities $\bar{P}(a)=P(a)$ and $\bar{Q}(a)=Q(a)$ hold simultaneously. It follows immediately from (49) and (50) that this happens if and only if b_{R} is a natural boundary condition constant for the energy E, i.e. if and only if b_{R} is equal to the ratio $(2mac/\hbar)Q(a)/P(a)$. In such a case E coincides with one of the eigenvalues E_i of the boundary value problem (28), (29) and $\bar{P}(a)=P_i(a)=P(a)$, $\bar{Q}(a)=Q_i(a)=Q(a)$.

We have arrived at the moment when we may derive a relativistic counterpart of the relation (11). Simple algebraic manipulations with (35), (36), (40) and (49) give

$$P(a) = \left(R(E)-\frac{b_{\mathrm{R}}}{b_{\mathrm{R}}^2+(2mac/\hbar)^2}\right)\left[(2mac/\hbar)Q(a)-b_{\mathrm{R}}P(a)\right]. \tag{52}$$

This relation must replace, in the single-channel case, the relation (37) which is erroneous unless $b_{\mathrm{R}}=0$. An analogous expression for the lower component obtained from (35), (36), (40) and (50) is

$$Q(a) = \left(\frac{b_{\mathrm{R}}}{(2mac/\hbar)}R(E)+\frac{(2mac/\hbar)}{b_{\mathrm{R}}^2+(2mac/\hbar)^2}\right)\left[(2mac/\hbar)Q(a)-b_{\mathrm{R}}P(a)\right]. \tag{53}$$

Equations (52) and (53) constitute a set of two algebraic homogeneous equations for $P(a)$ and $Q(a)$. This system is consistent since its determinant vanishes as may be easily verified.

Here it is appropriate to discuss the non-relativistic limit of the results obtained in this section. Choosing $b_{\mathrm{R}} = b_{\mathrm{N}} + \kappa$ and allowing $c \to \infty$ equations (27) and (52) give

$$P(a) = R(E)\left[aP'(a) - b_{\mathrm{N}}P(a)\right] \tag{54}$$

which is immediately recognized to be identical with (11) as one would expect. The same procedure applied to (48) and (49) shows that in the non-relativistic limit they become identical with (23) and (24). A proof of the equivalence of the non-relativistic limit of (50) and (25) is only slightly more involved.

In actual numerical calculations one must deal somehow with an infinite expansion in the definition of the R-matrix (36). A simple truncation of the series without any correction is inappropriate since distant R-matrix poles may significantly contribute to the sum which is, in general, very slowly convergent. Two methods allowing the minimization of an error due to the truncation have been proposed by Buttle [35] and Zvijac *et al* [36]. In all relativistic calculations performed so far the Buttle correction has been used and therefore here we discuss an application of this method. The error due to the truncation of the R-matrix expansion after the first M terms is partially compensated approximating in (52)

$$R(E) - \frac{b_{\mathrm{R}}}{b_{\mathrm{R}}^2 + (2mac/\hbar)^2} \simeq \frac{\hbar^2}{2ma}\sum_{i=1}^{M}\frac{P_i(a)P_i(a)}{E_i - E} - \frac{\hbar^2}{2ma}\sum_{i=1}^{M}\frac{P_i^{(0)}(a)P_i^{(0)}(a)}{E_i^{(0)} - E} + \frac{P^{(0)}(a)}{(2mac/\hbar)Q^{(0)}(a) - b_{\mathrm{R}}P^{(0)}(a)} \tag{55}$$

where $(P^{(0)}, Q^{(0)})^{\mathrm{T}}$ is a known solution to the initial-value problem (27) with V replaced by some suitable chosen potential $V^{(0)}$ while $\left\{(P_i^{(0)}, Q_i^{(0)})^{\mathrm{T}}\right\}$ and $\left\{E_i^{(0)}\right\}$ are eigenfunctions and eigenvalues of the corresponding boundary value problem (28), (29) again with V replaced by $V^{(0)}$.

It would be desirable to illustrate the results obtained in this section with some analytically solvable example. Unfortunately, we have not been able to find an example exactly related to the problem considered here. (In fact, if such an example could be easily constructed, it probably would have been found by Goertzel and Chang, indicating to them errors in their arguments.) Even in the simplest case of a free Dirac particle R-matrix poles are given by solutions of transcendental equations. We observe, however, that the R-matrix technique is a general mathematical tool which may be applied also to equations which are not related to any physical situation. In appendix A we generalize the results obtained in this section for the Dirac equation to a wider class of two coupled first-order linear differential equations. In appendix B we employ the results of this generalization and provide an analytically solvable example illustrating to some extent the results we have obtained in this section.

4. The relativistic multi-channel case

Below we generalize the results obtained in section 3 to the case of low-energy electron scattering from an N-electron atom. We intend to make this section self-contained and self-explanatory and therefore some overlap with the material presented in the previous section is unavoidable although we have attempted to minimize repetitions. The nucleus is assumed to be an infinitely heavy point charge $+Ze$. We neglect all second-order magnetic interactions (i.e. spin–spin, orbit–orbit and spin–other-orbit) as well as retardation effects. The Dirac equation for the system considered has the form

$$[H(\boldsymbol{X}) - E]\,\Psi(\boldsymbol{X}) = 0 \tag{56}$$

where H is the Dirac–Coulomb Hamiltonian

$$H(\boldsymbol{X}) = \sum_{k=1}^{N+1}\left(-\mathrm{i}c\hbar\boldsymbol{\alpha}_k\cdot\boldsymbol{\nabla}_k + \beta_k mc^2 - \frac{Ze^2}{r_k}\right) + \frac{1}{2}\sum_{j,k=1}^{N+1}\frac{e^2}{|\boldsymbol{r}_j - \boldsymbol{r}_k|} \tag{57}$$

with the matrices $\boldsymbol{\alpha}$ and β defined as usual [37] and E is a preselected total energy of the system including rest energies of the electrons. The subscript k refers to the kth electron and $\boldsymbol{X}$ stands collectively for spatial coordinates of $N+1$ electrons, i.e. $\boldsymbol{X} = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N+1})$. In the following we shall also find the abbreviation $\boldsymbol{R}_{-k} = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{k-1}, \boldsymbol{r}_{k+1}, \ldots, \boldsymbol{r}_{N+1})$ to be convenient. Moreover, throughout this section we denote $\boldsymbol{R}_{-(N+1)} \equiv \boldsymbol{R}$ and $\boldsymbol{r}_{N+1} \equiv \boldsymbol{r}$ wherever this does not lead to misunderstanding.

From now on we assume that $\Psi(\boldsymbol{X})$ is an eigenfunction of the total parity, the total angular momentum and its projection on a quantization axis with quantum numbers $\mathcal{P}$, $\mathcal{J}$ and $\mathcal{M}$, respectively. We restrict ourselves to those energies E for which only one electron may escape to infinity. A set of target states, which we wish to include in calculations, will be denoted by $\{\Phi_{\Gamma PJM}\}$, where P, J and M are the parity, total angular momentum and its projection quantum numbers of the target, respectively. All other quantum numbers characterizing the target state are denoted collectively by Γ. The functions $\Phi_{\Gamma PJM}(\boldsymbol{R})$ are combined with spherical spinors $\Omega_{\pm\kappa m}(\hat{\boldsymbol{r}})$ to form the channel functions for the large (Θ_γ) and small ($\widetilde{\Theta}_\gamma$) components

$$\Theta_\gamma(\boldsymbol{R}, \hat{\boldsymbol{r}}) = \sum_{mM}\Phi_{\Gamma PJM}(\boldsymbol{R})\begin{pmatrix}\Omega_{\kappa m}(\hat{\boldsymbol{r}})\\ 0\end{pmatrix}\langle JMjm \mid \mathcal{J}\mathcal{M}\rangle \tag{58}$$

$$\widetilde{\Theta}_\gamma(\boldsymbol{R}, \hat{\boldsymbol{r}}) = \sum_{mM}\Phi_{\Gamma PJM}(\boldsymbol{R})\begin{pmatrix}0\\ \Omega_{-\kappa m}(\hat{\boldsymbol{r}})\end{pmatrix}\langle JMjm \mid \mathcal{J}\mathcal{M}\rangle \tag{59}$$

where $\langle JMjm \mid \mathcal{J}\mathcal{M}\rangle$ is the Clebsch–Gordan coefficient. The composite index $\gamma = (\Gamma\mathcal{P}\mathcal{J}\mathcal{M}PJ\kappa)$ defines a scattering channel. The total wavefunction $\Psi(\boldsymbol{X})$ may then be written as

$$\Psi(\boldsymbol{X}) = \mathcal{A}\sum_\gamma\left(\Theta_\gamma(\boldsymbol{R}, \hat{\boldsymbol{r}})\frac{P_\gamma(r)}{r} + \mathrm{i}\widetilde{\Theta}_\gamma(\boldsymbol{R}, \hat{\boldsymbol{r}})\frac{Q_\gamma(r)}{r}\right) \tag{60}$$

where $P_\gamma(r)$ and $Q_\gamma(r)$ are the large and small components of the radial wavefunction of the scattered electron in the channel γ and $\mathcal{A}$ is the antisymmetrization operator.

To construct the R-matrix theory for the system under consideration we divide the three-dimensional configuration space of the system into two regions separated by an R-matrix sphere $\mathcal{V}$ of radius a centred at the nucleus. The radius of the sphere $\mathcal{V}$ is chosen such that outside the sphere exchange between the projectile and target electrons may be neglected. The reaction hypervolume $\mathcal{T}$ in the $3(N+1)$-dimensional configuration space of the system is defined as

$$\mathcal{T} = \{\boldsymbol{X} : \max(r_1, \ldots, r_{N+1}) \leqslant a\} \tag{61}$$

and is bounded by the hypersurface $\mathcal{S}$

$$\mathcal{S} = \{\boldsymbol{X} : \max(r_1, \ldots, r_{N+1}) = a\}\ . \tag{62}$$

We shall need a set $\{\Psi_K\}$ of eigenfunctions of a Hermitian operator $\mathcal{H} = H + L$, where the integral kernel of the Bloch surface operator L is

$$L(\boldsymbol{X}, \boldsymbol{X}') = \eta\sum_{k=1}^{N+1}\sum_\gamma\delta(r_k - a)\Theta_\gamma(\boldsymbol{R}_{-k}, \hat{\boldsymbol{r}}_k)\Theta_\gamma^+(\boldsymbol{R}'_{-k}, \hat{\boldsymbol{r}}'_k)$$
$$\times\frac{\delta(r'_k - a)}{a^2}\left(-\frac{\hbar^2}{2m}\frac{b_\gamma}{a} + \mathrm{i}c\hbar\hat{\boldsymbol{r}}'_k\cdot\boldsymbol{\alpha}_k\right)$$

$$+(1-\eta)\sum_{k=1}^{N+1}\sum_{\gamma}\delta(r_k-a)\widetilde{\Theta}_{\gamma}(\boldsymbol{R}_{-k},\hat{\boldsymbol{r}}_k)\widetilde{\Theta}_{\gamma}^{+}(\boldsymbol{R}'_{-k},\hat{\boldsymbol{r}}'_k)$$
$$\times\frac{\delta(r'_k-a)}{a^2}\left(2mc^2\frac{a}{b_\gamma}+\mathrm{i}c\hbar\hat{\boldsymbol{r}}'_k\cdot\boldsymbol{\alpha}_k\right) \tag{63}$$

and η is an arbitrary real number. The construction of the basis set $\{\Psi_K\}$ proceeds as follows. Let N_γ be a number of channels included in calculations. We generate N_γ single-particle radial basis sets $\{(p_{\gamma i}, q_{\gamma i})^{\mathrm{T}}\}$ solving a boundary value problem

$$\begin{pmatrix} mc^2-\epsilon_{\gamma i}+v_\gamma(r) & -c\hbar(\mathrm{d}/\mathrm{d}r-\kappa_\gamma/r) \\ c\hbar(\mathrm{d}/\mathrm{d}r+\kappa_\gamma/r) & -mc^2-\epsilon_{\gamma i}+v_\gamma(r)\end{pmatrix}\begin{pmatrix} p_{\gamma i}(r) \\ q_{\gamma i}(r)\end{pmatrix}=0 \qquad 0\leqslant r\leqslant a \tag{64}$$

$$p_{\gamma i}(0)=0 \qquad (2mac/\hbar)q_{\gamma i}(a)-b_\gamma p_{\gamma i}(a)=0 \tag{65}$$

where v_γ, suitable chosen potentials, and b_γ, the same real constant which appears in (63), may differ for different channels. We note that, as in the single-channel case, the constants b_γ do not coincide with the constant b used by Norrington and Grant [6, 7] and Thumm and Norcross [14, 18]. For a specific channel index γ, the functions $\{(p_{\gamma i}, q_{\gamma i})^{\mathrm{T}}\}$ form a complete orthonormal set for $0<r<a$, i.e.

$$\sum_i \begin{pmatrix} p_{\gamma i}(r) \\ q_{\gamma i}(r)\end{pmatrix}\begin{pmatrix} p_{\gamma i}(r') & q_{\gamma i}(r')\end{pmatrix}=\delta(r-r')\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \tag{66}$$

for $0<r<a$ and $0<r'<a$ but

$$\sum_i \begin{pmatrix} p_{\gamma i}(r) \\ q_{\gamma i}(r)\end{pmatrix}\begin{pmatrix} p_{\gamma i}(a) & q_{\gamma i}(a)\end{pmatrix}=A_\gamma\delta(r-a)\begin{pmatrix}1 & b_\gamma(\hbar/2mac)\\ b_\gamma(\hbar/2mac) & b_\gamma^2(\hbar/2mac)^2\end{pmatrix} \tag{67}$$

for $r'=a$ and $0<r\leqslant a$ because of the boundary condition (65). (From section 3 we know that $A_\gamma=(2mac/\hbar)^2/(b_\gamma^2+(2mac/\hbar)^2)$ but for the reasons explained in the introduction to this section we shall for the moment treat A_γ as an undetermined constant.) In the next step we combine the channel functions Θ_γ and $\widetilde{\Theta}_\gamma$ with the single-particle functions $p_{\gamma i}$ and $q_{\gamma i}$ and antisymmetrize the resulting function obtaining

$$\Xi_{\gamma i}(\boldsymbol{X})=\mathcal{A}\left(\Theta_\gamma(\boldsymbol{R},\hat{\boldsymbol{r}})\frac{p_{\gamma i}(r)}{r}+\mathrm{i}\widetilde{\Theta}_\gamma(\boldsymbol{R},\hat{\boldsymbol{r}})\frac{q_{\gamma i}(r)}{r}\right). \tag{68}$$

The functions $\{\Xi_{\gamma i}\}$ form the orthonormal set. Then, we diagonalize the operator $\mathcal{H}$ using as a primary basis the set $\{\Xi_{\gamma i}\}$ and get the needed eigenfunctions $\{\Psi_K\}$

$$\Psi_K(\boldsymbol{X})=\sum_{\gamma i}\Xi_{\gamma i}(\boldsymbol{X})U_{\gamma i,K} \tag{69}$$

where $U_{\gamma i,K}$ are elements of a unitary diagonalizing matrix. An eigenvalue of the operator $\mathcal{H}$ corresponding to the function Ψ_K will be denoted by E_K. We observe that the functions $\{\Xi_{\gamma i}\}$ and $\{\Psi_K\}$ satisfy the boundary conditions

$$\left(L\Xi_{\gamma i}\right)(\boldsymbol{X})=0 \qquad (L\Psi_K)(\boldsymbol{X})=0\,. \tag{70}$$

We may expand the total wavefunction of the system in the set $\{\Psi_K\}$

$$\Psi(\boldsymbol{X})=\sum_K C_K\Psi_K(\boldsymbol{X}) \tag{71}$$

where the expansion coefficients $C_K=\langle\Psi_K|\,\Psi\rangle$ are to be determined. It is expected that the expansion (71) is valid only in the interior of the reaction hypervolume $\mathcal{T}$ and *not* on the hypersurface $\mathcal{S}$ because of the restrictive boundary condition (70) satisfied by the basis functions $\{\Psi_K\}$. To find the expansion coefficients we add the term $L\Psi$ to both sides of

(56), substitute the expansion (71) into the left-hand side of the obtained expression and project the resulting equation onto one of the states Ψ_K obtaining

$$C_K = \frac{\langle \Psi_K |\, L\Psi\rangle}{E_K - E} \tag{72}$$

hence

$$\Psi(\boldsymbol{X}) = \sum_K \frac{\langle \Psi_K |\, L\Psi\rangle}{E_K - E} \Psi_K(\boldsymbol{X}) \,. \tag{73}$$

We emphasize again that this expansion is expected to be valid only in the interior of the reaction volume, $\mathcal{T} \setminus \mathcal{S}$. Projecting (73) onto the channel functions Θ_γ and $\widetilde{\Theta}_\gamma$ we have for the radial functions P_γ and Q_γ

$$\begin{pmatrix} P_\gamma(r) \\ Q_\gamma(r) \end{pmatrix} = \frac{\hbar^2}{2ma} \sum_K \sum_{\gamma'} \frac{y_{\gamma' K}(a)}{E_K - E} \left[(2mac/\hbar) Q_{\gamma'}(a) - b_{\gamma'} P_{\gamma'}(a)\right] \begin{pmatrix} y_{\gamma K}(r) \\ z_{\gamma K}(r) \end{pmatrix} \qquad 0 < r < a \tag{74}$$

and

$$\begin{pmatrix} P_\gamma(a) \\ Q_\gamma(a) \end{pmatrix} = \frac{\hbar^2}{2ma} \lim_{r\to a^-} \sum_K \sum_{\gamma'} \frac{y_{\gamma' K}(a)}{E_K - E} \left[(2mac/\hbar) Q_{\gamma'}(a) - b_{\gamma'} P_{\gamma'}(a)\right] \begin{pmatrix} y_{\gamma K}(r) \\ z_{\gamma K}(r) \end{pmatrix} \tag{75}$$

because of continuity of the functions P_γ and Q_γ at $r = a$. The functions $y_{\gamma K}$ and $z_{\gamma K}$ are linear combinations of the radial basis functions $p_{\gamma i}$ and $q_{\gamma i}$

$$\begin{pmatrix} y_{\gamma K}(r) \\ z_{\gamma K}(r) \end{pmatrix} = \sum_i \begin{pmatrix} p_{\gamma i}(r) \\ q_{\gamma i}(r) \end{pmatrix} U_{\gamma i, K} \,. \tag{76}$$

Now, we define a matrix $\mathcal{R}(E)$ by the relation

$$\mathbf{P}(a) = \mathcal{R}(E)\left[(2mac/\hbar)\mathbf{Q}(a) - \mathbf{b}\mathbf{P}(a)\right]. \tag{77}$$

Here $\mathbf{P}(a)$ and $\mathbf{Q}(a)$ are column vectors with N_γ rows and elements $P_\gamma(a)$ and $Q_\gamma(a)$ while $\mathbf{b}$ is a diagonal $N_\gamma \times N_\gamma$ matrix with elements $b_\gamma \delta_{\gamma\gamma'}$. It follows from equation (75) that the matrix $\mathcal{R}$ has elements

$$\mathcal{R}_{\gamma\gamma'}(E) = \frac{\hbar^2}{2ma} \lim_{r\to a^-} \sum_K \frac{y_{\gamma K}(r) y_{\gamma' K}(a)}{E_K - E} \tag{78}$$

and therefore may be written in the form

$$\mathcal{R}(E) = \frac{\hbar^2}{2ma} \lim_{r\to a^-} \sum_K \frac{\mathbf{Y}_K(r)\mathbf{Y}_K^{\mathrm{T}}(a)}{E_K - E} \tag{79}$$

where the superscript T denotes matrix transposition. The column vector $\mathbf{Y}_K(r)$ with N_γ rows has elements $y_{\gamma K}(r)$.

In actual calculations the expression (79) would be useless and must be somehow transformed to a more suitable form. To this end we introduce an auxiliary function $\bar{\Psi}$ defined by the expansion

$$\bar{\Psi}(\boldsymbol{X}) = \sum_K \frac{\langle \Psi_K |\, L\Psi\rangle}{E_K - E} \Psi_K(\boldsymbol{X}) \tag{80}$$

in the whole hypervolume $\mathcal{T}$ *including* the hypersurface $\mathcal{S}$. In the interior of the reaction hypervolume, $\mathcal{T} \setminus \mathcal{S}$, we have $\bar{\Psi}(\boldsymbol{X}) = \Psi(\boldsymbol{X})$ but on the hypersurface $\mathcal{S}$ equation (70) implies

$$\left(L\bar{\Psi}\right)(\boldsymbol{X}) = 0\,. \tag{81}$$

The expansion of $\bar{\Psi}$ in the basis of channel functions is

$$\bar{\Psi}(\boldsymbol{X}) = \mathcal{A}\sum_{\gamma}\left(\Theta_{\gamma}(\boldsymbol{R},\hat{\boldsymbol{r}})\frac{\bar{P}_{\gamma}(r)}{r} + \mathrm{i}\widetilde{\Theta}_{\gamma}(\boldsymbol{R},\hat{\boldsymbol{r}})\frac{\bar{Q}_{\gamma}(r)}{r}\right). \tag{82}$$

Equations (73), (74), (80) and (82) show that the functions $\bar{P}_{\gamma}$ and $\bar{Q}_{\gamma}$ are defined by the series

$$\begin{pmatrix}\bar{P}_{\gamma}(r)\\ \bar{Q}_{\gamma}(r)\end{pmatrix} = \frac{\hbar^2}{2ma}\sum_{K}\sum_{\gamma'}\frac{y_{\gamma' K}(a)}{E_K - E}\left[(2mac/\hbar)Q_{\gamma'}(a) - b_{\gamma'}P_{\gamma'}(a)\right]\begin{pmatrix}y_{\gamma K}(r)\\ z_{\gamma K}(r)\end{pmatrix} \qquad 0 < r \leqslant a \tag{83}$$

hence

$$\begin{pmatrix}\bar{P}_{\gamma}(r)\\ \bar{Q}_{\gamma}(r)\end{pmatrix} = \begin{pmatrix}P_{\gamma}(r)\\ Q_{\gamma}(r)\end{pmatrix} \qquad \text{for} \quad 0 < r < a \tag{84}$$

and

$$\begin{pmatrix}\bar{P}_{\gamma}(a)\\ \bar{Q}_{\gamma}(a)\end{pmatrix} = \frac{\hbar^2}{2ma}\sum_{K}\sum_{\gamma'}\frac{y_{\gamma' K}(a)}{E_K - E}\left[(2mac/\hbar)Q_{\gamma'}(a) - b_{\gamma'}P_{\gamma'}(a)\right]\begin{pmatrix}y_{\gamma K}(a)\\ z_{\gamma K}(a)\end{pmatrix} \qquad \text{for } r = a\,. \tag{85}$$

Moreover, equation (81) implies

$$(2mac/\hbar)\bar{Q}_{\gamma}(a) - b_{\gamma}\bar{P}_{\gamma}(a) = 0\,. \tag{86}$$

We rewrite the upper equation (85) in the matrix form

$$\bar{\mathsf{P}}(a) = \mathsf{R}(E)\left[(2mac/\hbar)\mathsf{Q}(a) - \mathsf{b}\mathsf{P}(a)\right] \tag{87}$$

where

$$\mathsf{R}(E) = \frac{\hbar^2}{2ma}\sum_{K}\frac{\mathsf{Y}_K(a)\mathsf{Y}_K^{\mathrm{T}}(a)}{E_K - E} \tag{88}$$

and other symbols have analogous meaning as in (77) and (79). The matrix R is the same matrix which has been used in [2–19].

To find the relation between the matrices $\mathcal{R}(E)$ and $\mathsf{R}(E)$ we derive a differential equation satisfied by the functions $\left\{(\bar{P}_{\gamma},\bar{Q}_{\gamma})^{\mathrm{T}}\right\}$ in a thin spherical layer $a - \varepsilon \leqslant r \leqslant a$ ($\varepsilon \to 0^{+}$) near the boundary of the sphere $\mathcal{V}$. Since the radius a of the sphere $\mathcal{V}$ has been chosen so that for $r \geqslant a$ the exchange between the projectile and the target electrons may be neglected, we assume that the same is true in the layer (if not, we simply increase a). Acting on both sides of (80) with the operator $\mathcal{H} - E$, utilizing (82) and projecting the resulting equation onto Θ_{γ} and $\widetilde{\Theta}_{\gamma}$ we get

$$\begin{aligned}&\begin{pmatrix}mc^2 - \epsilon_{\gamma} - c\hbar(\mathrm{d}/\mathrm{d}r - \kappa_{\gamma}/r)\\ c\hbar(\mathrm{d}/\mathrm{d}r + \kappa_{\gamma}/r) - mc^2 - \epsilon_{\gamma}\end{pmatrix}\begin{pmatrix}\bar{P}_{\gamma}(r)\\ \bar{Q}_{\gamma}(r)\end{pmatrix} + \sum_{\gamma'}V_{\gamma\gamma'}(r)\begin{pmatrix}\bar{P}_{\gamma'}(r)\\ \bar{Q}_{\gamma'}(r)\end{pmatrix}\\ &\quad = \frac{\hbar^2}{2ma}\sum_{K}\sum_{\gamma'}y_{\gamma' K}(a)\left[(2mac/\hbar)Q_{\gamma'}(a) - b_{\gamma'}P_{\gamma'}(a)\right]\begin{pmatrix}y_{\gamma K}(r)\\ z_{\gamma K}(r)\end{pmatrix}\\ &\quad a - \varepsilon \leqslant r \leqslant a\end{aligned} \tag{89}$$

where $V_{\gamma\gamma'}$ are elements of the potential matrix which couples the channels and ϵ_γ is the energy of the projectile in the channel γ (including the rest energy mc^2). This equation may be further transformed to the form

$$\begin{pmatrix} mc^2-\epsilon_\gamma & -c\hbar(\mathrm{d}/\mathrm{d}r-\kappa_\gamma/r) \\ c\hbar(\mathrm{d}/\mathrm{d}r+\kappa_\gamma/r) & -mc^2-\epsilon_\gamma \end{pmatrix}\begin{pmatrix} \bar{P}_\gamma(r) \\ \bar{Q}_\gamma(r) \end{pmatrix} + \sum_{\gamma'} V_{\gamma\gamma'}(r)\begin{pmatrix} \bar{P}_{\gamma'}(r) \\ \bar{Q}_{\gamma'}(r) \end{pmatrix}$$
$$= A_\gamma \frac{\hbar^2}{2ma}\left[(2mac/\hbar)Q_\gamma(a) - b_\gamma P_\gamma(a)\right]\delta(r-a)\begin{pmatrix} 1 \\ b_\gamma(\hbar/2mac) \end{pmatrix}$$
$$a-\varepsilon \leqslant r \leqslant a \tag{90}$$

which follows from the sequence of equalities

$$\sum_K y_{\gamma' K}(a)\begin{pmatrix} y_{\gamma K}(r) \\ z_{\gamma K}(r) \end{pmatrix} = \sum_{ijK} p_{\gamma' i}(a) U_{\gamma' i,K} U_{\gamma j,K}\begin{pmatrix} p_{\gamma j}(r) \\ q_{\gamma j}(r) \end{pmatrix}$$
$$= \sum_{ij} p_{\gamma' i}(a)\delta_{\gamma\gamma'}\delta_{ij}\begin{pmatrix} p_{\gamma j}(r) \\ q_{\gamma j}(r) \end{pmatrix} \tag{91}$$

and (67). Integrating both sides of (90) over the interval $a-\varepsilon \leqslant r \leqslant a$ we obtain

$$\begin{pmatrix} -c\hbar\left[\bar{Q}_\gamma(a) - Q_\gamma(a)\right] \\ c\hbar\left[\bar{P}_\gamma(a) - P_\gamma(a)\right] \end{pmatrix} = A_\gamma \frac{\hbar^2}{2ma}\left[(2mac/\hbar)Q_\gamma(a) - b_\gamma P_\gamma(a)\right]\begin{pmatrix} 1 \\ b_\gamma(\hbar/2mac) \end{pmatrix} \tag{92}$$

which together with (86) constitute a set of three algebraic equations for three unknowns A_γ, $\bar{P}_\gamma(a)$ and $\bar{Q}_\gamma(a)$. The solution to this system is

$$A_\gamma = \frac{(2mac/\hbar)^2}{b_\gamma^2 + (2mac/\hbar)^2} \tag{93}$$

$$\bar{P}_\gamma(a) = \frac{(2mac/\hbar)}{b_\gamma^2 + (2mac/\hbar)^2}\left[(2mac/\hbar)P_\gamma(a) + b_\gamma Q_\gamma(a)\right] \tag{94}$$

$$\bar{Q}_\gamma(a) = \frac{b_\gamma}{b_\gamma^2 + (2mac/\hbar)^2}\left[(2mac/\hbar)P_\gamma(a) + b_\gamma Q_\gamma(a)\right]. \tag{95}$$

Utilizing equations (77), (87) and (94) after simple transformations we obtain the desired relation between the matrices $\mathcal{R}(E)$ and $\mathbf{R}(E)$

$$\mathcal{R}(E) = \mathbf{R}(E) - \frac{\mathbf{b}}{\mathbf{b}^2 + (2mac/\hbar)^2}. \tag{96}$$

These results show that in general the operations $\lim_{r\to a^-}$ and $\sum_K$ in equations (75), (78) and (79) do not commute. For fixed $\mathbf{b} \neq 0$ the difference $\mathcal{R}(E) - \mathbf{R}(E)$ is of the order c^{-2}.

Equations (77) and (96) constitute the main result of this paper and because of their importance we rewrite them here together

$$\mathbf{P}(a) = \mathcal{R}(E)\left[(2mac/\hbar)\mathbf{Q}(a) - \mathbf{b}\mathbf{P}(a)\right] \tag{97}$$

$$\mathcal{R}(E) = \frac{\hbar^2}{2ma}\sum_K \frac{\mathbf{Y}_K(a)\mathbf{Y}_K^{\mathrm{T}}(a)}{E_K - E} - \frac{\mathbf{b}}{\mathbf{b}^2 + (2mac/\hbar)^2}. \tag{98}$$

The non-relativistic limit of these multi-channel equations is

$$\mathbf{P}(a) = \mathcal{R}_{\mathrm{N}}(E)\left[a\frac{\mathrm{d}\mathbf{P}(a)}{\mathrm{d}r} - (\mathbf{b} - \mathcal{K})\mathbf{P}(a)\right] \tag{99}$$

$$\mathcal{R}_{\mathrm{N}}(E) = \mathbf{R}_{\mathrm{N}}(E) = \frac{\hbar^2}{2ma} \sum_K \frac{\mathbf{Y}_K(a)\mathbf{Y}_K^{\mathrm{T}}(a)}{E_K - E} \tag{100}$$

where the diagonal matrix $\mathcal{K}$ has elements $\kappa_\gamma \delta_{\gamma\gamma'}$. Equations (99) and (100) become identical with the well known non-relativistic multi-channel expressions [1, 25–27] provided one defines in (99) a matrix of non-relativistic boundary-condition constants $\mathbf{b}_{\mathrm{N}} = \mathbf{b} - \mathcal{K}$.

Equations (25) and (26) of [3] should be replaced by (97) and (98) of the present paper. Comparison of our results with those obtained by Chang [3] shows that in his presentation of the relativistic R-matrix theory the term $-\mathbf{b}/(\mathbf{b}^2 + (2mac/\hbar)^2)$ in (98) has unfortunately been omitted. We shall show that results of numerical calculations performed so far within the framework of the relativistic R-matrix theory were not affected by this error. The reason for this is that in all these calculations the Buttle correction has been used. Indeed, truncating the series in the definition of the matrix element $\mathcal{R}_{\gamma\gamma'}(E)$ after $M_{\gamma\gamma'}$ terms and compensating partially the error due to this truncation with the Buttle correction we obtain

$$\begin{aligned}\mathcal{R}_{\gamma\gamma'}(E) &= R_{\gamma\gamma'}(E) - \frac{b_\gamma}{b_\gamma^2 + (2mac/\hbar)^2}\delta_{\gamma\gamma'} \\ &\simeq \frac{\hbar^2}{2ma}\sum_{K=1}^{M_{\gamma\gamma'}} \frac{y_{\gamma K}(a) y_{\gamma' K}(a)}{E_K - E} - \frac{\hbar^2}{2ma}\sum_{i=1}^{M_{\gamma\gamma}} \frac{p_{\gamma i}(a) p_{\gamma i}(a)}{\epsilon_{\gamma i} - \epsilon_\gamma}\delta_{\gamma\gamma'} \\ &\quad + \frac{p_\gamma(a)}{(2mac/\hbar) q_\gamma(a) - b_\gamma p_\gamma(a)}\,\delta_{\gamma\gamma'}\,.\end{aligned} \tag{101}$$

Here $p_{\gamma i}$ and $\epsilon_{\gamma i}$ have been defined by (64) and (65), ϵ_γ is the energy of the scattered electron in the channel γ and $(p_\gamma, q_\gamma)^{\mathrm{T}}$ is a solution to the equation

$$\begin{pmatrix} mc^2 - \epsilon_\gamma + v_\gamma(r) & -c\hbar(\mathrm{d}/\mathrm{d}r - \kappa_\gamma/r) \\ c\hbar(\mathrm{d}/\mathrm{d}r + \kappa_\gamma/r) & -mc^2 - \epsilon_\gamma + v_\gamma(r) \end{pmatrix} \begin{pmatrix} p_\gamma(r) \\ q_\gamma(r) \end{pmatrix} = 0 \qquad 0 \leqslant r \leqslant a \tag{102}$$

with an initial condition $p_\gamma(0) = 0$ (cf equation (64)). Substituting the approximate expression (101) into (97) we obtain exactly the same approximation which follows from (25)–(27) of Chang's paper [3] (even though the latter equations are incorrect). This is so because the errors occurring in (25)–(27) of [3] cancel when deriving the approximate relation. Since all numerical calculations were based on this approximate expression, they do not suffer from errors due to the incorrect presentation of the theory.

5. Conclusions

Unexpectedly, we have found an error in previous presentations of the relativistic R-matrix theory. We have shown that an origin of this error lies in an incorrect assumption that the relativistic expansion of the wavefunction converges to this function at the boundary of the reaction volume. Incorrectness of this assumption follows from incompleteness of a relativistic expansion basis on the surface of the R-matrix region. Despite claims to the contrary in the literature [22], we have proved that the R-matrix theory for the Dirac equation can be constructed since the extent of incompleteness of the relativistic expansion basis on the boundary can be found quantitatively. This permits a correct derivation of the relativistic theory, which has been presented both for single- and multi-channel cases. We have also indicated that in spite of being based on the incorrect theory, results of numerical relativistic R-matrix calculations performed so far fortuitously are not affected by these errors.

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Appendix A

In this appendix we present a generalization of the results obtained in section 3 for the Dirac operator to a more general family of 2×2 differential operators. This generalization will allow us to present in appendix B an illustrative analytical example.

We define an operator

$$H = \begin{pmatrix} h_{11}(r) & -\gamma(\mathrm{d}/\mathrm{d}r) + h_{12}(r) \\ \gamma(\mathrm{d}/\mathrm{d}r) + h_{21}(r) & h_{22}(r) \end{pmatrix} \tag{A1}$$

with h_{ij} real and $h_{ij} = h_{ji}$. The functions h_{ij} are assumed to be well behaving and γ is a real non-zero constant. We attempt to solve the equation

$$(H - E)\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = 0 \qquad 0 \leqslant r \leqslant a \tag{A2}$$

subject to an initial condition $P(0) = 0$. An auxiliary orthonormal basis set $\left\{(P_i, Q_i)^{\mathrm{T}}\right\}$ is generated by solving a Hermitian boundary value problem

$$(H - E_i)\begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} = 0 \qquad 0 \leqslant r \leqslant a \tag{A3}$$

$$P_i(0) = 0 \qquad \alpha P_i(a) + \beta Q_i(a) = 0 \tag{A4}$$

where α and β are some real constants. Since the remaining steps are almost identical with those described in section 3, we shall not repeat them here and present only final results:

$$\sum_i \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} \begin{pmatrix} P_i(a) & Q_i(a) \end{pmatrix} = \frac{\delta(r-a)}{\alpha^2+\beta^2} \begin{pmatrix} \beta^2 & -\alpha\beta \\ -\alpha\beta & \alpha^2 \end{pmatrix} \qquad 0 < r \leqslant a \tag{A5}$$

$$\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = \frac{\gamma}{\beta}[\alpha P(a) + \beta Q(a)] \sum_i \frac{P_i(a)}{E_i - E} \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} \qquad 0 < r < a \tag{A6}$$

$$P(a) = \left(R(E) + \frac{\alpha}{\alpha^2+\beta^2} \right)[\alpha P(a) + \beta Q(a)] \tag{A7}$$

$$Q(a) = \left(-\frac{\alpha}{\beta} R(E) + \frac{\beta}{\alpha^2+\beta^2} \right)[\alpha P(a) + \beta Q(a)] \tag{A8}$$

where the matrix R is defined by

$$R(E) = \frac{\gamma}{\beta} \sum_i \frac{P_i(a) P_i(a)}{E_i - E}\,. \tag{A9}$$

Appendix B

In this appendix we consider an analytically solvable example which illustrates to some extent the results we have obtained in section 3. We want to solve the equation

$$\begin{pmatrix} -k & -\mathrm{d}/\mathrm{d}r \\ \mathrm{d}/\mathrm{d}r & -k \end{pmatrix} \begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = 0 \qquad 0 \leqslant r \leqslant a \tag{B1}$$

subject to an initial condition $P(0) = 0$. This problem has an exact solution

$$\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = C \begin{pmatrix} \sin kr \\ \cos kr \end{pmatrix}. \tag{B2}$$

Basis functions $(P_n, Q_n)^{\mathrm{T}}$ are eigensolutions of a boundary value problem

$$\begin{pmatrix} -k_n & -\mathrm{d}/\mathrm{d}r \\ \mathrm{d}/\mathrm{d}r & -k_n \end{pmatrix} \begin{pmatrix} P_n(r) \\ Q_n(r) \end{pmatrix} = 0 \qquad 0 \leqslant r \leqslant a \tag{B3}$$

$$P_n(0) = 0 \qquad \alpha P_n(a) + \beta Q_n(a) = 0\,. \tag{B4}$$

In the following we shall parametrize α and β by

$$\alpha = \xi \cos\delta \qquad \beta = \xi \sin\delta \qquad (\xi \neq 0)\,. \tag{B5}$$

Normalized solutions of the boundary value problem (B3), (B4) are

$$\begin{pmatrix} P_n(r) \\ Q_n(r) \end{pmatrix} = \frac{1}{\sqrt{a}} \begin{pmatrix} \sin k_n r \\ \cos k_n r \end{pmatrix} \tag{B6}$$

where k_n is an nth root of the equation $\sin(k_n a + \delta) = 0$, i.e. $k_n a = -\delta + n\pi$, $n = 0, \mp 1, \mp 2, \ldots$. Comparison with (A1)–(A4) shows that the example considered here belongs to the family of problems discussed in appendix A. Therefore from (A7) we obtain immediately

$$R(k) = \frac{P(a)}{\alpha P(a) + \beta Q(a)} - \frac{\alpha}{\alpha^2 + \beta^2} = -\frac{\sin\delta \cot(ka + \delta)}{\xi}\,. \tag{B7}$$

The same result can be obtained from (A8). On the other hand, it follows from (A9) that the matrix R should also be given by the expansion

$$R(k) = \frac{\gamma}{\beta} \sum_n \frac{P_n(a) P_n(a)}{k_n - k} = \frac{1}{\xi \sin\delta} \sum_{n=-\infty}^{+\infty} \frac{\sin^2 k_n a}{k_n a - ka} \tag{B8}$$

which after some transformations may be rewritten in the form

$$R(k) = \frac{\sin\delta}{\xi} \sum_{n=0}^{+\infty} \frac{2(ka + \delta - \pi/2)}{(n + \frac{1}{2})^2 \pi^2 - (ka + \delta - \pi/2)^2}\,. \tag{B9}$$

The series occurring on the right-hand side of equation (B9) is easily recognized to be the partial fraction expansion of $\tan(ka + \delta - \pi/2)$ [38] and the final result is

$$R(k) = -\frac{\sin\delta \cot(ka + \delta)}{\xi} \tag{B10}$$

in agreement with (B7). Notice that if the term $\alpha/(\alpha^2 + \beta^2)$ in (A7) were omitted, as was done for the Dirac equation by Chang [3], equations (A7) and (A9) applied to the example considered here would give contradictory results.

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