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Quantum defect theory with long-range multipole potentials

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Abstract. The formula $\mathbf{K} = \mathcal{K}_{oo} - \mathcal{K}_{oc}(\mathcal{K}_{cc} + \tau)^{-1}\mathcal{K}_{co}$ is familiar in quantum defect theory: $\mathbf{K}$ is the reactance matrix for electron–ion collisions; $\mathcal{K}$ is a matrix with partitioning for open–open, open–closed, closed–open and closed–closed elements; and $\tau = \tan(\pi\nu)$ where ν is a diagonal matrix of effective quantum numbers in the closed channels. In the simplest case it may be assumed that $\mathcal{K}$ is a slowly varying function of the energy.

This formula has usually been obtained by assuming only a pure Coulomb potential at radial distances $r \geqslant r_0$, with r_0 finite. This paper discusses the derivation of a similar formula for the case in which long-range non-Coulomb potentials are included, behaving like $r^{-\lambda-1}$ for $r \geqslant r_0$, with $\lambda \geqslant 1$.

1. Introduction

A familiar formula in quantum defect theory (QDT) is

$$\mathbf{K} = \mathcal{K}_{oo} - \mathcal{K}_{oc}(\mathcal{K}_{cc} + \tau)^{-1}\mathcal{K}_{co} \tag{1}$$

where $\mathbf{K}$ is the reactance matrix for electron collisions with a positive ion, $\mathcal{K}$ is a matrix with partitioning for open–open, open–closed, closed–open and closed–closed channels and $\tau = \tan(\pi\nu)$ where ν is the diagonal matrix of effective quantum numbers in the closed channels. It may usually be assumed that $\mathcal{K}$ is a slowly varying function of the energy and that the main energy-variation of $\mathbf{K}$, due to resonance structures, is determined by the variation of $\tan(\pi\nu)$.

Let r_0 be a radial distance which is large compared with the mean radii of the target states. The formula has usually been derived assuming no potentials, other than Coulomb potentials, in the region of $r \geqslant r_0$ (see Seaton 1983, which will be referred to as S83: and section 4 of the present paper). In some collision problems an important role is played by outer-region multipole potentials, behaving like $r^{-\lambda-1}$ for $r \geqslant r_0$, with $\lambda \geqslant 1$. It is therefore desirable to generalize the formula to the case in which such potentials are included.

In an introductory essay to a book edited by Christian Jungen, Seaton (1996) described the problem as an awkward one which 'refuses to go away'. He concluded the essay by saying 'I obtained some formulae but never published them: they were too complicated and all the charm of QDT was lost'. There continues, however, to be an interest in the problem and an important recent advance has been made by Gorczyca *et al* (1996, to be referred to as GRPB). The present paper gives a detailed discussion of the problem.

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2. The collision problem

We consider electron collisions with an ion of charge z having energy levels E_i. We use scaled variables $r = z\rho$ where ρ is a radial co-ordinate in atomic units and scaled channel energies $\epsilon_i = (E - E_i)/z^2$ where E is the total energy and E and E_i are both in Rydbergs. Let there be N channels and take them to be in order of increasing E_i; $E_{i+1} \geqslant E_i$.

For $r \geqslant r_0$ the collision problem may be formulated in terms of a matrix of radial functions $\boldsymbol{F}(r)$ with elements F_{ij} where i specifies a channel and j a boundary condition. For $r \geqslant r_0$ the radial functions satisfy a system of coupled differential equations

$$h\boldsymbol{F} + \boldsymbol{W}\boldsymbol{F} = 0 \tag{2}$$

where

$$h = -\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{r^2} - \frac{2}{r} - \epsilon \tag{3}$$

and where $\boldsymbol{W}(r)$ is a symmetric matrix for the long-range multipole potentials: $W_{ii'}(r) = C_{ii'}/r^{\lambda+1}$ ($\lambda = 1$ for dipole potentials, $\lambda = 2$ for quadrupole potentials, etc).

Equation (2) is of second order and therefore has $2N$ linearly independent solutions. We suppose that the collision problem has been solved in the inner region of $r \leqslant r_0$ to give a value for the R-matrix,

$$\boldsymbol{R} = \boldsymbol{F}(\boldsymbol{F}')^{-1} \qquad \text{at} \quad r = r_0 \tag{4}$$

where $\boldsymbol{F}' = \mathrm{d}\boldsymbol{F}/\mathrm{d}r$. When the lower boundary condition (4) is imposed, equation (2) has N linearly independent solutions.

Let open channels have $\epsilon_i \geqslant 0$ and closed channels have $\epsilon_i < 0$, and let there be N_o open channels. For a closed channel i we obtain, in general, solutions $F_{ij}(r)$ which are exponentially increasing in the limit of r large. The physical solutions $\boldsymbol{G}(r)$ are required to be everywhere bounded, and are obtained on forming linear combinations of the columns of $\boldsymbol{F}(r)$. The matrix $\boldsymbol{G}$ has N rows and N_o columns.

Given that r_0 is large compared with the mean radii of the target states, it may be shown that $|W_{ii'}(r)| \ll 2/r$ for all ii' and all $r \geqslant r_0$. The terms in $\boldsymbol{W}$ can therefore always be handled using first-order perturbation theory.

2.1. The code STGF

Berrington *et al* (1987) describe a code, STGF, which handles terms in $\boldsymbol{W}$ using first-order perturbation theory without making use of QDT. That code can be used for any value of the energy but it is not well adapted to the problems of locating narrow resonances or for obtaining cross-sections averaged over resonances. We use STGF as a benchmark: results obtained employing other methods are compared with those from STGF.

3. Coulomb functions

Coulomb functions $y(r)$ are solutions of $hy = 0$. Here we use Coulomb functions s and c which are equal to $\pi^{1/2}$ times the Coulomb functions s and c defined in S83. For values of $|\epsilon|$ which are sufficiently small and values of r which are not too large, the functions s and c are slowly varying functions of ϵ.

For $\epsilon \geqslant 0$ the functions have asymptotic form $s \sim k^{-1/2}\sin(\zeta)$ and $c \sim k^{-1/2}\cos(\zeta)$ where $k = \epsilon^{1/2}$ and where ζ is the usual Coulomb phase function. For $\epsilon < 0$ one puts $\nu = 1/(-\epsilon)^{-1/2}$ and defines

$$\sigma = \sin(\pi\nu) \qquad \text{and} \qquad \gamma = \cos(\pi\nu). \tag{5}$$

One may then put (see equation (2.55) of S83)

$$s = (p\sigma - q\gamma), \qquad c = (p\gamma + q\sigma) \qquad (\epsilon < 0) \tag{6}$$

where

$$p = (-1)^l \xi/((2\pi\nu)^{1/2}K), \qquad q = (-1)^l \theta(\pi\nu^3/2)^{1/2}K \tag{7}$$

and where ξ and θ are defined in S83 and $K = [\nu^2\Gamma(\nu + l + 1)\Gamma(\nu - l)]^{-1/2}$. The functions θ and ξ have asymptotic forms

$$\theta \sim (2r/\nu)^{\nu} \exp(-r/\nu), \qquad \xi \sim (2r/\nu)^{-\nu} \exp(+r/\nu). \tag{8}$$

4. The QDT formula with no long-range potentials

With $\boldsymbol{W} = 0$ the functions $\boldsymbol{F}$ are linear combinations of the functions s and c. We put

$$\boldsymbol{F} = s + c\boldsymbol{\mathcal{K}}^{(0)} \tag{9}$$

which defines $\boldsymbol{\mathcal{K}}^{(0)}$. Using (4) we obtain

$$\boldsymbol{\mathcal{K}}^{(0)} = -(c - \boldsymbol{R}c')^{-1}(s - \boldsymbol{R}s') \tag{10}$$

which is the value of $\boldsymbol{\mathcal{K}}$ for the case of no outer-region multipole potentials.

One partitions $\boldsymbol{F}$ according to the scheme

$$\boldsymbol{F} = \begin{pmatrix} \boldsymbol{F}_{oo} & \boldsymbol{F}_{oc} \\ \boldsymbol{F}_{co} & \boldsymbol{F}_{cc} \end{pmatrix}, \tag{11}$$

where subscripts 'o' and 'c' are used for open and closed channels, and takes the physical solutions to be

$$\boldsymbol{G} = \boldsymbol{F} \begin{pmatrix} \boldsymbol{L}_{oo} \\ \boldsymbol{L}_{co} \end{pmatrix}. \tag{12}$$

Using (9) one then obtains

$$\boldsymbol{G}_{oo} = s\boldsymbol{L}_{oo} + c(\boldsymbol{\mathcal{K}}^{(0)}_{oo}\boldsymbol{L}_{oo} + \boldsymbol{\mathcal{K}}^{(0)}_{oc}\boldsymbol{L}_{co}) \tag{13}$$

and

$$\boldsymbol{G}_{co} = p[\gamma\boldsymbol{\mathcal{K}}^{(0)}_{co}\boldsymbol{L}_{oo} + (\sigma + \gamma\boldsymbol{\mathcal{K}}^{(0)}_{cc})\boldsymbol{L}_{co}] + q[\sigma\boldsymbol{\mathcal{K}}^{(0)}_{co}\boldsymbol{L}_{oo} + (-\gamma + \sigma\boldsymbol{\mathcal{K}}^{(0)}_{cc})\boldsymbol{L}_{co}]. \tag{14}$$

We now take $\boldsymbol{L}_{oo}$ and $\boldsymbol{L}_{co}$ to be such as to eliminate the exponentially increasing function p in (14),

$$\gamma\boldsymbol{\mathcal{K}}^{(0)}_{co}\boldsymbol{L}_{oo} + (\sigma + \gamma\boldsymbol{\mathcal{K}}^{(0)}_{cc})\boldsymbol{L}_{co} = 0, \tag{15}$$

and taking $\boldsymbol{L}_{oo} = 1$ we then obtain from (13)

$$\boldsymbol{G}_{oo} = s + c\mathbf{K} \tag{16}$$

where

$$\mathbf{K} = \boldsymbol{\mathcal{K}}^{(0)}_{oo} - \boldsymbol{\mathcal{K}}^{(0)}_{oc}(\tau + \boldsymbol{\mathcal{K}}^{(0)}_{cc})^{-1}\boldsymbol{\mathcal{K}}^{(0)}_{co} \tag{17}$$

and where $\tau = \sigma/\gamma = \tan(\pi\nu)$.

5. Perturbed outer-region functions

Let $\boldsymbol{S}$ and $\boldsymbol{C}$ be functions calculated allowing for $\boldsymbol{W}$ as a first-order perturbation,

$$h\boldsymbol{S} + \boldsymbol{W}s = 0, \qquad h\boldsymbol{C} + \boldsymbol{W}c = 0. \tag{18}$$

Let the Wronskian for any two functions a and b be $W(a, b) = ab' - a'b$. The Coulomb functions have Wronskians $W(c, s) = 1$ and $W(q, p) = 1$. We may therefore put

$$\boldsymbol{S} = s + s\langle cs\rangle - c\langle ss\rangle \qquad \text{and} \qquad \boldsymbol{C} = c + s\langle cc\rangle - c\langle sc\rangle \tag{19}$$

where

$$\langle ab\rangle = \int_{r_I}^{r} a\boldsymbol{W}b\,\mathrm{d}r, \tag{20}$$

and where a choice of the lower limit, r_I, provides a specification of the boundary conditions to be imposed on the functions.

In formulating the theory it is convenient to introduce r_1 as a value of r which is large but finite and to take $\boldsymbol{W}(r) = 0$ for $r \geqslant r_1$. All of our final results are independent of the choice of r_1. With two different choices for the lower limit r_I we obtain

$$\left.\begin{array}{lll} \boldsymbol{S} = s + s(cs) - c(ss), \quad \boldsymbol{C} = c + s(cc) - c(sc) & \text{for} & r \geqslant r_1, \\ \boldsymbol{S} = s, \quad \boldsymbol{C} = c & \text{at} & r = r_0, \end{array}\right\} \quad \text{with} \quad r_I = r_0 \tag{21}$$

$$\left.\begin{array}{lll} \boldsymbol{S} = s, \quad \boldsymbol{C} = c & \text{for} & r \geqslant r_1, \\ \boldsymbol{S} = s - s(cs) + c(ss), \quad \boldsymbol{C} = c - s(cc) + c(sc) & \text{at} & r = r_0, \end{array}\right\} \quad \text{with} \quad r_I = \infty \tag{22}$$

where we now use integrals

$$(\ldots) = \int_{r_0}^{r_1} \ldots\,. \tag{23}$$

6. Use of the perturbed functions

We calculate a perturbed reactance matrix $\mathbf{K}$ and then calculate the scattering matrix as $\mathbf{S} = (1 + \mathrm{i}\mathbf{K})(1 - \mathrm{i}\mathbf{K})^{-1}$: that gives the scattering matrix to be symmetric and unitary so long as $\mathbf{K}$ is symmetric and real.

6.1. Elimination of the exponentially increasing solutions

In order to study the elimination of the exponentially increasing functions we use functions $\boldsymbol{F}$ which are linear in the perturbation integrals. We therefore take $r_I = r_0$ in (20) and switch to the use of s and c for open channels and p and q for closed channels. We then have

$$\boldsymbol{S}_{\mathrm{oo}} = s + s\langle cs\rangle - c\langle ss\rangle, \tag{24}$$

$$\boldsymbol{S}_{\mathrm{oc}} = [s\langle cp\rangle - c\langle sp\rangle]\sigma - [s\langle cq\rangle - c\langle sq\rangle]\gamma, \tag{25}$$

$$\boldsymbol{S}_{\mathrm{co}} = p\langle qs\rangle - q\langle ps\rangle, \tag{26}$$

$$\boldsymbol{S}_{\mathrm{cc}} = [p + p\langle qp\rangle - q\langle pp\rangle]\sigma - [q + p\langle qq\rangle - q\langle pq\rangle]\gamma. \tag{27}$$

Similar equations for the sub-matrices of $\boldsymbol{C}$ can be obtained on making the following replacements in (24)–(27): $s \to c$, $c \to -s$, $q \to -p$ and $p \to q$.

We put

$$\boldsymbol{F} = \boldsymbol{S} + \boldsymbol{C}\boldsymbol{\mathcal{K}}^{(0)} \tag{28}$$

where, since $\boldsymbol{S} = s$ and $\boldsymbol{C} = c$ at $r = r_0$, $\boldsymbol{\mathcal{K}}^{(0)}$ is still defined by (10). The asymptotic forms for $\boldsymbol{G}$ are obtained using (12) and (28), and the asymptotic forms (21) for $\boldsymbol{S}$ and $\boldsymbol{C}$. We omit terms which go to zero in the limit of $r \to \infty$. Using integrations by parts† it may be shown that $q\langle ps\rangle$, $q\langle pc\rangle$ and $q\langle pq\rangle$ all go to zero in that limit. Defining

$$\boldsymbol{P} = s\langle cp\rangle - c\langle sp\rangle \qquad \text{and} \qquad \boldsymbol{Q} = p\langle qp\rangle - q\langle pp\rangle \tag{29}$$

it may be shown similarly that $\boldsymbol{P}$ and $\boldsymbol{Q}$ behave like $p/r^{\lambda+1}$ for r large.

After a little algebra we obtain the following asymptotic forms:

$$\boldsymbol{G}_{\mathrm{oo}} = s(\boldsymbol{A}\boldsymbol{L}_{\mathrm{oo}} + \boldsymbol{B}\boldsymbol{L}_{\mathrm{co}}) + c(\boldsymbol{C}\boldsymbol{L}_{\mathrm{oo}} + \boldsymbol{D}\boldsymbol{L}_{\mathrm{co}}) + \boldsymbol{P}\boldsymbol{T}, \tag{30}$$

$$\boldsymbol{G}_{\mathrm{co}} = p(\boldsymbol{X}\boldsymbol{L}_{\mathrm{oo}} + \boldsymbol{Y}\boldsymbol{L}_{\mathrm{co}}) + \boldsymbol{Q}\boldsymbol{T}, \tag{31}$$

where

$$\boldsymbol{A} = 1 + (cc)\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{oo}} + (cq)\sigma\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{co}} + (cs), \tag{32}$$

$$\boldsymbol{B} = (cc)\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{oc}} + (cq)(-\gamma + \sigma\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{cc}}), \tag{33}$$

$$\boldsymbol{C} = (1 - (sc))\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{oo}} - (ss) - (sq)\sigma\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{co}}, \tag{34}$$

$$\boldsymbol{D} = (1 - (sc))\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{oc}} - (sq)(-\gamma + \sigma\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{cc}}), \tag{35}$$

$$\boldsymbol{X} = (qs) + (qc)\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{oo}} + (\gamma + (qq)\sigma)\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{co}}, \tag{36}$$

$$\boldsymbol{Y} = (qc)\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{oc}} + (\gamma + (qq)\sigma)\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{cc}} + \sigma - (qq)\gamma \tag{37}$$

and

$$\boldsymbol{T} = \gamma\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{co}}\boldsymbol{L}_{\mathrm{oo}} + (\sigma + \gamma\boldsymbol{\mathcal{K}}^{(0)}_{\mathrm{cc}})\boldsymbol{L}_{\mathrm{co}}. \tag{38}$$

In equations (32)–(37) we use integrals $(\ldots) = \int_{r_0}^{\infty}$. We eliminate the increasing functions *to a consistent first order* in $\boldsymbol{W}$. For $\boldsymbol{W} = 0$ we have, from (15), $\boldsymbol{T} = 0$ and for $\boldsymbol{W} \neq 0$ we may therefore assume $\boldsymbol{T}$ to be of order $\boldsymbol{W}$. In (30) and (31) we therefore omit the terms $\boldsymbol{P}\boldsymbol{T}$ and $\boldsymbol{Q}\boldsymbol{T}$ which are of order $\boldsymbol{W}^2$.

For r large we require that $\boldsymbol{G}_{\mathrm{oo}} = s + c\mathsf{K}$ and that $\boldsymbol{G}_{\mathrm{co}}$ goes to zero. We therefore put

$$\boldsymbol{A}\boldsymbol{L}_{\mathrm{oo}} + \boldsymbol{B}\boldsymbol{L}_{\mathrm{co}} = 1, \tag{39}$$

$$\boldsymbol{C}\boldsymbol{L}_{\mathrm{oo}} + \boldsymbol{D}\boldsymbol{L}_{\mathrm{co}} = \mathsf{K}, \tag{40}$$

$$\boldsymbol{X}\boldsymbol{L}_{\mathrm{oo}} + \boldsymbol{Y}\boldsymbol{L}_{\mathrm{co}} = 0. \tag{41}$$

On solving (39) and (41) for $\boldsymbol{L}_{\mathrm{oo}}$ and $\boldsymbol{L}_{\mathrm{co}}$ we obtain from (40)

$$\mathsf{K} = \boldsymbol{C}\boldsymbol{A}^{-1} + (\boldsymbol{C}\boldsymbol{A}^{-1}\boldsymbol{B} - \boldsymbol{D})\Delta^{-1}\boldsymbol{X}\boldsymbol{A}^{-1} \tag{42}$$

where

$$\Delta = \boldsymbol{Y} - \boldsymbol{X}\boldsymbol{A}^{-1}\boldsymbol{B}. \tag{43}$$

These are the equations which MJS obtained 20 years ago. He did not like them, as being too cumbersome, and did not, therefore, publish them.

6.2. Variants on the method

6.2.1. Variant 1. Continuing to use $r_I = r_0$, from (21) and (28) we have, for $r \geqslant r_1$,

$$\boldsymbol{F} = \boldsymbol{S} + \boldsymbol{C}\boldsymbol{\mathcal{K}}^{(0)} = [s + s(cs) - c(ss)] + [c + s(cc) - c(sc)]\boldsymbol{\mathcal{K}}^{(0)} \tag{44}$$

$$= s[1 + (cs) + (cc)\boldsymbol{\mathcal{K}}^{(0)}] + c[-(ss) + \boldsymbol{\mathcal{K}}^{(0)} - (sc)\boldsymbol{\mathcal{K}}^{(0)}] \tag{45}$$

† The prototype of the integrals involved is given by:
$\exp(-\kappa r)\int r^{-\lambda-1}\exp[(\kappa + \mathrm{i}k)r]\,\mathrm{d}r = (\kappa + \mathrm{i}k)^{-1}\{r^{-\lambda-1}\exp(\mathrm{i}kr) + (\lambda + 1)\exp(-\kappa r)\int r^{-\lambda-2}\exp[(\kappa + \mathrm{i}k)r]\,\mathrm{d}r\}$.

and hence, on re-normalizing $\boldsymbol{F}$,

$$\boldsymbol{F} = s + c\boldsymbol{\mathcal{K}}^{(1)} \tag{46}$$

where

$$\boldsymbol{\mathcal{K}}^{(1)} = [-(ss) + \boldsymbol{\mathcal{K}}^{(0)} - (sc)\boldsymbol{\mathcal{K}}^{(0)}][1 + (cs) + (cc)\boldsymbol{\mathcal{K}}^{(0)}]^{-1}. \tag{47}$$

6.2.2. Variant 2. We now take the lower limit to be $r_I = \infty$ and put

$$\boldsymbol{F} = \boldsymbol{S} + \boldsymbol{C}\boldsymbol{\mathcal{K}}^{(2)} \tag{48}$$

where we now have $\boldsymbol{S} = s$ and $\boldsymbol{C} = s$ for $r \geqslant r_1$. From (4),

$$\boldsymbol{\mathcal{K}}^{(2)} = -(\boldsymbol{C} - \boldsymbol{R}\boldsymbol{C}')^{-1}(\boldsymbol{S} - \boldsymbol{R}\boldsymbol{S}') \qquad \text{at} \quad r = r_0, \tag{49}$$

where $\boldsymbol{S}$ and $\boldsymbol{C}$ at $r = r_0$ are given by (22). Using (10) we obtain

$$\boldsymbol{\mathcal{K}}^{(2)} = [1 + (sc) + \boldsymbol{\mathcal{K}}^{(0)}(cc)]^{-1}[-(ss) + \boldsymbol{\mathcal{K}}^{(0)} - \boldsymbol{\mathcal{K}}^{(0)}(cs)]. \tag{50}$$

Although, analytically, (49) and (50) give identical values for $\boldsymbol{\mathcal{K}}^{(2)}$, numerically, (50) is more accurate when c becomes large at $r = r_0$ as its inner turning point moves out beyond the R-matrix boundary with increasing l.

6.3. Symmetrization of K

We see that $\boldsymbol{\mathcal{K}}^{(2)}$ is the transpose of $\boldsymbol{\mathcal{K}}^{(1)}$. We require a symmetric matrix $\boldsymbol{\mathcal{K}}$ and therefore put

$$\boldsymbol{\mathcal{K}} = (\tfrac{1}{2})\left(\boldsymbol{\mathcal{K}}^{(1)} + \boldsymbol{\mathcal{K}}^{(2)}\right). \tag{51}$$

For $r \geqslant r_1$ we can then put $\boldsymbol{F} = s + c\boldsymbol{\mathcal{K}}$ and obtain, as in section 4,

$$\mathsf{K} = \boldsymbol{\mathcal{K}}_{\mathrm{oo}} - \boldsymbol{\mathcal{K}}_{\mathrm{oc}}(\tau + \boldsymbol{\mathcal{K}}_{\mathrm{cc}})^{-1}\boldsymbol{\mathcal{K}}_{\mathrm{co}}. \tag{52}$$

6.4. Summary on elimination of the increasing solutions

In section 6.1 we used functions $\boldsymbol{F}$ linear in the perturbation integrals. We obtained the expressions (30), (31) for the physical functions $\boldsymbol{G}$ in which the perturbation integrals involving the increasing functions p occur only in the terms $\boldsymbol{PT}$ and $\boldsymbol{QT}$ which are of second order in the perturbation. To a consistent first order we neglected those terms. But the method of section 6.1 did not give an expression for K of the desired form (1).

In section 6.2 we re-normalized the functions $\boldsymbol{F}$ to the forms (46) or (48) before forming the linear combinations to obtain $\boldsymbol{G}$. In those expressions the perturbation integrals occur in both the numerators and denominators on the right-hand sides of (47) and (50). We now make the assumption—without proof—that in (47) and (50) one can neglect all integrals involving the functions p, i.e. the closed-channel s and c functions can be replaced by $-q\gamma$ and $q\sigma$, respectively. We then obtain expressions of the form (1) involving only convergent integrals.

7. The method of GRPB

GRPB calculate $\boldsymbol{\mathcal{K}}$ using equations similar to (49), (50) of the present paper, and subsequently symmetrize $\boldsymbol{\mathcal{K}}$. Their method differs from that described in section 6 in that, in the elimination of divergent integrals, they use approximations which are less drastic.

Let us define points $a = r_0$, $b = r_1$ and $c = r_0 + \mathrm{i}(r_1 - r_0)$. All integrals around the closed coutour, $\int_{abca}$, are equal to zero. For open channels, GRPB use functions such as

$$\phi^+ = c + \mathrm{i}s \sim k^{-1/2}\exp(\mathrm{i}\zeta) \tag{53}$$

and consider integrals† $(\phi^+ p)$: then (cp) and (sp) are the real and imaginary parts of $(\phi^+ p)$. Along ac, ϕ^+ is exponentially decaying and p is oscillatory, so that the integral $\int_a^c$ is convergent in the limit of $r_1 \to \infty$: GRPB take r_1 to be such that adequate convergence is obtained. They replace the integral $\int_a^b$ by the integral $\int_a^c$, which implies neglect of the integral around the contour bc, which is divergent in the limit of $r_1 \to \infty$. They assert, without proof, that 'when we form the physical closed-channel solution ... these divergences cancel'. The discussion of section 6 provides some justification for their procedure.

In section 6.1 we neglected the terms $\boldsymbol{PT}$ and $\boldsymbol{QT}$ in (30), (31). In the method of GRPB one would retain the contribution from those terms from the integrals along ac and neglect only the divergent contribution from cb.

8. Some numerical results

We have made calculations for a simple model.

The model. We consider two channels with energies $E_1 = 0.0$, $E_2 = 0.5$; angular momenta $l_1 = 0$, $l_2 = 1$; inner-region boundary at $r_0 = 2$; outer-region charge $z = 1$. We shall consider energies E in the range $0 < E < E_2$ and shall refer to channel 1 as open (subscript 'o') and channel 2 as closed (subscript 'c'). The effective quantum number in the closed channel is $\nu = 1/[E_2 - E]^{-1/2}$.

The inner-region solutions. We assume no inner-region coupling between channels 'o' and 'c' and take the inner-region quantum defects to be μ_o and μ_c. Then at $r = r_0$ the inner-region functions are: $f_{oo} = (s_o \cos(\pi\mu_o) + c_o \sin(\pi\mu_o))$, $f_{oc} = 0$, $f_{co} = 0$, $f_{cc} = (s_c \cos(\pi\mu_c) + c_c \sin(\pi\mu_c))$. The R-matrix is $R_{oo} = f_{oo}/f'_{oo}$, $R_{oc} = 0$, $R_{co} = 0$, $R_{cc} = f_{cc}/f'_{cc}$.

The outer region. The only non-Coulomb interaction in the outer region is taken to be dipole coupling between channels 'o' and 'c': $W_{oo} = W_{cc} = 0$, $W_{oc} = W_{co} = C/r^2$. We take $C = 1.0$.

The two methods. Equation (51) is obtained on neglecting all integrals involving the increasing function p. We refer to that as method 1. The method of GRPB makes less drastic approximations and will be referred to as method 2.

We put $\mathbf{K}_{oo} = \tan(\pi\eta)$: then $\pi\eta$ is the elastic scattering phase shift. With $\mu_o = 0$, one obtains resonances in the vicinity of $\nu = (n - \mu_c)$, with $\eta \simeq \frac{1}{2}$ at $\nu \simeq (n - \mu_c)$. Figure 1 shows η for the $n = 4$ resonances with $\mu_c = 0$. Results from method 2 are shown as full curves, those from method 1 as dashed curves. The top part of the figure shows values of η. The differences in values of η from the two methods are seen to be fairly small: the differences between method 2 and STGF are indistinguishable on the scale used in the top part. The lower part shows, on a more expanded scale, values of $\delta\eta(1) = \eta(1) - \eta$ (STGF) and $\delta\eta(2) = \eta(2) - \eta$ (STGF). In the vicinity of $\nu = 4$ we have $\eta \simeq 0.5$ and $\tan(\pi\eta)$ is large: largish values of $\delta\eta$ then give fractional errors in $\tan(\pi\eta)$ which are quite small. It is seen that method 1 gives errors much larger than those from method 2.

Figure 2 shows the elements of the matrix $\mathcal{K}$ for $3.5 \leqslant \nu \leqslant 4.5$. It is seen that method 2 gives $\mathcal{K}$ to be nearly constant in that range, but that method 1 gives much more marked

† Strictly speaking, they consider integrals $(\phi^+ s_c)$ and $(\phi^+ c_c)$ where $s_c = (p\sigma - q\gamma)$ and $c_c = (p\gamma + q\sigma)$. The contributions from q are convergent.

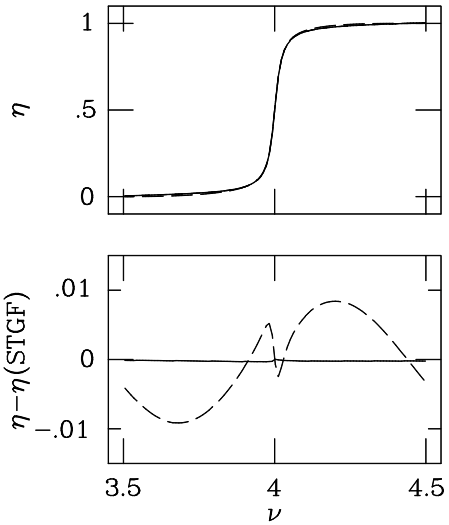

Figure 1. Values of η for $\mu_c = 0$ (the elastic-scattering phase-shift is $\pi\eta$). Full curves, method 2; dashed curves, method 1. The upper plot shows values of η, and the lower plot values of $\eta - \eta$ (STGF).

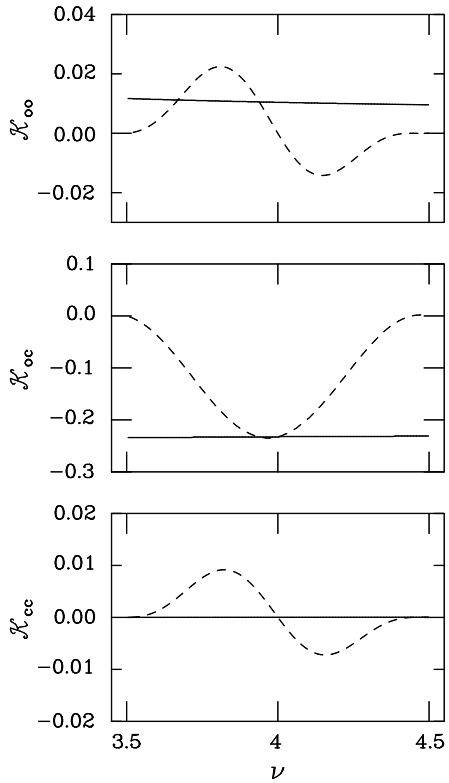

Figure 2. The elements of the matrix $\mathcal{K}$ for $\mu_c = 0$. Curves as for figure 1.

variations. This is to be expected since method 1 uses the closed-channel function q which is not slowly varying with energy while method 2 uses closed-channel s and c functions which are.

For $\mu_c = 0.5$ the resonances are much narrower than those for $\mu_c = 0$. Figure 3 shows values of η for $3.4 \leqslant \nu \leqslant 3.6$. It is seen again that the differences between values of η from the two methods are fairly small, but that method 2 is much more accurate than method 1. For the two-channel case the variants (47) and (50) are identical. For the case of $\mu_c = 0.5$ we find that the matrices in the denominator of those expressions have a singularity in the vicinity of $\nu = 3.43$. Figure 4 shows that leads to some rather wild variations in the elements of $\mathcal{K}$ for method 1. There is, however, no similar wild variation in η (see figure 3).

9. Discussion

The multipole potentials are handled using perturbation theory. In order to study systematically the elimination of exponentially increasing functions p, it is necessary to use functions $\boldsymbol{F}$ which are linear in the perturbation integrals. In section 6.1 we showed that results correct to a consistent first order in the perturbations are obtained if one neglects all integrals involving the functions p. In that section we obtained a somewhat ugly expression for $\mathbf{K}$ which does not

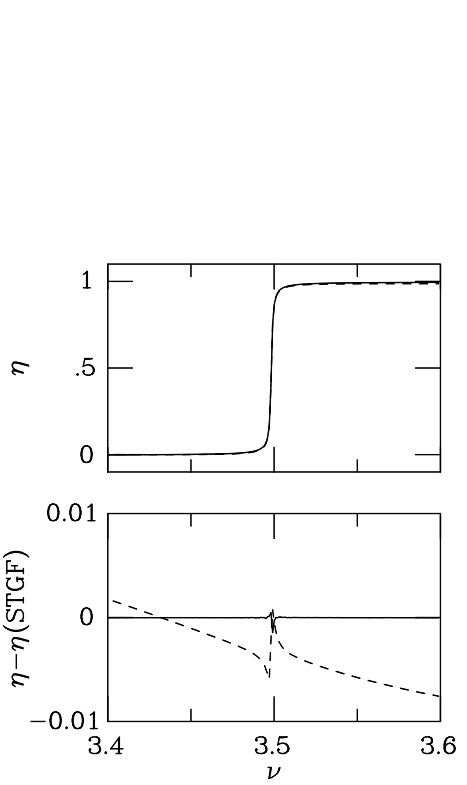

Figure 3. As figure 1, for $\mu_c = 0.5$.

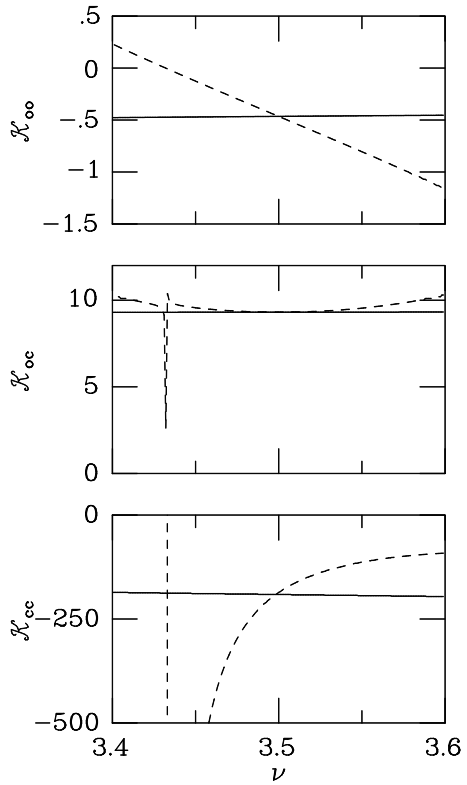

Figure 4. As figure 2, for $\mu_c = 0.5$.

have the form of (1). In section 6.2 we obtained two variants, one with $\mathbf{K}$ of the form $\boldsymbol{B}\boldsymbol{A}^{-1}$ and the other with the form $\boldsymbol{A}^{-1}\boldsymbol{B}$. Taking the mean we obtained a symmetric $\boldsymbol{\mathcal{K}}$ which can be used in (1). In section 8 that was referred to as method 1.

Less drastic approximations are made in the work of GRPB. In their work the perturbation integrals involving p are evaluated in the complex plane and the only approximation is to neglect contributions from a contour on which $|r| \to \infty$. In section 8 that was referred to as method 2.

We have presented some numerical results for a simple model. The values for $\mathbf{K}$ from method 2 are more accurate than those from method 1. More important is the fact that method 2 gives matrices $\boldsymbol{\mathcal{K}}$ which are much more slowly varying as functions of energy. In the present paper we have considered only two simple examples, but we note that in the work of GRPB many other examples were considered and found to give equally satisfactory results. The practical usefulness of equation (1) is that, if $\boldsymbol{\mathcal{K}}$ is slowly varying, it need be calculated only for a small number of energies. The scattering matrix is $\mathbf{S} = (1 + \mathrm{i}\mathbf{K})(1 - \mathrm{i}\mathbf{K})^{-1}$. Defining $\boldsymbol{\mathcal{S}} = (1 + \mathrm{i}\boldsymbol{\mathcal{K}})(1 - \mathrm{i}\boldsymbol{\mathcal{K}})^{-1}$ one obtains

$$\mathbf{S} = \boldsymbol{\mathcal{S}}_{oo} - \boldsymbol{\mathcal{S}}_{oc}[\boldsymbol{\mathcal{S}}_{cc} - \exp(-2\pi\mathrm{i}\nu)]^{-1}\boldsymbol{\mathcal{S}}_{co} \tag{54}$$

which can be used to locate positions and widths of resonances and to obtain cross-sections averaged over energy (see S83).

It should be noted that we have not achieved a complete mathematical derivation of the formulae used in methods 1 and 2, although they are rendered plausible by the discussion of section 6.1. Extensive numerical testing shows that method 2 does indeed give accurate results.

10. The computer codes

The original version of STGF was written by MJS. With various modifications it has been used extensively in the work of the Opacity Project (The Opacity Project Team 1995) and the subsequent Iron Project (Hummer *et al* 1993). The subroutine CORINT used in the work of GRPB for the calculation of the perturbation integrals was written by Dr F Robicheaux. A version of STGF incorporating the methods of GRPB has been written by NRB and will be used in a new project, RmaX, which will be mainly concerned with the calculation of data important for x-ray astronomy.

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