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A theoretical determination of the depth of the surface effect on impurity in semiconductors

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Abstract. From a previously obtained set of generalised spheroidal wave equations for a hydrogenic system in half-space, a method is developed for the determination of the depth of the surface effect on the eigenstates of donor impurity in semiconductors. As a concrete example of an application, the depths of the surface effect for the first 22 impurity states in GaAs are calculated using this method.

1. Introduction

Within the framework of effective-mass theory, a shallow donor impurity in a semiconductor with a surface can be treated as a hydrogenic system in half-space. The dominant potential function is chosen to be Coulombic in the interior, with an infinite barrier at the surface. The Schrödinger equation of such a system is shown to be separable in prolate spheroidal coordinates and a set of generalised spheroidal wave equations results from the separation (Shan *et al* 1985). The general properties of this set of equations have been investigated in great detail (Shan (1987); hereafter referred to as I), and exact solutions for a large number of eigenstates have been obtained in a sufficiently large range of system-centre–surface distance (Shan *et al* (1987); hereafter referred to as II). Much quantum mechanical study of this set of equations remains to be done; progress is currently steady. In the meantime, the results in I and II are ready for application to surface problems in semiconductor physics.

Consider an impurity positioned at a distance d from the surface of a semiconductor. It is quite obvious that the surface effect on the impurity is largest when $d = 0$ and decreases as d increases. The results calculated in II show that there is a distance, sufficiently large but finite, at which the surface effect essentially dwindles away to nothing. This distance, denoted d_s , is called the ‘depth of the surface effect’. d_s provides a quantitative measure of how far the influence of the surface on the impurity may extend. The purpose of the present paper is to develop a method of calculating the depth of the surface effect on donor impurity in semiconductors. As in I and II, the relevant formulae in this method are obtained using some of the existing mathematical methods and techniques of molecular physics with appropriate modifications.

2. The magnitude of the surface effect

The basic equations resulting from separation of variables in the Schrödinger equation for an impurity in a semiconductor with a surface are (Shan *et al* 1985)

$$(d/d\xi)[(\xi^2 - 1)(d/d\xi)M(\xi)] + [A - m^2/(\xi^2 - 1) + \frac{1}{4}R^2E\xi^2 + R\xi]M(\xi) = 0 \quad (1)$$

$$(d/d\eta)[(1 - \eta^2)(d/d\eta)N(\eta)] + [-A - m^2/(1 - \eta^2) - \frac{1}{4}R^2E\eta^2 + R|\eta|]N(\eta) = 0 \quad (2)$$

$$\left(\frac{d^2}{d\varphi^2} + m^2\right)\Phi(\varphi) = 0. \quad (3)$$

Equations (1) and (2) are called 'generalised spheroidal wave equations'. The (unnormalised) solution of (3) is $\Phi(\varphi) = \exp(\pm im\varphi)$ where m is zero or a positive integer. In equations (1) and (2), $R \equiv 2d$ is twice the distance between the impurity and the boundary surface and is measured in units of effective first Bohr radius $a_e \equiv \hbar^2\varepsilon/m^*e^2$, where ε is the dielectric constant of the semiconductor and m^* is the effective mass of the electron. The energy eigenvalue E is measured from the conduction band edge in units of the effective Rydberg $R^* \equiv e^4m^*/2\varepsilon^2\hbar^2$. A is a separation constant. Equations (1) and (2) have been solved exactly in II. A careful analysis shows that, as a function of R , the energy eigenvalue $E(R)$ displays faithfully and in detail the surface effect on the impurity system. It is advantageous to define the magnitude of the surface effect as

$$Y_s(R) \equiv (E(R) - E(\infty))/(E(0) - E(\infty)) \quad (4)$$

to account quantitatively for the surface effect, where $E(0) = -1/n^2$ and $E(\infty) = -1/N^2$. n is the spherical principal quantum number in the quasi-united-atom (QUA) limit and N the parabolic principal quantum number in the quasi-separated-atom (QSA) limit as shown in I. $Y_s(R)$ has the properties that $Y_s(0) = 1$ and $Y_s(\infty) = 0$, and $Y_s(R)$ decreases monotonically from 1 to 0 as R increases from 0 to ∞ , as can be easily seen from the variation of $E(R)$ with R obtained in II. These properties are common to the $Y_s(R)$ of all eigenstates of the impurity system. $Y_s(R)$ tells us numerically how large the surface effect on an impurity at R is. Thus 'magnitude of the surface effect' is an appropriate description for $Y_s(R)$.

3. The depth of the surface effect

The depth of the surface effect, d_s , can be defined by means of (4). Strictly speaking, d_s must be infinity in order to make $Y_s(R = 2d_s)$ equal to zero. However, a definition for d_s with such a severe restriction, although rigorous in a mathematical sense, is hardly useful in physical applications. In the problems concerned with impurity in semiconductors, some experimental constants often have to be used as input data, e.g. ε and m^* . The experimental values of these constants usually have three to four significant figures. Therefore, the number of reliable figures in the calculated numerical results is at best three or four. A distance d for which $Y_s(2d)$ has a vanishingly small value of the order of 10^{-4} (or 10^{-5}) ought to be large enough to be designated physically, although not mathematically, the depth of the surface effect, d_s . That is,

$$Y_s(2d_s) = 10^{-4} \quad (\text{or } 10^{-5}). \quad (5)$$

Y_s given by (5) is practically equal to zero, its first four or five figures only being taken

into account to match the number of significant figures of the other quantities. The boundary surface exerts no substantial influence over an impurity at a distance d_s from it.

4. Asymptotic expansion of the energy eigenvalue

Calculating the depth of the surface effect, d_s , from (4) and (5) involves calculating the energy eigenvalue $E(R)$. One way of calculating $E(R)$ is to solve equations (1) and (2) simultaneously, as has been done in II. The calculation must start from $R = 0$ and advance step by step with small increments ΔR until $R = 2d_s$ is reached. This will require a lot of effort. If we are only calculating d_s , such a calculation procedure is not economical in computation time, because not all the calculations in the interval of smaller R s are necessary. Only the energy eigenvalues at larger R s around $2d_s$ are needed for calculating the depth of the surface effect. The energy eigenvalues in this region of R can be obtained from an asymptotic expansion of $E(R)$. The most efficient and economical way of determining the depth of the surface effect is the incorporation of the asymptotic expansion into the combination of equations (4) and (5). The asymptotic expansion of $E(R)$ can be obtained by following a procedure similar to that of Power (1974). Let $p^2 \equiv -\frac{1}{4}R^2E$ and $A' \equiv A - p^2$, as defined in I. The eigenvalues $E(R)$ at large but finite R are given by

$$E(R) = -1/(N + \delta T)^2 = -1/N^2 + 2\delta T/N^3 + O(\delta T^2) + \dots \tag{6}$$

$$\begin{aligned} \delta T = (4p)^{2\chi} 2^{-2D} e^{-2p} [T!(T+m)!]^{-1} \{ & 1 + (1/4p)(-6\chi^2 - 2\omega + 2D^2) \\ & + (1/32p^2)[36\chi^4 + (64 \ln 2 - 56)\chi^3 - 4\chi + 24\chi^2\omega \\ & + 4\omega^2 - 8\chi\omega + D[(8 - 64 \ln 2)\chi^2 + 8\omega - 12] \\ & + D^2(-24\chi^2 - 8\omega + 44\chi) - 12D^3 + 4D^4\} + O(1/p^3) \end{aligned} \tag{7}$$

where

$$D = R/2p \tag{8}$$

$$\chi = T + \frac{1}{2}(m + 1) + \delta T \tag{9}$$

$$\omega = \frac{1}{4}(1 - m^2) \quad N = m + 1 + S + T.$$

N , S and T are the parabolic quantum numbers in the QSA limit as defined in I. The derivation of (6) and (7) is given in the Appendix. It is easily seen that $\delta T \rightarrow 0$ as $R \rightarrow \infty$ (the QSA limit). The practical way of using these formulae to calculate the energy eigenvalue is as follows. For a given value of R and a given eigenstate labelled by the set of spherical quantum numbers nlm in the QUA limit, we first obtain the parabolic quantum numbers N , S , T and m in the QSA limit from equations (30) and (22) of I. Then δT is calculated from (7), in which p , D and χ are approximated by their values in the QSA limit, i.e. $p \rightarrow R/2N$, $D \rightarrow N$ and $\chi \rightarrow T + \frac{1}{2}(m + 1)$. Terms of the order of $1/p^3$ or higher are dropped. Putting this δT in (6) and omitting the terms of the order of δT^2 and higher, we then have the energy eigenvalue of state nlm at R . The energy eigenvalues calculated using this asymptotic expansion for several sample states are listed in table 1. The exact energy eigenvalues obtained in II are also included in this table for comparison. The ranges of R in this table are selected, by visual inspection of the energy curves in II, to be roughly in the vicinity of $2d_s$. It may be seen that the eigenvalues obtained from (6)

Table 1. Energy eigenvalues in the asymptotic region. E is in $0.1 R$ and R^* in a_e .

State	R	E	
		Asymptotic expansion	Exact
2p σ	7.0	-9.938373906	-9.937709483
	8.0	-9.973872974	-9.973838869
	9.0	-9.989125285	-9.989150049
	10.0	-9.995536876	-9.995551569
4d π	17.0	-0.1099416373	-0.1100193938
	18.0	-0.1102055673	-0.1102657223
	19.0	-0.1104120108	-0.1104577922
	20.0	-0.1105728690	-0.1106072598
	25.0	-0.1109705015	-0.1109777610
5f σ	32.0	-0.1108109218	-0.1108211134
	34.0	-0.1109272629	-0.1109331825
	36.0	-0.1109996380	-0.1110029569
	38.0	-0.1110441220	-0.1110459375
	40.0	-0.1110711752	-0.1110721513
5g φ	38.0	-0.6217039259	-0.6216618585
	40.0	-0.6225964257	-0.6225787962
	42.0	-0.6232617871	-0.6232552506
	44.0	-0.6237524684	-0.6237505569
6f δ	30.0	-0.3973756361	-0.3975032763
	32.0	-0.3980400820	-0.3981417494
	34.0	-0.3985431489	-0.3986209997
	36.0	-0.3989216518	-0.3989796711
	38.0	-0.3992048649	-0.3992472689

and (7) are in practice close enough to the exact results.

5. Numerical results and discussion

The semiconductor GaAs is used as an example for the numerical calculations. Useful parameters are $m^* = 0.0665 m_e$ and $\epsilon = 12.5$ (Summers *et al* 1970). The effective Bohr radius $a_e = 99.469 \text{ \AA}$ and the effective Rydberg $R^* = 5.790 \text{ meV}$. The depth of the surface effect, d_s , is computed by the Newton-Raphson method (Dodes 1978). The numerical results obtained from $Y_s = 10^{-4}$ and $Y_s = 10^{-5}$ for the first 22 states are tabulated in tables 2 and 3, respectively. The energy eigenvalue in each state at $R = 2d_s$ is also computed and given in the last column of the table and it may easily be seen that this eigenvalue is actually equal to the energy eigenvalue in the QSA limit. This suffices to demonstrate the fact that the depth of the surface effect, d_s , in the second column of these tables is computed correctly. The negative of the derivative of E with respect to d , which is $-2dE/dR$, is the force due to the presence of the boundary surface of the semiconductor. On physical grounds this force is for each state expected to vanish at $R = 2d_s$. The numerical results in the third columns of these tables show that this is indeed the case.

We present here only the results calculated from $Y_s = 10^{-4}$ and 10^{-5} . However, where less precision in the determination of d_s with $Y_s = 10^{-3}$ is required, the expansion formulae (6) and (7) are still within the scope of applicability.

The present method can also be applied to the Wannier exciton. m^* is replaced by

Table 2. The depth of the surface effect on impurity in GaAs calculated from $Y_s = 10^{-4}$. The energy is in meV and the length in Å.

State	d_s	$-(dE/dR) _{R=2d_s}$	$-E(2d_s)$
2pσ	595.245	$0.6858358546 \times 10^{-4}$	5.78956
3pσ	1023.782	$0.6405782659 \times 10^{-5}$	1.44741
3dπ	1362.653	$0.6454468695 \times 10^{-5}$	1.44741
4pσ	1351.210	$0.1539710667 \times 10^{-5}$	0.64330
4dπ	1836.192	$0.1538426362 \times 10^{-5}$	0.64330
4fσ	1702.725	$0.8693246637 \times 10^{-5}$	1.44741
4fδ	2265.967	$0.1528629673 \times 10^{-5}$	0.64330
5pσ	1604.419	$0.5581834305 \times 10^{-6}$	0.36186
5dπ	2217.532	$0.5508367166 \times 10^{-6}$	0.36186
5fσ	2312.311	$0.2229813416 \times 10^{-5}$	0.64330
5fδ	2767.272	$0.5445254258 \times 10^{-6}$	0.36126
5gπ	2786.437	$0.2210662338 \times 10^{-5}$	0.64330
5gφ	3283.822	$0.5379400526 \times 10^{-6}$	0.36186
6pσ	1793.115	$0.2537520651 \times 10^{-6}$	0.23159
6dπ	2516.137	$0.2473233722 \times 10^{-6}$	0.23159
6fσ	2815.703	$0.8374599525 \times 10^{-6}$	0.36186
6fδ	3175.421	$0.2433578413 \times 10^{-6}$	0.23159
6gπ	3426.539	$0.8263204538 \times 10^{-6}$	0.36186
6gφ	3801.020	$0.2400388827 \times 10^{-6}$	0.22159
6hσ	3260.256	$0.2569809792 \times 10^{-5}$	0.64330
6hδ	3993.215	$0.8150650921 \times 10^{-6}$	0.36186
6hγ	4400.869	$0.2366541165 \times 10^{-6}$	0.23159

Table 3. The depth of the surface effect on impurity in GaAs calculated from $Y_s = 10^{-5}$. The energy is in meV and the length in Å.

State	d_s	$-(dE/dR) _{R=2d_s}$	$-E(2d_s)$
2pσ	719.371	$0.6973015562 \times 10^{-5}$	5.78995
3pσ	1270.253	$0.6495074435 \times 10^{-6}$	1.44749
3dπ	1626.288	$0.6534028902 \times 10^{-6}$	1.44749
4pσ	1712.121	$0.1545426159 \times 10^{-6}$	0.64333
4dπ	2227.280	$0.1546995816 \times 10^{-6}$	0.64333
4fσ	1980.129	$0.8809808119 \times 10^{-6}$	1.44749
4fδ	2681.578	$0.1541753260 \times 10^{-6}$	0.64333
5pσ	2068.715	$0.5526147047 \times 10^{-7}$	0.36187
5dπ	2728.459	$0.5490653011 \times 10^{-7}$	0.36187
5fσ	2727.942	$0.2250521312 \times 10^{-6}$	0.64333
5fδ	3314.408	$0.5451319719 \times 10^{-7}$	0.36187
5gπ	3221.645	$0.2237715646 \times 10^{-6}$	0.64333
5gφ	3862.611	$0.5407932967 \times 10^{-7}$	0.36187
6pσ	2351.616	$0.2481730358 \times 10^{-7}$	0.23160
6dπ	3140.566	$0.2444841230 \times 10^{-7}$	0.23160
6fσ	3363.308	$0.8391236149 \times 10^{-7}$	0.36187
6fδ	3848.893	$0.2419776570 \times 10^{-7}$	0.23160
6gπ	4003.402	$0.8316341966 \times 10^{-7}$	0.36187
6gφ	4515.845	$0.2396739883 \times 10^{-7}$	0.23160
6hσ	3720.575	$0.2606780266 \times 10^{-6}$	0.64333
6hδ	4596.941	$0.8238885078 \times 10^{-7}$	0.36187
6hγ	5153.733	$0.2372270943 \times 10^{-7}$	0.23160

the reduced mass calculated from the effective masses of the electron and the hole, and d (as well as d_s) is the distance between the centre of mass of the electron-hole system and the boundary surface (Shan *et al* 1985).

In conclusion, it is worth mentioning that our objective in the present paper is the development of a simple, easily applicable method to be used solely for the determination of the depth of the surface effect. In order to obtain the relevant formulae in manageable forms, mathematical rigour has to some extent been sacrificed. A rigorously derived expansion formula for $E(R)$ would consist of a large number of terms and would be valid in the interval covering large R as well as the R s whose values are somewhat smaller than $2d_s$. However, such an expansion formula for $E(R)$ would not be more suitable for the determination of the depth of the surface effect because (6) and (7) are already good enough for this purpose.

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Appendix. Derivation of (6) and (7)

Following Power (1974), let the solution $M(\xi)$ of (1) be

$$M(\xi) = (\xi^2 - 1)^{m/2} \exp[-p(\xi - 1)]M_1[2p(\xi - 1)]. \tag{A1}$$

$M_1[2p(\xi - 1)]$ satisfies the following differential equation:

$$(L(u, p, m, C) - A'_\xi)M(u) = 0 \tag{A2}$$

where

$$u = 2p(\xi - 1) \quad C = R/2p$$

and

$$L(u, p, m, C) = u(u + 4p) d^2/du^2 + [-u^2 + 2u(m + 1 - 2p) + 4p(m + 1)] \times d/du + m(m + 1) - 2p(m + 1 - C)(1 + u/2p). \tag{A3}$$

When R is large but finite, p is also a large parameter. Dividing (A2) through by $4p$ and retaining the leading terms, we have

$$[u d^2/du^2 + (m + 1 - u) d/du + \frac{1}{2}(C - m - 1 - A'_\xi/2p)]M_1(u) = 0. \tag{A4}$$

The solution for M_1 is given by

$$M_1(u) \simeq M(\frac{1}{2}(m + 1 - C + A'_\xi/2p), m + 1, u) \tag{A5}$$

where M is the confluent hypergeometric function, and

$$[(S + m)!/S!m!]M(-S, m + 1, u) = L^m_{S+m}(u) \tag{A6}$$

where $L^m_{S+m}(u)$ is the associated Laguerre polynomial. As $R \rightarrow \infty$, $M_1(u)$ becomes $L^m_{S+m}(u)$, as obtained in I. Hence

$$\frac{1}{2}(C - m - 1 - A'_\xi/2p) = S + \delta S \tag{A7}$$

with $\delta S \rightarrow 0$ as $R \rightarrow \infty$. For small δS , we have

$$1/\Gamma(-S - \delta S) \simeq (-1)^{S+1}S!\delta S. \tag{A8}$$

When u is very large, the confluent hypergeometric function becomes

$$M(-S - \delta S, m + 1, u) \approx \frac{s!m!}{(S + m)!} L_{S+m}^m(u) + \frac{(-1)^{S+1}m!}{(S + m)!} \frac{e^u \delta S}{u^{S+m+1}} \sum_j \frac{(S + j)!(S + m + 1)!}{j!u^j}. \tag{A9}$$

We must let $\delta S = 0$ even for finite R , otherwise the second term in (A9) diverges as $\exp(p\xi)$ as $\xi \rightarrow \infty$. Thus, for our initial approximation, we take

$$A'_{\xi} \approx -2p(2S + m + 1) + 2pC. \tag{A10}$$

As for equation (2), we let the solution $N(\eta)$ be as follows.

For $-1 \leq \eta \leq 0$

$$N(\eta) = (1 - \eta^2)^{m/2} \exp[-p(1 + \eta)]N_1^{(-)}[2p(1 + \eta)]. \tag{A11}$$

$N_1^{(-)}$ satisfies the following equation:

$$(L(v, -p, m, D) - A'_\eta)N_1^{(-)}(v) = 0 \tag{A12}$$

where $v = 2p(1 + \eta)$ for $0 \leq v \leq 2p$ and $D = R/2p$.

For $0 \leq \eta \leq 1$

$$N(\eta) = (1 - \eta^2)^{m/2} \exp[-p(1 - \eta)]N_1^{(+)}[2p(1 - \eta)]. \tag{A13}$$

We then have

$$(L(w, -p, m, D) - A'_\eta)N_1^{(+)}(w) = 0 \tag{A14}$$

where $w = 2p(1 - \eta)$ for $0 \leq w \leq 2p$.

Through a procedure completely analogous to that described above, we obtain

$$N_1^{(-)}(v) \approx M(\frac{1}{2}(m + 1 - D - A'_\eta/2p), m + 1, v) \tag{A15}$$

$$N_1^{(+)}(w) \approx M(\frac{1}{2}(m + 1 + D - A'_\eta/2p), m + 1, w) \tag{A16}$$

$$A'_\eta \approx 2p[2(T + \delta T) + m + 1] - 2pD \tag{A17}$$

with $\delta T \rightarrow 0$ as $R \rightarrow 0$. Using (A9) for $N_1^{(-)}(v)$ and $N_1^{(+)}(w)$, we must have a non-zero δT so that $N_1^{(-)}(v)$ and $N_1^{(+)}(w)$ can satisfy their boundary condition $N_1^{(-)}(2p) = N_1^{(+)}(2p) = 0$. If we take $\delta T \approx \exp(-2p)$, the two terms in (A9) will be of comparable magnitude and cancel each other to give zero.

In the following derivation of δT we shall use the modified comparison method (Slavyanov 1967, Komarov and Slavyanov 1968, Power 1974). In the region $-1 \leq \eta \leq 0$ we use a solution for $N(\eta)$

$$N(\eta) = M_{x,m/2}(2pt(\eta))/[t'(\eta)(1 - \eta^2)]^{1/2} \tag{A18}$$

where $M_{x,m/2}$ is the Whittaker function (Abramowitz and Stegun 1964). Then

$$(t')^2 - 1 + \frac{2}{p} \left(\frac{A'/2p + (R/2p)\eta}{1 - \eta^2} - \frac{\chi(t')^2}{t} \right) + \frac{1 - m^2}{4p^2} \left[\frac{4}{(1 - \eta^2)^2} - \left(\frac{t'}{t} \right)^2 \right] - \frac{1}{2p^2} \left[\frac{t'''}{t'} - \frac{3}{2} \left(\frac{t''}{t'} \right)^2 \right] = 0. \tag{A19}$$

Here the subscript η of A' has been dropped for simplicity. $\eta = -1$ still gives a regular

singular point in the transformed equation and it gives the condition

$$t(-1) = 0. \quad (\text{A20})$$

The expansion of $A'/2p$ is obtained from the 'quantum condition' (Komarov and Slavyanov 1968)

$$\frac{A'}{2p} = -D + 2\chi t'(-1) + \frac{1-m^2}{4p} \left(\frac{t''(-1)}{t'(-1)} - 1 \right). \quad (\text{A21})$$

A lengthy calculation gives

$$\begin{aligned} t(\eta) = 1 + \eta + \frac{1}{p} \left[(\chi - D) \ln \left(\frac{1-\eta}{2} \right) \right] + \frac{1}{p^2} \left(\frac{\chi(\chi - D)}{1+\eta} \ln \frac{1-\eta}{2} - \frac{(\chi - D)^2 + \omega}{2(1-\eta)} \right. \\ \left. + \frac{1}{4} [(\chi - D)^2 + \omega] + \frac{1}{2} \chi(\chi - D) \right) + \frac{1}{p^3} \left(-\frac{\chi(\chi - D)^2}{2(1+\eta)^2} \ln^2 \frac{1-\eta}{2} \right. \\ \left. + \frac{(3\chi^2 + \omega)(\chi - D)}{2(1+\eta)^2} \ln \frac{1-\eta}{2} - \frac{\chi[(\chi - D)^2 + \omega]}{2(1-\eta)} \right. \\ \left. - \frac{(\chi - D)[(\chi - D) + \omega + 1]}{4(1-\eta)^2} + \frac{(3\chi^2 + \omega)(\chi - D)}{4(1+\eta)} \right. \\ \left. + \frac{1}{16} (10\chi^3 - 18\chi^2 D + 9\chi D^2 - 2\omega D - D^3) \right. \\ \left. + 6\omega\chi + \chi - D \right) + O(1/p^4) \end{aligned} \quad (\text{A22})$$

and

$$\begin{aligned} A' = 2p(2\chi - D) - 2(\chi^2 + \omega - \chi D) - (1/2p)[2\chi(\chi^2 + \omega) \\ - (3\chi^2 + \omega)D + \chi D^2] + O(1/p^2) \end{aligned} \quad (\text{A23})$$

where $\omega = \frac{1}{4}(1 - m^2)$ and $\chi = T + \frac{1}{2}(m + 1) + \delta T$. In the region $0 \leq \eta \leq 1$, we simply make the replacements

$$\chi \rightarrow \chi' \quad \eta \rightarrow -\eta \quad D \rightarrow -D \quad (\text{A24})$$

in the formulae derived for $-1 \leq \eta \leq 0$. A' is unchanged after the replacements. Thus

$$\chi = \chi' \quad (\text{A25})$$

i.e. $T = T'$. We also have the following relations:

$$t(\eta; p, \chi, D) = t(\eta; -p, -\chi, -D) \quad (\text{A26})$$

$$A'(p, \chi, d, \omega) = A'(-p, -\chi, -D, \omega). \quad (\text{A27})$$

Let a new function $G(\eta; p, \chi, D)$ be defined (Power 1974) by

$$N(\eta) = (1 - \eta^2)^{-1/2} [(-1)^{(m+1)/2} G(\eta; p, \chi, D) + G(\eta; -p, -\chi, -D)] \quad (\text{A28})$$

in the region $-1 \leq \eta \leq 0$. The boundary condition $N(\eta = 0) = 0$ demands

$$(-1)^{(m+1)/2} G(0; p, \chi, D) + G(0; -p, -\chi, -D) = 0 \quad (\text{A29})$$

where

$$\begin{aligned}
 G(0; p, \chi, D) &= m!(-2p)^\chi 2^{-D} e^{-p} [\Gamma(\frac{1}{2}(m+1) + \chi)]^{-1} \\
 &\times \{ [1 + (1/4p)(-3\chi^2 + 4\chi - \omega - 2D + D^2) + (1/32p^2)\{\chi^4(10 - 4 \ln 2) \\
 &+ \chi^3(32 \ln 2 - 52) + 64\chi^2 - 2\chi + (4 + 4 \ln 2)\chi^2\omega \\
 &+ 2\omega^2 - 12\chi^2\omega + D[(4 \ln 2)\chi^3 + (16 - 32 \ln 2)\chi^2 \\
 &- (24 + 4\omega \ln 2)\chi + 8\omega - 6] + D^2[(4 \ln 2 - 8)\chi^2 \\
 &+ 30\chi + 20] + D^3(-10 - 4\chi \ln 2) + D^4\} + O(1/p^3) \}. \quad (A30)
 \end{aligned}$$

Substituting (A8) and (A30) in (A29) we obtain

$$\begin{aligned}
 \delta T &= (4p)^{2\chi} 2^{-2D} e^{-2p} [T!(T+m)!]^{-1} \{ [1 + (1/4p)(-6\chi^2 - 2\omega + 2D^2) \\
 &+ (1/32p^2)\{36\chi^4 + (64 \ln 2 - 56)\chi^3 - 4\chi + 24\chi^2\omega + 4\omega^2 \\
 &- 8\chi\omega + D[(8 - 64 \ln 2)\chi^2 + 8\omega - 12] + D^2(-24\chi^2 - 8\omega + 44\chi) \\
 &- 12D^3 + 4D^4\} + O(1/p^3) \}. \quad (A31)
 \end{aligned}$$

The asymptotic expansion of A' is obtained from (A23):

$$\begin{aligned}
 A' &= A'_{\delta T=0} + (2R/N)(1 - \chi)\delta T - (N/R)[2\chi(\chi^2 + \omega) - (3\chi^2 + \omega)N \\
 &+ \chi N^2 - 3\chi^2 + \omega - 4N\chi + N^2]\delta T. \quad (A32)
 \end{aligned}$$

As $R \rightarrow \infty$ (the QSA limit), $E = -1/N^2$ and $N = m + 1 + S + T$ as obtained in I. When R is large but finite, we make the replacements $T \rightarrow T + \delta T$, $N \rightarrow N + \delta T$; then

$$E = -1/(N + \delta T)^2 = -1/N^2 + (2/N^3)\delta T + O(\delta T^2).$$

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