

Two-electron perturbation problems and Pollaczek polynomials

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys. A: Math. Gen. 24 4989

(<http://iopscience.iop.org/0305-4470/24/21/013>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 01/06/2010 at 13:59

Please note that [terms and conditions apply](#).

Two-electron perturbation problems and Pollaczek polynomials

G I Watson

Department of Theoretical Physics, University of Oxford, Oxford, OX1 3NP, UK

Received 7 February 1991

Abstract. Exact wavefunctions are found for two-particle atomic perturbation problems, as expansions in a discrete basis involving Pollaczek polynomials. The solutions contain no arbitrary parameters and fully satisfy the boundary conditions. For the case of the long-range interaction between two ground-state hydrogen atoms, the expansion coefficients reduce to closed form, yielding exact integral representations for the van der Waals dispersion coefficients. The extension to the helium perturbation problem is discussed. The treatment complements studies involving formal power series with logarithmic terms.

1. Introduction

The practical usefulness of formal solutions to the few-particle atomic Schrödinger equation depends on the properties of the expansion of the wavefunction. One choice is power series with logarithmic terms. Considerable progress has been made in obtaining solutions and compacting the resulting series, but the serious problem of formulating and applying the boundary conditions to determine the physical solution remains (Gottschalk and Maslen 1985, Abbott and Maslen 1987, Gottschalk *et al* 1987). The consequences of the boundary conditions are not fully understood.

One alternative is to select basis functions which naturally reflect the structure of the problem. For few-particle perturbation problems the obvious choice, namely the eigenfunctions of the unperturbed Hamiltonian, form a complete set. This basis avoids normalizability difficulties, but often leads to multiple continuum integrals which are intractable both analytically and numerically. For this reason the completeness of these eigenfunctions is sometimes regarded as having no more than formal significance.

A third possibility is in some ways intermediate between the first two: the wavefunction may be expanded in a discrete (L^2) basis. Koga and co-workers (Koga 1985a, b, 1986, 1989, Koga and Matsumoto 1985, Koga and Uji-ie 1986, 1987a, b) applied a discrete basis successfully to the momentum space perturbation equations for the van der Waals interaction between two hydrogen atoms, and related problems. A truncated basis set yielded highly accurate numerical values for the expansion coefficients and the energy eigenvalues. However the possibility of analytical solutions for the coefficients was not considered, nor did the role of the boundary conditions emerge clearly.

In this paper it is shown that the analysis simplifies when the wavefunction is expanded in terms of Pollaczek polynomials (Pollaczek 1949, Szegő 1950, 1975, Erdélyi *et al* 1953, Bank and Ismail 1985, Broad 1985). Exact solutions, valid to arbitrary order in the multipole expansion, have the form of integrals over the Pollaczek weight function. The treatment includes the helium perturbation problem; although the solutions for this case are complicated, they naturally satisfy the exact boundary conditions for the wavefunction. The solutions can be interpreted as arising from a mixed expansion involving both the eigenfunction basis and the discrete basis. Finally, the solutions are applied to an efficient calculation of van der Waals dispersion coefficients.

Broad's (1985) notation $p_n^l(x) \equiv P_n^{l+1}(x, -1, 1)$ and $q_n^{+l}(x)$ for Pollaczek functions of the first and second kind, respectively, is used throughout this paper.

2. The Fock transformation

Fock (1935) introduced a special transformation for his treatment of the hydrogen atom in momentum space. Geometrically, momentum space is envisioned as a hyperplane embedded in a four-dimensional space. The momentum vector \mathbf{p} is mapped onto the hypersphere of radius p_0 centred at the origin, by stereographic projection with the projective origin $(0, 0, 0, -p_0)$. If $\Omega = (\alpha, \theta, \phi)$ are polar coordinates on the hypersphere, θ and ϕ are the usual spherical polar angles for \mathbf{p} , and $p = p_0 \tan(\alpha/2)$. The momentum volume element in terms of Fock variables is

$$d\mathbf{p} = \left(\frac{(p_0^2 + p^2)}{(2p_0)} \right)^3 d\Omega \quad (2.1)$$

where $d\Omega = \sin^2 \alpha \sin \theta d\alpha d\theta d\phi$ is the surface element on the hypersphere in four dimensions.

The utility of the Fock representation results from the expansion (Judd 1975) of the Coulomb kernel,

$$|p - p'|^{-2} = 8\pi^2 p_0^2 (p_0^2 + p^2)^{-1} (p_0^2 + p'^2)^{-1} \sum_{nlm} n^{-1} Y_{nlm}^*(\Omega') Y_{nlm}(\Omega) \quad (2.2)$$

in which the four-dimensional spherical harmonics, Y_{nlm} , are defined by

$$Y_{nlm}(\Omega) = (-2i)^l l! \left(\frac{2}{\pi} \right)^{1/2} A_{nl} \sin^l \alpha C_{n-l-1}^{l+1}(\cos \alpha) Y_{lm}(\theta, \phi). \quad (2.3)$$

Here Y_{lm} is the usual three-dimensional spherical harmonic, C_{n-l-1}^{l+1} is a Gegenbauer polynomial (Abramowitz and Stegun 1972), and $A_{nl} = [n(n-l-1)!/(n+l)!]^{1/2}$.

The functions Y_{nlm} form a complete orthonormal basis for the set of square-integrable functions on the hypersphere (Vilenkin 1968, p 468), and are orthonormal with respect to the measure $d\Omega$. Further properties associated with tensor coupling of angular momenta are given by Judd (1975) and Abbott (1986).

3. Complete basis sets

3.1. Eigenfunction basis

The normalized bound states of the hydrogen atom (Podolsky and Pauling 1929, Fock 1935) are

$$\chi_{nlm}(\mathbf{p}) = 4n^{-5/2}(n^{-2} + p^2)^{-2}Y_{nlm}(\Omega^{(n)}) \quad (3.1)$$

where the symbol $\Omega^{(n)}$ indicates a Fock transformation with $p_0 = n^{-1} = \sqrt{-2E}$. These functions do not form a complete set unless the continuum states are included; thus the expansion of a general momentum space function is an infinite sum over the discrete bound states plus an integral over the continuum.

Unnormalized continuum states are defined by the analytic continuation of (3.1) to imaginary n , accomplished by rewriting the Gegenbauer polynomial in (2.3) as a hypergeometric function.

3.2. Laguerre-type basis

The completeness property of the four-dimensional spherical harmonics suggests a choice of discrete basis functions. We define

$$\phi_{nlm}(\mathbf{p}) = (-1)^n A_{nl}(1 + p^2)^{-2}Y_{nlm}(\Omega). \quad (3.2)$$

It is understood here and in future equations that when p and Ω appear together without superscripts they are related by a Fock transformation with $p_0 = 1$. The functions ϕ_{nlm} are complete and orthogonal with respect to the measure $(1 + p^2)dp$. Integrals of the type $\int \phi_{nlm}^* \phi_{n'l'm'} dp$ occur frequently in this work; they may be reduced using the identity (Koga and Matsumoto 1985)

$$\begin{aligned} -4(1 + p^2)^{-1} \phi_{nlm} &= [(n - l - 1)/(n - 1)] \phi_{n-1lm} - 2\phi_{nlm} \\ &+ [(n + l + 1)/(n + 1)] \phi_{n+1lm}. \end{aligned} \quad (3.3)$$

The basis functions ϕ_{nlm} are essentially those used by Koga *et al* in their work on the van der Waals problem, except for combinatorial factors included for convenience. In the configuration space representation,

$$\phi_{nlm}(\mathbf{r}) = -(1/2)n^{-1}A_{nl}^2 e^{-r}(2r)^l L_{n-l-1}^{2l+1}(2r)Y_{lm}(\theta, \phi). \quad (3.4)$$

These functions have been applied extensively in so-called L^2 basis calculations of potential scattering and ionization processes. Many of the results in this paper are related to such work, particularly in connection with equivalent quadrature, Stieltjes imaging, and J -matrix methods (Heller *et al* 1973, Heller 1975, Yamani and Reinhardt 1975, Broad 1978, 1985).

3.3. Change of basis

Consider the momentum space Schrödinger equation for the hydrogen atom, in atomic units,

$$(E - p^2/2)\phi(p) + (2\pi^2)^{-1} \int |p - q|^{-2} \phi(q) dq = 0 \quad (3.5)$$

where the integral is over all space. Expanding the wavefunction in the $\{\phi_{nlm}\}$ basis, $\phi = \sum a_{nlm} \phi_{nlm}$, and using the kernel expansion (2.2) together with the identity (3.3), we obtain

$$(n + l)a_{n+1lm} - 2[(n - 1)x + 1]a_{nlm} + (n + l)a_{n-1lm} = 0 \\ n - l = 1, 2, 3, \dots \quad (3.6)$$

where $x = (2E - 1)/(2E + 1)$. This recurrence relation is satisfied by the Pollaczek polynomial $p_{n-l-1}^l(x)$, the other linearly independent solution being excluded by the condition $a_{llm} = 0$. Normalising the solution by examining the limit $p \rightarrow 0$, we find

$$\chi_{nlm} = 4n^{-1/2} J_{nl} \sum_{k=l+1}^{\infty} p_{k-l-1}^l(x_n) \phi_{klm} \quad (3.7)$$

where $x_n = (1 + n^2)/(1 - n^2)$ and

$$J_{nl} = A_{nl}^{-1} (4n)^{l+1} (1 - n)^{n-l-1} (1 + n)^{-n-l-1}. \quad (3.8)$$

Thus we identify the Pollaczek polynomials as the transformation coefficients in changing from the eigenfunction basis to the set $\{\phi_{nlm}\}$. The formula holds for any n corresponding to both bound and unbound states χ_{nlm} . An equivalent formula in position space was obtained by Broad (1985) and, in a finite basis form, by Yamani and Reinhardt (1975).

4. The van der Waals perturbation problem

The H(1s)–H(1s) system of interest involves two hydrogen atoms interacting at long range. Under the infinite nuclear masses approximation, the problem reduces to that of two electrons moving in the potential of two fixed protons. The long-range effects may be studied systematically using perturbation series in inverse powers of the internuclear separation R . The effects of wavefunction symmetry may be neglected, since the exchange energy vanishes to all orders in the perturbation expansion (Alrichs 1976, Morgan and Simon 1980). Relativistic corrections enter at $O(R^{-4})$ in the energy.

This problem's difficulties are typical of few-particle systems. The Schrödinger equation is not separable, and has no solutions in the form of power series in the electron coordinates: it is necessary to include logarithmic terms (Tulub 1969, Tulub *et al* 1971, Abbott 1986). Consequently early work was concentrated on approximate methods, which yielded accurate values for the energy eigenvalues, but poor approximations to the exact wavefunction.

More recently, a discrete basis technique has been applied to the H(1s)-H(1s) and related systems with considerable success. Koga (1985a, b, 1986, 1989), Koga and Matsumoto (1985) and Koga and Uji-ie (1986, 1987a, b) calculated leading-order interaction energies for a range of two- and three-body problems. Their method depends on solving a two-dimensional recurrence relation by matrix truncation.

In this section we express the recurrence relation in a form closely resembling the equation defining the Pollaczek polynomials, preparing for the exact solution in section 5. The treatment is valid to arbitrary order in the multipole expansion.

The first-order perturbation equations can be written

$$(H_0 + 1)\psi_{ll'}(1, 2) = 4(1 + p_1^2)^{-1}(1 + p_2^2)^{-1}B_{ll'}(1, 2) \quad (4.1)$$

where (1,2) represents (p_1, p_2) and $H_0 = H_0^{(1)} + H_0^{(2)}$ is given by

$$H_0^{(1)}\Phi(p_1, p_2) = (p_1^2/2)\Phi(p_1, p_2) - (2\pi^2)^{-1} \int q^{-2}\Phi(p_1 - q, p_2) dq \quad (4.2)$$

and a similar expression for $H_0^{(2)}$ has the momenta interchanged. The functions $B_{ll'}(1, 2)$ are generated from the multipole expansion of the interaction potential; the general formula is given by Koga and Uji-ie (1986). The functions $\psi_{ll'}$ are defined by the corresponding expansion of the first-order wavefunction, $\Psi_1 = \sum R^{-l-l'-1}\psi_{ll'}$. Expanding $\psi_{ll'}$ in the series

$$\begin{aligned} \psi_{ll'}(1, 2) = & \sum_{nn'} \beta_{nn'}^{ll'} \sum_{m=-<}^< [(l-m)!(l+m)!(l'-m)!(l'+m)!]^{-1/2} \\ & \times \phi_{nlm}(1)\phi_{n'l'-m}(2) \end{aligned} \quad (4.3)$$

where $<$ is the lesser of l and l' , yields the recurrence relation to be solved,

$$\begin{aligned} (n' - 1)[(n - l)\beta_{n+1n'} - 2n\beta_{nn'} + (n + l)\beta_{n-1n'}] \\ + (n - 1)[(n' - l')\beta_{nn'+1} - 2n'\beta_{nn'} + (n' + l')\beta_{nn'-1}] = R_{nn'} \end{aligned} \quad (4.4)$$

in which

$$\begin{aligned} R_{nn'} = & (-1)^l 2^{2-l-l'} (l+l')!(2l+2)!(2l'+2)![(2l+1)(2l'+1)]^{-1/2} \\ & \times (\delta_{n,l+1} - \delta_{n,l+2})(\delta_{n',l'+1} - \delta_{n',l'+2}). \end{aligned} \quad (4.5)$$

In the recurrence relation (4.4), the superscripts have been dropped for convenience.

The extension to more complex two-electron perturbation problems is straightforward. For the helium isoelectronic sequence, neglecting relativistic effects and spin, the expansion coefficients for the first-order perturbation wavefunction satisfy an equation differing from (4.4) only in the inhomogeneous term $R_{nn'}$. The exact solution presented in the next section thus includes the perturbation problems of both the H(1s)-H(1s) system and the helium isoelectronic sequence as special cases.

5. Solution of the recurrence relation

The general solution of the recurrence relation (4.4) contains an infinite number of adjustable parameters. Applying the appropriate boundary condition fixes uniquely the wavefunction and energy eigenvalue. The exact solution presented here satisfies the condition that the coefficients decay exponentially as a function of the indices. This boundary condition, equivalent to the matrix truncation procedure used in numerical work by Koga and co-workers, is discussed further in section 6.

Multiplying (4.4) by $n'^{-1}A_{n'l}^2 p_{n'-l-1}^{l'}(x)$, summing over n' and using the recurrence relation defining $p_n^l(x)$ gives

$$(n - l)S_{n+1} - 2[(n - 1)(2 - x) + 1]S_n + (n + l)S_{n-1} = Q_n(x) \tag{5.1}$$

where

$$S_n(x) = \sum_{n'=l'+1}^{\infty} (1 - n'^{-1})A_{n'l'}^2 p_{n'-l'-1}^{l'}(x)\beta_{nn'} \tag{5.2}$$

and

$$Q_n(x) = \sum_{n'=l'+1}^{\infty} n'^{-1}A_{n'l'}^2 p_{n'-l'-1}^{l'}(x)R_{nn'}. \tag{5.3}$$

The solution of (5.1) satisfying the stated boundary condition is readily shown to be

$$S_n(x) = (1/2) \sum_{n'=l'+1}^{\infty} n'^{-1}A_{n'l'}^2 Q_{n'}(x) p_{n_<-l-1}^l(2-x) q_{n_>-l-1}^{+l}(2-x) \tag{5.4}$$

where $n_<$ ($n_>$) is the lesser (greater) of n and n' . Thus the problem is reduced to evaluating the sums (5.3) and (5.4) and computing the inversion integral

$$\beta_{nn'} = \int_{-\infty}^{\infty} S_n(x) p_{n'-l'-1}^{l'}(x) \rho_{l'}(x) dx \tag{5.5}$$

where $\rho_l(x)$ is the orthogonality measure (Broad 1985),

$$\int_{-\infty}^{\infty} p_m^l(x) p_n^l(x) \rho_l(x) dx = \delta_{mn} (n + 1)_{2l+1} / (n + l) \tag{5.6}$$

of the Pollaczek polynomials. Equations (5.4) and (5.5), giving the expansion coefficients in terms of the inhomogeneous term, are the principal results of this paper. The auxiliary function $S_n(x)$ has a direct interpretation as the expansion coefficients in the eigenfunction basis, as discussed in section 6.

For the van der Waals interaction, both sums collapse to *exact* solutions for $S_n(x)$ to arbitrary order in the perturbation expansion,

$$S_n^{ll'}(x) = (-1)^{l+1} 2^{4-l-l'} (l + l')! l! [(2l + 1)(2l' + 1)]^{-1/2} \times (x - 1) [l(x - 1) q_{n-l-1}^{+l}(2-x) - (2l + 1)! \delta_{n,l+1}]. \tag{5.7}$$

These expressions form the basis for a numerical determination of the van der Waals dispersion coefficients in section 7.

For the helium perturbation problem, the solutions are more complicated, being multiply infinite series with coefficients of the form (5.5). Their significance lies in the fact that they obey the exact boundary conditions for the wavefunction, in contrast with techniques based on formal power series expansions, which generally yield solutions containing a number of undetermined coefficients (Abbott 1986). Although the physical solution can in principle be extracted by requiring that the wavefunction be normalizable, no general procedure for eliminating these extra degrees of freedom exists. The discrete basis treatment circumvents this problem by transferring the boundary conditions to a simple constraint on the coefficients. Normalisability of the solutions is implicit in the procedure.

6. Boundary conditions

We now show that the quantity $S_n(x)$ has a direct interpretation involving the eigenfunction basis. Initially we restrict attention to a single momentum variable. Combining the discrete basis expansion $\phi = \sum a_{nlm} \phi_{nlm}$ with

$$a_{nlm} = \int_{-\infty}^{\infty} S(x) p_{n-l-1}^l(x) \rho_l(x) dx \quad (6.1)$$

and using the change of basis formula (3.7), yields the relation

$$\phi(\mathbf{p}) = 2^{2l-1} \int_{-\infty}^{\infty} \sum_{lm} [k^{1/2} J_{kl}^{-1} \chi_{klm}(\mathbf{p})] S_{lm}(x) \rho_l(x) dx \quad (6.2)$$

where $k^2 = (x-1)/(x+1)$. Hence the values of $S(x)$ at the spectral points (corresponding to allowed energies) are the coefficients in the expansion of ϕ in terms of the eigenfunctions of the unperturbed Hamiltonian. In the two-particle wavefunctions, we have applied the transformation (6.1) to only one of the momentum variables. Thus we interpret $S_n(x)$ as the coefficients in a mixed expansion involving both the discrete and the eigenfunction bases.

We turn now to the origin of the boundary conditions used in the previous section to obtain a unique solution of the recurrence relation. The general solution of (5.1) consists of the particular solution already obtained plus an arbitrary multiple of the homogeneous solution, $p_{n-l-1}^l(2-x)$. When substituted into (6.2), this homogeneous solution gives rise to additional terms in the wavefunction of the type $\chi_{lm}(x, \mathbf{p}_1) \chi_{l'm'}(2-x, \mathbf{p}_2)$, where $\chi_{lm}(x, \mathbf{p}) = \chi_{klm}(\mathbf{p})$. These are excited states of the unperturbed system with the same energy as the state ϕ_0 . Thus, degenerate perturbation theory must be applied. The spurious terms arise because in the discrete basis the Hamiltonian is not diagonal in the degenerate subspace. Thus the prescription of exponentially decaying coefficients eliminates contributions from the excited states, which are incompatible with the physical situation.

7. Van der Waals dispersion energy

The first-order energy in the perturbation expansion vanishes due to the orthogonality of the spherical harmonics. Thus the leading-order dispersion energy is the second-order correction, given by a matrix element, $E_2 = \langle \Psi_0 | V | \Psi_1 \rangle$, of the interaction potential. In the framework of the multipole expansion, we may calculate an energy contribution from each $\psi_{ll'}$ separately, since the cross terms vanish by orthogonality. Hence the quantity of interest is

$$E_{ll'} = -4 \int (1 + p_1^2)^{-1} (1 + p_2^2)^{-1} B_{ll'}(1, 2) \psi_{ll'}^*(1, 2) \, dp_1 \, dp_2. \quad (7.1)$$

Then the coefficients in the expansion $E_2 = C_6 R^{-6} + C_8 R^{-8} + C_{10} R^{-10} + \dots$ are given by

$$C_{2n} = \sum_{l=1}^{n-2} E_{l, n-l-1}. \quad (7.2)$$

This series yields the asymptotic dispersion energy up to terms of order R^{-10} , since the third-order perturbation energy is $O(R^{-11})$.

Due to the simple form of $B_{ll'}$ in the Fock representation, the integrals (7.1) collapse to a linear combination of just four β coefficients. These are known from section 5 as integrals over $S_n^{ll'}$ and the Pollaczek weight function. Collecting functions of x , we arrive at the result

$$E_{ll'} = 2^{-2l-2l'-1} (2l+2l')! \left[l(l'+1)^{-1} l'^{-2} (4l'^3 + 11l'^2 + 8l' + 2) - l'^{-1} (l'+2)(2l'+1) \right. \\ \left. + 2l^2 l'^2 [(2l+1)!(2l'+1)!]^{-1} \int_{-\infty}^{\infty} (x-1)^4 q_0^{+l} (2-x) \rho_{l'}(x) \, dx \right]. \quad (7.3)$$

A further quantity of interest is the coefficient W_4 of the leading-order relativistic energy correction proportional to $\alpha^2 R^{-4}$. Following Koga (1985b), we have

$$W_4 = (1/6) \beta_{22}^{ll'} = 1 + (1/72) \int_{-\infty}^{\infty} (x-1)^2 q_0^{+2} (2-x) \rho_1(x) \, dx. \quad (7.4)$$

The Pollaczek function q_0^{+l} may be computed numerically from the continued fraction expansion,

$$q_0^{+l}(x) = -2(2l)! a_0 / \{b_0 - a_1 [b_1 - a_2 / (b_2 - \dots)]\} \quad (7.5)$$

where $a_n = (n+2l+1)/(n+1)$ and $b_n = 2[(n+l)x+1]/(n+1)$. Thus (7.3) and (7.4) provide a particularly simple method of calculating the interaction constants. Results of such a calculation are presented in table 1. The values are accurate to within one unit in the last (15th) decimal place. Our results agree perfectly with those of Koga (1989), and with those of Thakkar (1988) obtained using a pseudostate

Table 1. Second order van der Waals dispersion coefficients. $A (m)$ means $A \times 10^m$.

n	$-C_n$
6	6.499 026 705 405 84
8	1.243 990 835 836 22 (2)
10	3.285 828 414 967 42 (3)
12	1.214 860 208 968 61 (5)
14	6.060 772 689 192 12 (6)
16	3.937 506 393 999 18 (8)
18	3.234 218 715 849 38 (10)
20	3.278 573 440 416 62 (12)
22	4.021 082 847 685 36 (14)
24	5.868 996 334 559 96 (16)
26	1.005 294 993 336 29 (19)
28	1.996 944 940 887 58 (21)
30	4.553 288 866 634 74 (23)
W_4	0.462 806 538 843 273

technique. However, our calculations do not generalize readily to the non-additive three-body interaction coefficients.

The details of the calculation are unremarkable. Integrals of the type $\int f(x)\rho_l(x) dx$ were evaluated using a standard integration routine and by direct summation of the infinite series. The convergence of the series was accelerated dramatically by asymptotic estimation of the truncation error: if $f(-1) \neq 0$, the leading-order correction is

$$\sum_{n=N}^{\infty} 2n(n^2-1)^{-1} J_{n1}^2 f(x_n) = 2^{4l+4} e^{-4} f(-1) (N+1) N^{-3} + O(N^{-4}). \quad (7.6)$$

The expansion coefficients $\beta_{nn}^{ll'}$ may also be computed accurately and efficiently by this method. Given that stable algorithms for calculating the Pollaczek polynomials and functions exist (Broad 1985), the computational effort involved does not grow rapidly with n and n' . This may be compared with matrix truncation methods, which require solution of a set of linear equations whose size grows as $O(nn')$. These considerations may be significant in further calculations involving slowly convergent series of β coefficients (see, for example, Koga and Uji-ie 1987b).

8. Conclusions

This work has been motivated primarily by the search for exact solutions: the dispersion coefficients have been calculated accurately by other methods, but relatively little is known about the exact wavefunction. In this work, the series expansions for the wavefunction are exact, but converge rather slowly. In this sense they are of direct interest only to the extent that they can be compacted into closed form. The fact that the integral formula for the coefficients does not appear to reduce is not promising in this regard.

More encouraging are the results concerning the role of boundary conditions in this treatment. A discrete basis approach entirely avoids the problem of undetermined

coefficients, which is a major complication in more direct methods. The physical conditions of the problem translate naturally into a condition on the expansion coefficients. It is hoped that further investigations will lead to a better understanding of the consequences of boundary conditions on few-particle wavefunctions. Progress is likely to be made by relating the discrete basis solutions to formal power-series solutions already known. The optimum procedure will involve a combination of techniques.

Acknowledgments

It is a pleasure to thank Dr E N Maslen for invaluable guidance throughout the course of this work, and for helpful comments on the manuscript. Part of this research was supported by a Hackett Studentship from the University of Western Australia.

References

- Abbott P C 1986 *PhD Thesis* University of Western Australia
Abbott P C and Maslen E N 1987 *J. Phys. A: Math. Gen.* **20** 2043–75
Abramowitz M and Stegun J A 1972 *Handbook of Mathematical Functions* (New York: Dover)
Alrichs R 1976 *Theor. Chim. Acta* **41** 7–15
Bank E and Ismail M E H 1985 *Constr. Approx.* **1** 103–19
Broad J T 1978 *Phys. Rev. A* **18** 1012–27
— 1985 *Phys. Rev. A* **31** 1494–514
Erdélyi A, Magnus W, Oberhettinger F and Tricomi F G 1953 *Higher Transcendental Functions* (New York: McGraw-Hill)
Fock V 1935 *Z. Phys.* **98** 145–54
Gottschalk J E, Abbott P C and Maslen E N 1987 *J. Phys. A: Math. Gen.* **20** 2077–104
Gottschalk J E and Maslen E N 1985 *J. Phys. A: Math. Gen.* **18** 1687–96
Heller E J, Reinhardt W P and Yamani H A 1973 *J. Comput. Phys.* **13** 536–50
Heller E J 1975 *Phys. Rev. A* **12** 1222–31
Judd B R 1975 *Angular Momentum Theory for Diatomic Molecules* (New York: Academic)
Koga T 1985a *J. Chem. Phys.* **82** 2022–25
— 1985b *J. Chem. Phys.* **83** 6304–06
— 1986 *J. Chem. Phys.* **84** 1636–9
— 1989 *J. Chem. Phys.* **90** 605–6
Koga T and Matsumoto S 1985 *J. Chem. Phys.* **82** 5127–32
Koga T and Uji-ie M 1986 *J. Chem. Phys.* **84** 335–40
— 1987a *J. Chem. Phys.* **86** 2854–8
— 1987b *J. Chem. Phys.* **87** 1137–41
Morgan J D III and Simon B 1980 *Int. J. Quant. Chem.* **17** 1143–66
Podolsky and Pauling 1929 *Phys. Rev.* **34** 109–16
Pollaczek F 1949 *C.R. Acad. Sci.* **228** 1363–5
Szegő G 1950 *Proc. Am. Math. Soc.* **1** 731–7
— 1975 *Orthogonal Polynomials (AMS Colloquium Publications 23)* 4th edn (Providence, RI: American Mathematical Society)
Thakkar A J 1988 *J. Chem. Phys.* **89** 2092–8
Tulub A V 1969 *Sov. Phys.—Dokl.* **13** 936–8
Tulub A V, Bal'makov M D and Khallaf S A 1971 *Sov. Phys.—Dokl.* **16** 18–20
Vilenkin N Ja 1968 *Special Functions and the Theory of Group Representations* (Providence, RI: American Mathematical Society)
Yamani H A and Reinhardt W P 1975 *Phys. Rev. A* **11** 1144–56