Computer Physics Communications 47 (1987) 207–212
North-Holland, Amsterdam

THE GENERATION OF CONTINUUM ORBITALS FOR MOLECULAR *R*-MATRIX CALCULATIONS USING LAGRANGE ORTHOGONALISATION

Jonathan TENNYSON

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, England

P.G. BURKE and K.A. BERRINGTON

Department of Applied Mathematics and Theoretical Physics, The Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland

Received 11 June 1987

A method is presented whereby a given set of single-channel continuum functions can be used to generate a set of multi-channel orbitals which are orthogonal to a specified number of target molecular orbitals with the same symmetry. The procedure uses the single-channel functions as a basis set expansion which is Lagrange orthogonalised to the target orbitals by searching for the zeros of a determinant. Sample calculations on a variety of diatomic targets, such as H_2^+ and CO, show the method is reliable and does not suffer from the linear dependence problems frequently encountered with other orthogonalisation procedures. A straightforward generalisation of the method allows continuum orbitals to be generated which are adapted to anisotropic terms in the potential.

1. Introduction

The *R*-matrix method provides a natural formalism for the representation of electron–molecule collisions. It allows use to be made of the expertise developed by quantum chemists in handling the complicated interactions when the scattered electron is close to the molecular target and the experience acquired by atomic physicists in solving for the asymptotic motion of the electron. An important addition that needs to be made to any electronic structure code when adapting it for scattering calculations is that functions must be developed to represent the continuum. In the *R*-matrix method these functions represent the portion of the discretised continuum that lies in the internal region of the calculation – typically a sphere of radius about $10 a_0$.

The first molecular *R*-matrix calculations of this type [1] represented the continuum using functions, Slater Type Orbitals, often used to represent bound electronic states. These calculations were successful for low scattering energies but at higher energies difficulties were encountered due to linearly dependent orbitals. Linear dependence is often encountered in highly accurate electronic structure calculations [2], but is a more severe problem in scattering calculations because of the need to represent a large range of continuum energies.

In response to this problem, Burke et al. [3] suggested the use of numerical functions to represent the continuum. These functions were expressed as a partial wave expansion about the molecular centre of mass

$$F(\boldsymbol{r}) = \sum_{l,\, i} r^{-1} u^m_{l,i}(r) Y_{l,m}(\hat{\boldsymbol{r}}) a_i, \tag{1}$$

where $Y_{l,m}$ is a spherical harmonic. For a diatomic target m but not l is conserved. The radial basis functions $u^m_{l,i}$ were generated as solutions of the model problem:

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} - V_0(r) + k_i^2 \right) u^m_{l,i}(r) = \sum_{l' \neq l} V^m_{l,l'}(r) u^m_{l',i}(r) + \sum_q^p \lambda^m_{i,q} P^m_{l',q}(r) \tag{2}$$

0010-4655/87/$03.50
(North-Holland Physics Publishing Division)

subject to the boundary conditions, for an R-matrix of radius a,

$$\left.\begin{aligned} &u^m_{l,i}(0)=0 \\ &\frac{a}{u^m_{l,i}}\left.\frac{\mathrm{d}u^m_{l,i}}{\mathrm{d}r}\right|_{r=a}=b \end{aligned}\right\} \quad \text{for all } l \text{ and } i. \tag{3}$$

The use of these fixed boundary conditions requires a Buttle correction [4] to be applied to the final R-matrices. The orthogonality constraints in (2) are equivalent to requiring all the solutions, $u^m_{l,i}$ to be orthogonal to a set of orbitals:

$$\sum_l \int_0^a u^m_{l,i}(r)P^m_{l,q}(r)\,\mathrm{d}r=0 \quad \text{for all } i \text{ and } q, \tag{4}$$

where in (2) and (4) $P^m_{l,q}$ are the components of the single-centred expansion of the occupied target molecular orbital (MO) ϕ^m_q

$$\phi^m_q(\boldsymbol{r})=\sum_l r^{-1}P^m_{l,q}(r)Y_{l,m}(\hat{\boldsymbol{r}}). \tag{5}$$

In (2) $\lambda^m_{i,q}$ is thus a Lagrangian multiplier which ensures orthogonality to the p occupied target MOs. As some virtual target MOs are also usually retained in the orbital set, to allow for short range effects due to higher partial waves (often called correlation) and polarisation, it is still necessary to Schmidt orthogonalise the continuum orbitals to the complete set of target MOs.

In (2), $V^m_{l,l'}$ represents the coupling due to anisotropic terms in the potential; it can be expressed as sums over the expansion of the molecular target potential V_λ [5]:

$$V^m_{l,l'}(r)=\sum_\lambda g_\lambda(l,\,l',\,m)V_\lambda(r), \tag{6}$$

where $g_\lambda(l,\,l',\,m)$ is a Gaunt coefficient. In practice, all calculations have only included the isotropic part of this potential V_0 which means that there is no coupling between the single channel basis functions due to the model target potential.

The calculations of Burke et al. [3] gave a good representation of electron–N_2 scattering over a considerable energy range. However the method employed had two disadvantages. Firstly, solutions of (2) satisfying the Lagrange orthogonality constraint proved difficult to find. Secondly, and more seriously, the method gives rise to a very large number of single channel basis functions. This is because each solution of (2) must necessarily, because of the orthogonality constraint, be a linear combination of different $u_{l,i}$. The large number of basis functions implied by this procedure means that it was found to be intractable for more complicated problems, such as coupled electronic state calculations or scattering from heteronuclear targets.

As a response to this, subsequent molecular R-matrix calculations [6–14] dropped the strict orthogonality implied by eq. (4) and used single-channel continuum functions which are not orthogonal to the occupied target MOs. These functions were then orthogonalised, usually using Schmidth orthogonalisation, to the entire (occupied and virtual) target MO set. This simplified procedure does not suffer from either of the problems outlined above. The success of the quoted calculations for both electron [6–12] and positron [13] molecule collisions, and photoionisation [14] is a testimony to its usefulness. However for certain targets (see for example refs. [11,12]), the orbital sets generated in this fashion showed severe linear dependence problems. These problems were found to be worst for light–heavy systems such as HF and CH^+ for which no successful calculations at all could be performed.

In this work we propose a new method of obtaining continuum orbitals which are, to a good approximation, Lagrange orthogonalised to a specified set of target MOs without encountering any of the problems of the original procedure of Burke et al. [3]. We demonstrate the utility of the procedure by giving sample results for electron scattering from H_2^+ and CO.

2. Theory

What we require is a set of continuum functions, $u^m_{l,i}(r)$, which are orthogonal to the target MOs but can be expressed in terms of one set single channel functions for all i and a given $(l,\,m)$. Such a set can be written

$$u^m_{l,i}(r)=\sum_j a^m_{l,j,i}v^m_{l,j}(r), \tag{7}$$

where $v^m_{l,j}(r)$ is the single channel function of energy $k^2_{l,j}$ which is the solution of (2) with the right hand side set to zero. In principle there are an infinite number of such solutions which constitute a complete orthonormal set. In calculations which use these single-channel functions directly as a basis, all the solutions with $k^2_{l,j}$ less than some maximum value of k^2 are usually included in the basis. Typical maxima for k^2 are 2–3 times the maximum energy of the scattering electron [3,6–12]. These solutions are easily found [15].

To find the expansion coefficients $a^m_{l,j,i}$ one substitutes (7) into (2) to give

$$\sum_j \left(k_i^2 - k^2_{l,j}\right) v^m_{l,j}(r) a^m_{l,j,i} = \sum_{j'} \sum_{l'} \left(V^m_{l,l'}(r) - \delta_{l,l'} V^m_0(r)\right) v^m_{l',j'}(r) a^m_{l',j',i} + \sum_q \lambda^m_{i,q} P^m_{l,q}(r), \tag{8}$$

where use has been made of the fact that $v^m_{l,j}$ is a solution of the left hand side of (2). Solutions to (8) must be found for all l and i.

Multiplying (8) by $v^m_{l,j}$ and integrating over r from 0 to a gives

$$\left(k_i^2 - k^2_{l,j}\right) a^m_{l,j,i} = \sum_{j'} \sum_{l'} b_{l,j,l',j'} a^m_{l',j',i} + \sum_q c_{l,j,q} \lambda^m_{i,q} \tag{9}$$

for all l, i, j; where

$$b_{l,j,l',j'} = \int_0^a v^m_{l,j}(r) \left(V^m_{l,l'}(r) - \delta_{l,l'} V^m_0(r)\right) v^m_{l',j'}(r)\, \mathrm{d}r \tag{10}$$

and

$$c_{l,j,q} = \int_0^a v^m_{l,j}(r) P^m_{l,q}(r)\, \mathrm{d}r. \tag{11}$$

Substituting (7) into the Lagrange orthogonalisation condition (4) gives the extra equations

$$\sum_l \sum_j c_{l,j,q} a^m_{l,j,i} = 0 \tag{12}$$

which must be satisfied for each i.

(9) and (12) form a set of homogeneous equations in the coefficients $a^m_{l,j,i}$ and $\lambda^m_{l,q}$. They only have non-zero solutions when the determinant of the corresponding matrix is zero. This occurs when the solution of (2) can be expanded in terms of the single channel functions as in (7).

3. Method of solution

As we have defined two equations, (9) and (12), that need to be satisfied, the solutions are found in two steps. First one diagonalises the symmetric matrix

$$B_{l,j,l',j'} = \delta_{l,l'} \delta_{j,j'} k^2_{l,j} + b_{l,j,l',j'}, \tag{13}$$

where (l, j) and (l', j') are row and column indices respectively. Let k^2_μ and $h_{l,j,\mu}$ be the eigenvalues and normalised eigenvectors of $\mathbf{B}$ respectively. Then eq. (9) can be solved to give

$$a^m_{l,j,i} = \sum_\mu \sum_{l',j'} \sum_q \frac{h_{l,j,\mu} h_{l',j',\mu}}{k_i^2 - k_\mu^2} c_{l',j',q} \lambda^m_{i,q}. \tag{14}$$

Substituting (14) into (12) yields a set of equations for each i which can be expressed most simply as

$$\sum_{q'} C_{q,q'} \lambda^m_{i,q'} = 0. \tag{15}$$

The matrix $\mathbf{C}$ has dimension p by p, where p is number of target MOs to which the continuum is to be Lagrange orthogonalised, and is defined by

$$C_{q,q'} = \sum_\mu \sum_{l',j'} \sum_{l,j} c_{l,j,q} \frac{h_{l,j,\mu} h_{l',j',\mu}}{k_i^2 - k_\mu^2} c_{l',j',q'}. \tag{16}$$

Non-trivial solutions of (15) are given by Det $|\mathbf{C}(k_i^2)| = 0$. That is, the eigenvalues k_i^2 of (2) are given by the zeros of the determinant. At a zero we can arbitrarily set $\lambda^m_{i,1} = 1$ and determine $\lambda^m_{i,q}$ ($q = 2$, p) by solving (15). The corresponding $a^m_{l,j,i}$ are given by (14) and the unnormalised eigenvectors by (7). These eigenvectors can then be simply normalised.

There are two possible simplifying assumptions to the above procedure. Firstly, if no Lagrange orthogonalisation is required, i.e. $p = 0$, then the k_i^2 are simply k_μ^2 and the $a^m_{l,j,i}$ are given by $h_{l,j,i}$. Secondly, if mixing due to anisotropic terms in the potential can be neglected, i.e. $b_{l,j.l',j'} = 0$, then the diagonalisation of **B** is no longer required. In this case eqs. (14) and (16) reduce to:

$$a^m_{l,j,i} = \sum_q \frac{c_{l,j,\mu} \lambda^m_{i,q}}{k_i^2 - k_{l,j}^2} \tag{17}$$

and

$$C_{q,q'} = \sum_{l,\,j} \frac{c_{l,j,q} c_{l,j,q'}}{k_i^2 - k_{l,j}^2}. \tag{18}$$

It is this simplified procedure which is considered in the next section.

4. Computational implementation

The theory given above allows single channel continuum functions to be adapted for anisotropy in the potential as well as Lagrange orthogonalised to the target MOs. We will only consider examples requiring orthogonalisation. This is because experience has shown that the solutions we obtain for scattering problems are not highly sensitive to the choice of model potential, providing there are no problems with linear dependence. For example in positron–H_2 calculations [13] very similar results were obtained when the numerical functions were generated using a model potential appropriate for electron–H_2, $-V_0(r)$, and positron–H_2 scattering, $V_0(r)$.

In implementing the procedure derived above there are a number of numerical considerations that need to be addressed. The basis of the procedure is the search for zeroes in the determinant of **C**. However $\mathbf{C}(k^2)$ has a pole every time k^2 equals $k^2_{l,j}$ (or k^2_μ). Thus any scan of **C** for the sign change which imply a zero must avoid these poles. As the pole positions are known before the search starts this is not a difficult problem, the search is divided into regions defined by $k_s^2 + \epsilon \le k^2 \le k^2_{s+1} - \epsilon$. In this scheme s runs over all the poles in energy order. As some continuum functions, particularly those with high l and/or j, are very nearly orthogonal to the target MOs, k_i^2 may lie very close to $k^2_{l,j}$ (or k^2_μ). This means that ϵ has to be chosen small or solutions will be missed, values in the region of 10^{-11} to 10^{-12} Ry were found to give satisfactory results. Conversely it was found that relatively few grid points were needed between the neighbouring poles as once a sign change in **C** is found a Newton iteration procedure can be used to speedily find the poles to high accuracy – a tolerance of about 0.01ϵ being typical.

Of course, if the single channel continuum functions are already exactly orthogonal to the target MOs, the k_i^2 equals $k^2_{l,j}$ and the procedure will suffer numerical difficulties because of the indeterminacy of **C**. In practice it was found for that these problems were not great, but for the case of a homonuclear diatomic target, separate orthogonalisation steps were implemented for orbitals with g and u symmetry. This was done despite the fact that the overlap integrals [16], from which the $c_{l,j,q}$ were constructed (see (11)), were read into the code only in $C_{\infty v}$ symmetry.

Table 1 shows the pole positions for a calculation of electron scattering from CO in its equilibrium geometry. The numerical functions of column (a) correspond to the low-lying continuum

Table 1
Continuum function pole positions below 1 Ry for electron–CO scattering calculation with Σ ($m = 0$) symmetry. (a) $k^2_{l,j}$ for an isotropic model CO potential [6]. (b) k_i^2 given by Lagrange orthogonalisation to the 5 occupied σ CO molecular orbitals; the largest expansion coefficient, $a^m_{l,j,i}$, is given for each pole

(a)			(b)				
l	j	$k^2_{l,j}$ (Ry)	i	k_i^2 (Ry)	l	j	$a^m_{l,j,i}$
0	0	−2.48611	1	0.05423	0	1	0.94
1	0	−0.33793	2	0.09336	1	1	0.97
0	1	0.02865	3	0.15139	2	0	0.99
1	1	0.08152	4	0.24726	3	0	1.00
2	0	0.14914	5	0.36743	4	0	1.00
3	0	0.24724	6	0.42208	0	2	0.75
0	2	0.26249	7	0.50982	5	0	1.00
4	0	0.36744	8	0.53023	1	3	0.76
1	2	0.43531	9	0.60806	2	1	0.67
5	0	0.50982	10	0.67417	6	0	1.00
2	1	0.53542	11	0.75676	3	1	1.00
6	0	0.67417	12	0.99215	4	1	1.00
0	3	0.73982					
3	1	0.75718					
4	1	0.99239					

functions used by Salvini et al. [6], who then Schmidt orthogonalised them to the target MOs. The functions whose pole positions are shown in column (b) were obtained by Lagrange orthogonalisation a set of 58 functions (all those with $k_{l,j}^2 < 9$ Ry) to the 5 occupied σ orbitals of the CO target. The resulting set has 5 fewer orbitals and it can be seen from table 1 that 3 of the functions removed come from the low energy region below 1 Ry. Table 1 also shows that even in this low energy region, several of the functions are almost unchanged by the Lagrange orthogonalisation procedure.

Scattering calculations performed with (a) the complete set of 58 continuum orbitals and (b) the 53 continuum orbitals that result from the Lagrange orthogonalisation gave similar results. As the expansion (7) is only exact in the limit of an infinite set of functions $v_{l,k}^m$, one would expect procedure (a), when it does not suffer from linear dependence problems, to give higher eigenphase sums. This is indeed observed. However the difference is not great, for example the $^2\Sigma$ shape resonance found at 1.4896 Ry in the SEP model [6] using procedure (a) is raised by only 3×10^{-7} Ry using procedure (b).

Table 2 compares eigenphase sums for a two electronic state calculation on electron-H_2^+ at the H_2 equilibrium separation of $1.4a_0$. The calculations closely followed those of Tennyson et al. [7] and differ only in the orthogonalisation procedure used. It can be seen that the eigenphase sums are closely parallel and that the resonance parameters are in good agreement. In this case the Schmidt orthogonalisation procedure gave orbitals with large coefficients, several greater than 100. Coefficients of this size are associated with linear dependence. For this reason, Tennyson et al. used a precursor of the current Lagrange orthogonalisation procedure [15], which was found only to give satisfactory results for hydrogenic systems. In the Lagrange orthogonalised orbital set (b) there are no coefficients greater than 4.

Table 2
Eigenphase sums as a function of energy for a $^2\Sigma_g$ two electronic state electron-H_2^+ calculation. (a) Schmidt orthogonalisation. (b) Lagrange plus Schmidt orthogonalisation. The energy (E) and width (Γ) of the lowest resonance are also given

k^2 (Ry)	η (radians) (a)	(b)
0.04	−0.061	−0.064
0.09	−0.060	−0.064
0.16	−0.057	−0.063
0.25	−0.052	−0.058
0.36	−0.044	−0.049
0.49	−0.028	−0.030
0.64	0.010	0.009
0.81	0.155	0.137
1.00	2.702	2.628
E (Ry)	0.94721	0.94739
Γ (Ry)	0.05559	0.05559

5. Concluding remarks

We have developed a procedure for generating tractable continuum orbital sets which are Lagrange orthogonalised to the molecular orbitals of a given target. This procedure has been tested for electron scattering from diatomic targets including H_2^+, H_2, N_2, CO, CH^+ and HF and found satisfactory. In cases where there are no problems with linear dependence, it can be argued on variational grounds that use of the procedure will always result in a lowering of the computed eigenphase sums. However, cases where this loss is significant are exactly those for which use of this procedure is unnecessary. Conversely, there are systems for which linear dependence problems have in the past proved a major obstacle to performing molecular R-matrix scattering calculations. These difficulties are removed by the current procedure and calculations are being performed on two such systems, HF [17] and CH^+ [18]. The results of these calculations will be reported elsewhere.

Acknowledgement

We are grateful Dr. C.J. Noble and Dr. L.A. Morgan for advice and use of their codes during the course of this work.

References

[1] C.J. Noble, P.G. Burke and S. Salvini, J. Phys. B 15 (1982) 3779.

[2] S. Wilson, Advan. Chem. Phys. 67 (1987) 439.

[3] P.G. Burke, C.J. Noble and S. Salvini, J. Phys. B 16 (1983) L113.

[4] P.J.A. Buttle, Phys. Rev. 160 (1967) 691.

[5] P.G. Burke and A.L. Sinfailam, J. Phys. B 3 (1970) 641.

[6] S. Salvini, P.G. Burke and C.J. Noble, J. Phys. B 17 (1984) 2549.

[7] J. Tennyson, C.J. Noble and S. Salvini, J. Phys. B 17 (1984) 905.
J. Tennyson and C.J. Noble, J. Phys. B 18 (1985) 155.

[8] L.A. Morgan and C.J. Noble, J. Phys. B 17 (1984) L369.

[9] K.L. Baluja, C.J. Noble and J. Tennyson, J. Phys. B 18 (1985) L851.

[10] L.A. Morgan, J. Phys. B 19 (1986) L439.

[11] C.J. Noble and P.G. Burke, J. Phys. B 19 (1986) L35.

[12] J. Tennyson and C.J. Noble, J. Phys. B 19 (1986) 4025.

[13] J. Tennyson, J. Phys. B 19 (1986) 4255.

[14] J. Tennyson, C.J. Noble and P.G. Burke, Intern. J. Quantum Chem. 19 (1986) 1033.
J. Tennyson, J. Phys. B 20 (1987) L375.

[15] S. Salvini, Ph.D. Thesis, The Queen's University of Belfast (1983).

[16] C.J. Noble, Daresbury Laboratory Technical Memorandum DL/SCI/TMT33T (1982).

[17] L.A. Morgan, to be published.

[18] J. Tennyson, to be published.