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1978 J. Phys. A: Math. Gen. 11 833

(http://iopscience.iop.org/0305-4470/11/5/014)

J. Phys. A: Math. Gen., Vol. 11, No. 5, 1978. Printed in Great Britain

On the treatment of symmetry properties in the generator coordinate method†

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Received 19 July 1977, in final form 20 January 1978

Abstract. The problem of generating symmetry adapted wavefunctions, within the framework of the generator coordinate method, is examined. Results for the discretisation technique and the natural state formalism are applied to the quartic anharmonic oscillator.

1. Introduction

If the Hamiltonian of a quantum system has an unitary constant of motion, there is an operator S such that

$$[H, S] = 0 \qquad \text{and} \qquad S^+ = S^{-1} \tag{1}$$

where S^+ is the adjoint and S^{-1} the inverse of S. One can easily prove that an exact eigenstate of H is also an eigenfunction of S‡ (see e.g. Löwdin 1962). The question whether this property can be extended to approximate variational wavefunctions has been studied by Laskowski and Löwdin (1972). They showed that a sufficient condition is the stability of the variational subspace $\mathcal{H}_v$ under the symmetry operation S. Here stability means that if $\psi(x)$ belongs to $\mathcal{H}_v$ so does $S\psi(x)$. In this case S is also a constant of motion of the projected Hamiltonian $H_v = P_v H P_v$, where P_v is the projector onto $\mathcal{H}_v$, so that the theorem follows immediately. The aim of this paper is to apply the results of Laskowski and Löwdin to a space of generator coordinate (GC) trial functions (Griffin and Wheeler 1957). For the sake of simplicity we restrict ourselves to a single unitary transformation S having its eigenvalues $s_1, s_2, \ldots, s_k$ on the unit circle in the complex plane. The more general case where H is invariant under a group of unitary transformations can be treated in an analogous way (Löwdin 1962). The quartic anharmonic oscillator will be used as an illustrative example.

2. Symmetry properties of generator coordinate wavefunctions under the Brink–Weiguny condition

In the generator coordinate method (GCM) a variational subspace is generated by

† Part of this work was carried out during the author's stay at the Department of Quantum Chemistry, Uppsala University, and supported by the Interuniversitair Instituut voor Kernwetenschappen (Belgium) and the Swedish Institute (Sweden).

‡ For this purpose it is sufficient to assume that S is normal, i.e. $SS^+ = S^+S$.

0305-4770/78/0005-0833$02.00

taking linear superpositions

$$\psi(x)=\int f(a)\phi(x|a)\,\mathrm{d}a \qquad \|\psi\|<+\infty \tag{2}$$

of continuously labelled basis functions $\phi(x|a)$ with adjustable weight functions $f(a)$. Brink and Weiguny (1968) showed that the space $\mathcal{H}_{GC}$ spanned in this way is stable under S provided that the $\phi(x|a)$ are closed under S in the sense that†

$$S\phi(x|a)=\phi(x|\sigma(a)). \tag{3}$$

This implies that to each symmetry operation S there corresponds a transformation $\sigma(a)$ defined in the space of generator coordinates.

From From the Brink–Weiguny (BW) condition it is easy to verify the stability of $\mathcal{H}_{GC}$ under S. Indeed one has

$$\begin{aligned} S\psi(x)&=\int g(a)\phi(x|a)\,\mathrm{d}a \\ g(a)&=f(\sigma^{-1}(a))/|J(a)| \end{aligned} \tag{4}$$

where $J(a)$ is the Jacobian and $\sigma^{-1}(a)$ the inverse of the transformation $\sigma(a)=a'$. Consequently the solutions of the eigenvalue problem

$$H_{GC}\psi(x)=E\psi(x); \qquad \|\psi\|<+\infty \tag{5}$$

for the projected Hamiltonian $H_{GC}=P_{GC}HP_{GC}$, will be eigenfunctions of S. Under the BW condition the GC wavefunctions are symmetry adapted. We will verify this result for two explicit representations of the formal eigenvalue problem (5).

2.1. The Hill–Wheeler representation

Applying the variational principle directly to the GC trial function (2) one finds that the weight functions which yield stationary energy values must satisfy the Hill–Wheeler (HW) integral equation

$$\int (H(a,a')-EA(a,a'))f(a')\,\mathrm{d}a'=0. \tag{6}$$

Here $H(a,a')$ and $A(a,a')$ are respectively the well known Hamiltonian and overlap kernels which are Hermitian. The BW condition implies further that

$$\begin{aligned} H(\sigma(a),\sigma(a'))&=H(a,a')=H(\sigma^{-1}(a),\sigma^{-1}(a')) \\ A(\sigma(a),\sigma(a'))&=A(a,a')=A(\sigma^{-1}(a),\sigma^{-1}(a')) \end{aligned} \tag{7}$$

which are kernel symmetries induced by (3). Combining (7) with the HW equation one arrives at the result

$$\int (H(a,a')-EA(a,a'))f(\sigma^{-1}(a))/|J(a)|\,\mathrm{d}a=0. \tag{8}$$

Comparing this with the original HW equation and using (4) we conclude that, if $f(a)$ is

† In this case of a continuous group this condition should be taken for the infinitesimal elements (Brink and Weiguny 1968).

a solution to (8), $f(a)$ and $g(a)$ are proportional. Consequently $S\psi(x) \sim \psi(x)$, i.e. the GC wavefunctions are eigenfunctions of S.

2.2. The natural state representation

The projected Schrödinger equation (5) is purely conceptual since the projector P_{GC} is not known explicitly. This drawback can be removed by constructing a basis for the space $\mathscr{H}_{GC}$. Recently a formalism which provides a complete orthonormal set for $\mathscr{H}_{GC}$ has been suggested (Lathouwers 1976a). We give here a short summary which at the same time introduces the necessary notation.

It is a general strategy to choose the intrinsic functions $\phi(x|a)$ to be square integrable in x for all values of a. In this case one can always normalise $\phi(x|a)$ such that it is square integrable in both x and a. Whenever the variables of a square integrable function have been divided into two subsets one can define the so called left- and right-iterated kernels:

$$\begin{aligned} A(a, a') &= \int \phi^*(x|a)\phi(x|a')\,\mathrm{d}x \\ X(x, x') &= \int \phi(x|a)\phi^*(x'|a)\,\mathrm{d}a \end{aligned} \tag{9}$$

which are both Hermitian and positive (Schmidt 1907a, b, c). The spectral properties of $A(a, a')$ and $X(x, x')$ are strongly connected. In fact one can show that they have the same, positive eigenvalues $\lambda_0 \geqslant \lambda_1 \geqslant \ldots > 0$ which have zero as their only possible point of accumulation. The associated eigenfunctions are related by simple integral transform having $\phi(x|a)$ as transformation kernel:

$$\begin{aligned} &\int A(a, a')b_n(a')\,\mathrm{d}a' = \lambda_n b_n(a) \qquad \int X(x, x')y_n(x')\,\mathrm{d}x' = \lambda_n y_n(x) \\ &b_n(a) = \frac{1}{\lambda_n^{1/2}} \int y_n(x)\phi^*(x|a)\,\mathrm{d}x \qquad y_n(x) = \frac{1}{\lambda_n^{1/2}} \int b_n(a)\phi(x|a)\,\mathrm{d}a. \end{aligned} \tag{10}$$

The extended Hilbert–Schmidt theorem (see e.g. Tricomi 1957) then states that the intrinsic function has a norm convergent expansion of the form

$$\phi(x|a) = \sum_{n=0}^{\infty} \lambda_n^{1/2} y_n(x) b_n^*(a) \tag{11}$$

which is unique up to a phase convention in $\lambda_n^{1/2}$. The expansions of the final wavefunction in terms of natural states used in density matrix theory are of the type (11). In view of this analogy and the optimal convergence of (11) we will refer to this series as the natural expansion of the intrinsic functions. The $y_n(x)$ and $b_n(a)$ are termed coordinate natural states (CNS) and generator coordinate natural states (GCNS) respectively.

It is easy to show that $\mathscr{H}_{GC}$ coincides with the space spanned by the CNS. Consequently we can now replace the formal projected Schrödinger equation (5) by the matrix eigenvalue problem

$$\sum_{n=0}^{\infty} H_{mn}^{GC} c_n = E c_m \qquad \sum_{n=0}^{\infty} |c_n|^2 < +\infty \tag{12}$$

where $H^{GC}_{mn} = \int y^*_m(x) H y_n(x)\,dx$. The question now arises of how the BW condition affects the properties of the natural states and the structure of the secular equation. In order to answer this question we consider the projection operators:

$$P_k = \prod_{l \neq k} (S - s_l I)/(s_k - s_l) \tag{13}$$

associated with the eigenvalues s_k. They are idempotent, Hermitian, mutually exclusive and generate a resolution of the identity

$$P_k^2 = P_k \qquad P_k^+ = P_k \qquad P_k P_l = 0 \qquad \sum_{k=1}^{K} P_k = I. \tag{14}$$

In other words they divide the Hilbert space into orthogonal subspaces associated with a specific symmetry. Furthermore one has the relations

$$SP_k = P_k S = s_k P_k. \tag{15}$$

The BW condition together with (15) implies that

$$S\phi^k(x|a) = \phi^k(x|\sigma(a)) = s_k \phi^k(x|a) \tag{16}$$

where $\phi^k(x|a) = P_k \phi(x|a)$ is the component of the intrinsic state in the subspace characterised by P_k. The following set of equalities then holds:

$$\begin{aligned}
&\int b_n(a)\phi^k(x|a)\,da \\
&\quad = \int b_n(\sigma(a))\phi^k(x|\sigma(a))\,d\sigma(a) \\
&\quad = s_k \int b_n(\sigma(a))\phi^k(x|a)\,d\sigma(a) \\
&\quad = s_k \int b_n(\sigma(a))\phi^k(x|a)|J(a)|\,da.
\end{aligned} \tag{17}$$

If, for fixed n and k, these integrals are not identically vanishing (17) reflects a property of the GCNS $b_n(a)$ which we can mark by assigning to it the label k. Identifying the first and last integrals we can conclude that

$$b^k_n(a) = s_k b^k_n(\sigma(a))|J(a)|. \tag{18}$$

This relation expresses the symmetry property of the GCNS induced by the BW condition. Via the integral transforms (10) we can derive the corresponding property for the CNS. It follows that

$$\begin{aligned}
Sy^k_n(x) &= \frac{1}{\lambda_n^{1/2}} \int b^k_n(a)\phi(x|\sigma(a))\,da \\
&= \frac{s_k}{\lambda_n^{1/2}} \int b^k_n(\sigma(a))\phi(x|\sigma(a))|J(a)|\,da = s_k y^k_n(x)
\end{aligned} \tag{19}$$

which combined with (13) implies that

$$P_k y^k_n(x) = y^k_n(x). \tag{20}$$

We have thus proved that, under the BW condition, the CNS are eigenstates of S. They

can be divided into subsets situated in one of the subspaces characterised by the projectors P_k. Consequently the matrix H^{GC}_{mn} will be block diagonal and the secular equation (12) will split into K different eigenvalue problems, one for each symmetry type s_k.

3. Conservation of symmetry in approximation schemes

The question now arises whether the approximation schemes, which can be drawn from the Hill–Wheeler and natural state representations, conserve the symmetry properties demonstrated above.

3.1. The discretisation technique

The most straightforward and commonly used procedure to solve approximately the HW equation is to replace the integral by a summation. This leads to a generalised matrix eigenvalue problem

$$\sum_{j=1}^{N} (H_{ij} - EA_{ij})c_j = 0 \tag{21}$$

where $H_{ij} = H(a_i, a_j)$, $A_{ij} = A(a_i, a_j)$ and $a_1, a_2, \ldots, a_N$ is a set of mesh points. Clearly (21) is nothing but the diagonalisation of the Hamiltonian in the non-orthogonal basis $\phi(x|a_1), \phi(x|a_2), \ldots, \phi(x|a_N)$. Several suggestions for choosing a relevant set of mesh points have been made: equidistant, by a quadrature rule, via an energy criterion, ... (for a review see e.g. Van Leuven and Bouten 1975). However in either of these cases there is no reason why the subspace spanned by $\{\phi(x|a_i)\}$ is stable under S even though the BW condition may hold. Consequently the approximate wavefunctions will in general not be symmetry adapted. This can of course be remedied by first projecting $\phi(x|a)$ on one of the symmetry subspaces, i.e. by using $\phi^k(x|a)$ as an intrinsic state. However in realistic cases this may turn out to be a rather laborious task.

As an alternative one can consider the functions $\phi(x|a_0)$, $S\phi(x|a_0)$, $\ldots, S^{K-1}\phi(x|a_0)$ where the initial point a_0 is, e.g., the value of the GC's which minimises the energy of $\phi(x|a)$. Using the reduced Cayley–Hamilton equation

$$\prod_{k=1}^{K} (S - s_k I) = 0$$

it is easy to show that the above set is stable under S. On the other hand, according to the BW condition the functions can be written as $\phi(x|a_i)$ where $a_{i+1} = \sigma(a_i)$. Thus by starting out from an initial point and taking as the next point the value of the function σ in the previous point one generates a set of mesh points for which the associated subspace is stable under S. The process can be continued by taking a_K as the point which combined with $a_0, a_1, \ldots a_{K-1}$ gives the lowest ground state and then repeating the procedure with a_K as a starting value†. The advantage of this combined energy–symmetry algorithm over the plain discretisation procedure is evident. It generates

† The procedure also makes sense when, as for continuous groups, S has infinitely many eigenvalues but only a finite number of them are present in the variational subspace.

mesh points in a way which is at the same time simple and 'cheap' and produces symmetry adapted wavefunctions.

3.2. Truncation of the natural expansion

Upper bounds to the GC eigenvalues can be found by diagonalising the Hamiltonian in the space spanned by the first N coordinate natural states, i.e. by solving the matrix equation for the $N \times N$ upper left corner of H^{GC}_{mn}. It is easy to see that this is equivalent to replacing the original intrinsic function by its natural expansion truncated after N terms. In view of the convergence properties of the natural expansion one could say that this approximation scheme preserves a maximum amount of intrinsic information.

The CNS corresponding to the eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_N$ can be grouped into subsets situated in the subspaces characterised by $P_1, P_2, \ldots, P_K$ (see § 2.2.). Since the latter are orthogonal the $N \times N$ Hamiltonian matrix will be block diagonal, each block corresponding to one of the symmetry types $s_1, s_2, \ldots, s_K$. Consequently the secular equation can be broken up into K independent matrix eigenvalue problems which can be treated separately. We conclude that, under the BW condition, the truncation of the natural expansion is a symmetry-conserving approximation.

4. Illustration: the quartic anharmonic oscillator

As an illustration we will consider the quartic anharmonic oscillator

$$H = -\frac{1}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 + \lambda x^4. \tag{23}$$

Like the simple harmonic oscillator ($\lambda = 0$) this operator is parity invariant, i.e.

$$[H, S] = 0 \qquad S\psi(x) = \psi(-x). \tag{24}$$

For $\lambda \geqslant 0$ H has bound states which we try to describe in terms of translated Gaussian intrinsic states

$$\phi(x|a) = \left(\frac{4s}{\pi}\right)^{1/4} \exp(-ra^2)\exp[-2s(x-a)^2] \tag{25}$$

where the exponential normalisation factor is included in order to make all kernels appearing in (25) square integrable. According to a theorem of Wiener (1933) the above continuously labelled set is complete. The GCM will therefore be exact and approximation schemes can be tested effectively. In addition it is clear that the $\phi(x|a)$ are closed under S since

$$S\phi(x|a) = \phi(-x|a) = \phi(x|-a) \tag{26}$$

such that $\sigma(a) = -a$ and $|J(a)| = 1$.

The Hill–Wheeler kernels are easily calculated:

$$A(a, a') = \exp(-ra^2)\exp[-s(a-a')^2]\exp(-ra'^2) \tag{27}$$

$$H(a,a')=A(a,a')\left\{\frac{1}{2m}[2s-4s^2(a-a')^2]+\frac{m\omega^2}{2}\left[\frac{1}{8s}+\left(\frac{a+a'}{2}\right)^2\right]\right.$$
$$\left.+\lambda\left[\frac{3}{4}\left(\frac{1}{4s}\right)^2+\frac{3}{4s}\left(\frac{a+a'}{2}\right)^2+\left(\frac{a+a'}{2}\right)^4\right]\right\}. \tag{28}$$

They are invariant under inversion of both variables:

$$H(a,a')=H(-a,-a') \qquad A(a,a')=A(-a,-a') \tag{29}$$

which are the kernel symmetries corresponding to (24). As mentioned earlier the discretisation of the HW equation for (27) and (28) will not lead to symmetry adapted wavefunctions. One can remedy this drawback by projecting out the correct symmetries before the variation. Here S has two eigenvalues, $+1$ and -1, which are both infinitely degenerate since every even or odd function is an eigenfunction of S.

The corresponding projectors onto positive and negative parity subspaces are

$$P_\pm=(I\bullet S)/2. \tag{30}$$

The kernels for the projected intrinsic states $P_\pm\phi(x|a)$ are therefore given by

$$\begin{aligned}H^\pm(a,a')&=\tfrac{1}{4}(H(a,a')\pm H(-a,a')\pm H(a,-a')+H(-a,-a'))\\ A^\pm(a,a')&=\tfrac{1}{4}(A(a,a')\pm A(-a,a')\pm A(a,-a')+A(-a,-a')).\end{aligned} \tag{31}$$

Discretisation of the corresponding HW equations leads to even (+) or odd (−) wavefunctions.

In order to apply the natural state formalism one first has to solve the eigenvalue problem for the overlap kernel $\Delta(a,a')$. In the Gaussian case (27) analytical solutions for eigenvalues and eigenfunctions have been found (Lathouwers 1976a):

$$\lambda_n=\left(\frac{\pi}{r+s+\gamma}\right)^{1/2}\left(\frac{s}{r+s+\gamma}\right)^n \qquad b_n(a)=\psi_n(a|\gamma) \tag{32}$$

where $\gamma=[r(r+2s)]^{1/2}$ and we have used the notation (H_n is a Hermite function)

$$\begin{aligned}\psi_n(z|\eta)&=N_n(\eta)\exp(-\eta z^2)H_n(\sqrt{2\eta}z)\\ N_n(\eta)&=(2\eta)^{1/4}(\sqrt{\pi}2^n n!)^{-1/2}\end{aligned} \tag{33}$$

for oscillator eigenstates. The associated coordinate natural states can be derived from (10) by direct integration. The result reads

$$y_n(x)=\psi_n(x|\sigma) \qquad \sigma=\frac{2s(\gamma+r)}{(2s+\gamma+r)}. \tag{34}$$

Both the CNS and the GCNS are scaled oscillator eigenstates. They are even or odd according to whether n is even or odd. Hence, the labels + and − should be assigned in the following way:

$$\begin{aligned}\lambda_n^+&=\lambda_{2n} & \lambda_n^-&=\lambda_{2n+1}\\ b_n^+(a)&=b_{2n}(a) & b_n^-(a)&=b_{2n+1}(a)\\ y_n^+(x)&=y_{2n}(x) & y_n^-(x)&=y_{2n+1}(x).\end{aligned} \tag{35}$$

The non-zero values of the matrix elements of H^{GC}_{mn} are given by

$$\begin{aligned} H^{GC}_{nn} &= 2\sigma(n+\tfrac{1}{2})+\left(\frac{1}{4\sigma}-\sigma\right)<n|x^2|n\rangle+\frac{\lambda}{(2\sigma)^2}\langle n|x^4|n\rangle \\ H^{GC}_{nn\pm2} &= \left(\frac{1}{4\sigma}-\sigma\right)<n|x^2|n\pm2\rangle+\frac{\lambda}{(2\sigma)^2}\langle n|x^4|n\pm2\rangle \\ H^{GC}_{nn\pm4} &= \frac{\lambda}{(2\sigma)^2}\langle n|x^4|n\pm4\rangle \end{aligned} \tag{36}$$

where the brackets denote integrals of powers between oscillator eigenstates $\psi_n(x|\frac{1}{2})$. These quantities can be calculated in closed form (Brändas and Reid 1975) of from recursion relations between Hermite polynomials

$$\begin{aligned} &\langle n|x^2|n\rangle = \tfrac{1}{2}(2n+1) \\ &\langle n|x^2|n+2\rangle = \tfrac{1}{2}[(n+1)(n+2)]^{1/2} \\ &\langle n|x^4|n\rangle = \tfrac{3}{4}(2n^2+2n+1) \\ &\langle n|x^4|n+2\rangle = \tfrac{1}{2}(2n+3)[(n+1)/(n+2)]^{1/2} \\ &\langle n|x^4|n+4\rangle = \tfrac{1}{4}[(n+1)(n+2)(n+3)(n+4)]^{1/2}. \end{aligned} \tag{37}$$

In view of the symmetry properties of the CNS's the Hamiltonian matrix of order $2N$ factorises into two N-dimensional blocks corresponding to positive and negative parity.

In table 1 we have listed some results for the ground and first excited states of the quartic anharmonic oscillator at different values of the coupling strength λ. Three discretisation procedures were considered. D1 and D2 correspond to discretisation of the unprojected (equations (27), (28)) and projected (equation (31)) kernels respectively. In both cases each point was selected such as to give the lowest possible energy if combined with the ones already chosen (Caurier 1975). In D3 the combined energy–symmetry algorithm was used. Here this means that if a point a_i is chosen the

Table 1. Results for the ground and first excited states of the quartic anharmonic oscillator. The calculations were done with the scale factors $2s = \sigma = 1$. This value minimises the expectation value $\langle\psi_0(\sigma)|H|\psi_0(\sigma)\rangle$ at $\lambda = 1$. Figures in parentheses indicate the dimension needed for stability on the fifth decimal place.

	λ	D1	D2	D3	NSD	'Exact'
	0·1	0·559158 (7)	0·559146 (4)	0·559154 (17)	0·559146 (5)	0·559146
E_0	0·5	0·696183 (9)	0·696190 (4)	0·696177 (13)	0·696176 (6)	0·696176
	1·0	0·803788 (11)	0·803926 (4)†	0·803773 (17)	0·803771 (7)	0·803770
	0·1	1·769507 (9)	1·769503 (5)	1·769503 (11)	1·769503 (7)	1·769503
E_1	0·5	2·324424 (11)	2·324438 (5)†	2·324411 (15)	2·324407 (6)	2·324406
	1·0	2·737914 (15)	2·739201 (5)†	2·737898 (21)	2·737893 (8)	2·737892

† program interrupted for approximate linear dependence.

next one is $-a_i$ since $\sigma(a) = -a$. The column marked NSD (natural state diagonalisation) is generated by diagonalising matrices defined by (36)–(37).

5. Discussion

Comparing the D1 and NSD results it is clear that the latter are by far superior. More accurate energy values are obtained with fewer basis states and the NSD wavefunctions have the proper symmetry. The NSD is also more economical. The computer time needed to produce the above results was roughly a factor 50 larger for D1 as compared to NSD. This is due to the time-consuming scanning of a grid in order to find the energetically most favourable mesh points.

Symmetry has been restored in D2 and D3. In the case of projection before variation this advantage is largely destroyed by the rapid occurrence of approximate linear dependences†. This is a consequence of the fact that one is selecting basis functions in a smaller space (in this case half the space). The chosen states resemble each other more which leads to larger overlaps; a familiar origin of approximate linear dependences. D3 produces results of higher accuracy than D1. The number of basis functions is in most cases larger. However, the necessary computer time is less since only half the number of points are to be selected while the others are prescribed by symmetry. This advantage will become more pronounced when several s_k are involved or when one is dealing with a group of symmetry operations. Thus in realistic cases, where the calculation of matrix elements between projected states may become very difficult, D3 provides a way to avoid projection before variation.

In view of the above results, the combined energy–symmetry algorithm is probably the best discretisation alternative to the diagonalisation in natural states.

6. Conclusions

In this paper we have verified that, both in the Hill–Wheeler and in the natural state representations, the GCM wavefunctions are symmetry adapted if the Brink–Weiguny condition is satisfied. From the practical point of view we derived an algorithm for choosing mesh points which guarantees that this property is conserved in the discretisation technique. On the other hand it was shown that the truncation of the natural expansion leads to a splitting, according to symmetry, of the secular equation. A numerical test on the quartic anharmonic oscillator showed that the diagonalisation in natural states is qualitatively and economically superior to the discretisation techniques among which the one equipped with the suggested energy–symmetry algorithm was most competitive.

Acknowledgments

The author would like to thank Professor P O Löwdin for hospitality at the Department of Quantum Chemistry, University of Uppsala. The critical reading of the manuscript by Professors M Bouten and P Van Leuven and the computational help of Dr F Arickx are gratefully acknowledged.

† This means that the overlap matrix is numerically singular (see e.g. Lathouwers 1976b).

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