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On the Method of Solving Constrained Secular Equations

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A new method is proposed for solving constrained secular equations. It incorporates the two methods which have been used so far, namely, perturbation and parametrization. The present method has the advantages of both of the previous methods and none of their disadvantages. This is illustrated by an example.

1. Introduction

In the method of constrained variations [1, 2], the system of equations one has to solve are:

$$[\boldsymbol{H} + \Lambda \boldsymbol{C} - E\mathbf{1}]\,\boldsymbol{a} = 0\,, \tag{1.1}$$

$$\boldsymbol{a}^{\dagger}\boldsymbol{C}\boldsymbol{a} = 0\,, \tag{1.2}$$

where $\boldsymbol{H}$ and $\boldsymbol{C}$ are the matrix representations of the Hamiltonian and constraint operators respectively.

Two methods have been proposed for solving the system of Eqs. (1.1) and (1.2), namely, perturbation and parametrization. In both methods, one considers the situation in which Λ (the correct value of the Lagrangian multiplier) is replaced by a parameter λ in Eqs. (1.1) and (1.2):

$$[\boldsymbol{H} + \lambda \boldsymbol{C} - E(\lambda)\,\mathbf{1}]\,\boldsymbol{a}(\lambda) = 0\,, \tag{1.3}$$

$$C(\lambda) = \boldsymbol{a}^{\dagger}(\lambda)\,\boldsymbol{C}\boldsymbol{a}(\lambda)\,, \tag{1.4}$$

and the correct value of $\lambda(=\Lambda)$ is determined by:

$$C(\Lambda) = 0\,. \tag{1.5}$$

In practice, one uses the most convenient basis set, namely, the eigenvectors of $\boldsymbol{H}$.

2. Perturbation

In the perturbation approach [1], one treats λ as a perturbation parameter and $\boldsymbol{C}$ as a perturbation matrix. Byers Brown [1] has shown that

$$C(\lambda) = \sum_{l} \lambda^{l} C_{l} \tag{2.1}$$

where

$$C_l = (l+1)\, E^{(l+1)} \tag{2.2}$$

and $E^{(l+1)}$ are the perturbation energies. Λ is then given by

$$0 = C(\Lambda) = \sum_l \Lambda^l C_l\,, \tag{2.3}$$

and can be obtained by inverting (2.3) ($\theta = -C_0/C_1$):

$$\Lambda = \sum_k a_k \theta^k\,. \tag{2.4}$$

The advantage of this approach is that no arbitrary choice of parameter values is needed. On the other hand, this procedure suffers from the drawback that the power series in Eq. (2.4) may not converge fast enough, especially for a small basis set [2]. (See also Example in Section 4.)

3. Parametrization

In the parametrization procedure, one solves Eq. (1.4) for selected values of λ, and the correct value of $\lambda(=\Lambda)$ is obtained by examining $C(\lambda)$ until $C(\Lambda)=0$.

This method suffers from the disadvantage that the choice of selected values of λ is somewhat arbitrary, even with the help of the perturbation approach to obtain an intial guess. The choice of both the intervals for λ and of the factor by which this interval is decreased from one cycle to the next in a simple iterative Newton's method may be too arbitrary for workers without previous experience in constrained variations.

4. Perturbation-Iteration

Theory

In practice, one has to truncate the series in Eq. (2.4). We consider

$$\Lambda_0 = \sum_{l=0}^{N} a_l \theta^l \tag{4.1}$$

as an initial value for an iterative scheme in which a new value Λ_{n+1} is obtained from the preceding one Λ_n (the value after n iterations).

The perturbation series in Eq. (2.1) is a Maclaurin's series expansion about $\lambda = 0$. During each iteration, say the $(n+1)$th, in the present method, $C(\lambda)$ is expanded in a truncated Taylor's series around $\lambda = \Lambda_n$

$$C(\Lambda_n + \chi) = C(\Lambda_n) + \sum_{l=1}^{N} \chi^l D_l(\Lambda_n)\,, \tag{4.2}$$

where

$$D_l(\Lambda_n) = \frac{1}{l!}\left[\frac{d^l C(\lambda)}{d\lambda}\right]_{\lambda=\Lambda_n}. \tag{4.3}$$

It can readily be shown that

$$D_l(\Lambda_n) = \sum_{k=l}^{N} \binom{k}{l} \Lambda_n^{k-l} C_k + O(C_{N+1}), \tag{4.4}$$

where $\binom{k}{l}$ are the binomial coefficients, C_k are given by Eq. (2.2), and $O(C_{N+1})$ is neglected in practice. The crucial point in the present method is that $C(\Lambda_n)$ in Eq. (4.2) is obtained from Eq. (1.4) and *not* from D_0. Setting both sides of Eq. (4.2) equal to zero and inverting the power series in χ, one gets a value for χ and hence a new value for the Lagrangian multiplier

$$\Lambda_{n+1} = \Lambda_n + \chi . \tag{4.5}$$

Program

A subroutine has been written by the author for seventh order perturbation calculations. This yields $C_0, C_1, \ldots, C_6$. Another subroutine handles the inversion of sixth order polynomials. The rest of the program is straightforward.

The perturbation-iteration procedure stops when any one of three criteria is met: (1) when the number of cycles reaches some maximum N_{cy}, (2) when $|C(\Lambda_n)| < \varepsilon_c$ (such as 10^{-7}), or (3) when $|x| < \varepsilon_x$ (such as 10^{-6}).

The desired values of N_{cy}, ε_c and ε_x are part of the input data.

The other input data required are $\boldsymbol{\varepsilon}$, $\boldsymbol{C}$, and a few control parameters for optional printing (of intermediate results) and optional punching of the final constrained vector $\boldsymbol{a}$.

This program, with complete documentation, will be submitted to Quantum Chemistry Program Exchange.

Example

The case of force constraint studied by Chong and Rasiel [2] is chosen as example in this work. The input data are:

$$\boldsymbol{\varepsilon} = (-9.058791, \quad -8.908329, \quad -6.618735)$$

$$\boldsymbol{C} = \begin{bmatrix} -0.968705 & 1.260620 & -10.542866 \\ 1.260620 & 6.875227 & -13.565059 \\ -10.542866 & -13.565059 & 0.387417 \end{bmatrix}.$$

For this example, the perturbation energies $E^{(1)}$ to $E^{(7)}$ are -0.968705, -56.11495, $+1558.06$, -1.03604×10^5, 5.51799×10^6, -2.76201×10^8, and 1.25172×10^{10}.

The disadvantage of the perturbation approach can be seen from the following:

$$10^3 \Lambda = -8.63144 + 3.10287 + 0.14366 - 0.89861$$
$$+ 0.23057 + 0.33785 + O(\theta^7) .$$

Thus, truncation of the power series after the term $E^{(3)}$, $E^{(5)}$, and $E^{(7)}$ leads to -5.5286, -6.2835, and -5.7151 respectively for the value of $10^3 \Lambda$, compared to the correct value of -5.93501 [2]. The drawback of the parametrization approach has already been mentioned.

In the present method of perturbation-iteration, $\Lambda_0 = -5.7151 \times 10^{-3}$, $\Lambda_1 = -5.93600 \times 10^{-3}$, $\Lambda_2 = -5.93500 \times 10^{-3}$ and $\Lambda_3 = -5.93501 \times 10^{-3}$. The computational time on an IBM 7044 is about 1 second.

5. Discussion

The present method of perturbation-iteration is an incorporation of both perturbation and parametrization. It enjoys the advantages of both and does not suffer from the disadvantages of either.

It is hoped that, with the availability of this perturbation-iteration method and the computer program in FORTRAN IV, more workers may be encouraged to try the method of constrained variation.

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References

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