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Relationes

Parameters for Multiple Constraints

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A simple procedure is outlined, to obtain good initial guesses for the parameters for multiple constraints.

Early papers [1–4] on the method of constrained variations were mainly concerned with the formulation of the constrained variation principle and the methods of solving the constrained secular equation. More recently, the purpose of constrained variations has been established [5–9]. Therefore, as long as accurate wavefunctions are beyond our reach (especially for systems with more than four electrons), we expect to see more applications of constrained variations in the near future. The object of this note is to add to the methodology of constrained variations.

The two methods of solving constrained secular equations are perturbation [1–3] and parametrization [2]. For single constraints, the perturbation approach is used to obtain good initial guesses for the parametrization method [2, 8]. However, this procedure becomes tedious for double constraints and formidable for multiple constraints in general. In this note, we show how simple it is to obtain good initial guesses for the parameters for multiple constraints and to arrive at the correct values for the parameters.

In a recent investigation [8], we discovered that, for double constraints, the equations

$$\left.\begin{aligned} C_1(\lambda_1, \lambda_2) &= A_{10} + A_{11}\lambda_1 + A_{12}\lambda_2 \\ C_2(\lambda_1, \lambda_2) &= A_{20} + A_{21}\lambda_1 + A_{22}\lambda_2 \end{aligned}\right\} \tag{1}$$

holds to a very good approximation. This empirical linearity can be used to great advantage, both in determining good initial guesses for the λ's and in finding their correct values. For N constraints, there are $N(N+1)A$ coefficients, which can be calculated from the values of the N C_j's at $(N+1)$ sets of λ's.

To obtain good initial guesses, the free variation and the results of single constraints provide $(N+1)$ such sets. In this case, the A_{j0} coefficients are simply the expectation values of the constraint operators obtained with the free variational wavefunction; and the A_{jj} coefficients are given by

$$A_{jj} = -A_{j0}/\ell_j, \tag{2}$$

where ℓ_j is the value of λ_j which satisfies the single constraint $C_j = 0$. For double constraints, the other A coefficients are

$$\left.\begin{aligned} A_{12} &= [C_1(0, \ell_2) - A_{10}]/\ell_2, \\ A_{21} &= [C_2(\ell_1, 0) - A_{20}]/\ell_1. \end{aligned}\right\} \tag{3}$$

Table. *Good initial guesses for the parameters in double constraints. The correct values of the parameters are given in parentheses*

Constraints	Ref.	λ_1	λ_2
F_H and F_{Li}	3	2.985×10^{-4} (2.987×10^{-4})	4.129×10^{-4} (4.129×10^{-4})
F and V	3	4.114×10^{-4} (4.111×10^{-4})	-1.742×10^{-4} (-1.740×10^{-4})
F_{Li} and V	3	4.115×10^{-4} (4.111×10^{-4})	-1.805×10^{-4} (-1.804×10^{-4})
F_H and V	3	5.735×10^{-5} (5.737×10^{-5})	-1.757×10^{-4} (-1.756×10^{-4})
$M_1 - M_2$ and $M_2 - M_3$ for ψ_5	8	1.468 (1.460)	0.3954 (0.3907)
$M_1 - M_2$ and $M_2 - M_3$ for ψ_7	8	-0.02549 (-0.02548)	0.03957 (0.03957)

Then, good initial guesses for λ_1^0 and λ_2^0, the correct parameters for double constraints, can be calculated by setting $C_1 = C_2 = 0$ in Eq. (1). This procedure is tested on the four cases of double constraints studied by Chong and Byers Brown [3] and on the two examples in our recent paper [8]. The results, summarized in the table show how good the initial guesses are.

The empirical linearity in Eq. (1) has been used [8] to find better and better values of λ_1 and λ_2 until the correct values are obtained. The algebra is straightforward: using values of C_1 and C_2 at three sets of (λ_1, λ_2) around the previous estimates, we solve for the six A's and then for better λ_1 and λ_2. In practice [8], one iteration has been sufficient.

It is straightforward to extend the present scheme to multiple constraints, provide that similar linearity holds to a good approximation and that the constraints are linearly independent. Since this procedure involves only solving simultaneous linear algebraic equations, it is much simpler than multiple perturbation.

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