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Some Remarks on the Linear Dependence Problem in Variational Calculations*

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Introduction

While the use of nonorthogonal basis functions in atomic and molecular calculations, employing the Ritz variational method, renders the wave function more flexible [*1*, *5*], it can, under certain unfavourable circumstances, cause the so-called "linear dependence" problem [*1*], or more correctly, the "near linear dependence" problem. When the linear dependence problem arises in a variational calculation, the calculated results usually become unstable [*3*]; it also causes a loss of the accuracy [*6*]. Occasionally, one can remove this difficulty by dropping the "bad" functions from the wave function. However, this is not a satisfactory solution, since this problem is most likely to happen when two or more similar functions, centered on the same spatial point, are included in the wave function. The effect, on the calculated results, of excluding the "bad" functions, instead of using a suitable set of parameters for the functions, is usually not assessed; but, in view of the circumstances where this difficulty is most probable, this effect, if assessed, might prove to be a rather significant loss.

Furthermore, because of the difficulty in explicitly handling the nonlinear parameters as a continuous variable in a calculation based on the variational principle, it is customary to choose an initial set of values for these parameters around which one then searches for the optimal values. By varying the nonlinear parameters over a sufficiently wide range, one can, in principle, obtain the absolute energy minimum attainable with the basis set. However, this is impractical, in most cases, because of the economical factor and the higher possibility of running into the linear dependence problem. As a consequence, it necessitates, on the one hand, a much larger basis set in order to attain a certain energy [*5*]. On the other hand, it may lead to a peculiar situation where different people find different local energy minima**.

A Method of Avoiding the Linear Dependence Problem

In this report, a method of avoiding the linear dependence problem, and consequently, of giving full flexibility to the wave function is described.

Let us assume a set of square-integrable functions, $\{f_i(\alpha_i, \beta_i)\}$, $i = 1, 2, \ldots, n$, where α_i and β_i are nonlinear parameters, such as the exponential parameters of elliptical orbitals [*7*]. We will use the convention that parameters with a subscript, such as α_i and β_i, have been assigned some constant values while those without a subscript, e.g., α and β, are to be regarded as variables. We will further assume that the set $\{f_i(\alpha_i, \beta_i)\}$ does not give any linear dependence problem. To this set of

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** For example, J. C. Browne [J. chem. Physics **41**, 3495 (1964)], using a seven-term wave function, given in Tab. 4 therein, with the parameters listed in Tab. 5 thereof, obtained a total energy of -7.7269 a.u. for LiH^+ at the nuclear distance of 4.25 a_0. However, if the parameters are changed to $\alpha(3) = 3.45$, $\beta(3) = 2.70$, $\alpha(4) = 4.80$, and $\beta(4) = 2.94$, one obtains -7.7274 a.u. at the same nuclear distance.

functions, we want to add another function, $f_{n+1}(\alpha, \beta)$, and determine the values of α and β, which can be used with the original set, free of the linear dependence problem. For simplicity, we will assume that the functions f_j, $j = 1, 2, \ldots, n, n+1$, are normalised to unity.

The lowest root $\lambda_{\min} \geq 0$, of the equation

$$\begin{vmatrix} (f_1 f_1) - \lambda & (f_1 f_2) & \ldots. & (f_1 f_n) \\ (f_2 f_1) & (f_2 f_2) - \lambda & \ldots. & (f_2 f_n) \\ \ldots. & \ldots. & \ldots. & \ldots. \\ (f_n f_1) & (f_n f_2) & \ldots. & (f_n f_n) - \lambda \end{vmatrix} = 0 \qquad (1)$$

where

$$(f_i f_j) \equiv \int f_i(\alpha_i, \beta_i)\, f_j(a_j, \beta_j)\, dv \qquad (2)$$

is defined as the "measure of linear independence" [2, 6]. Since the linear dependence problem arises when $\lambda_{\min}$ is very small*, to avoid this difficulty we want to find the domain of the variables, α and β, over which $\lambda_{\min}$ satisfies the condition, $\lambda_{\min} \geq$ constant. Let us set up the equation

$$\begin{vmatrix} 1-\lambda & (f_1 f_2) & \ldots. & \ldots. & (f_1 f_n) & g_1(\alpha, \beta) \\ (f_2 f_1) & 1-\lambda & \ldots. & \ldots. & (f_2 f_n) & g_2(\alpha, \beta) \\ \ldots. & \ldots. & \ldots. & \ldots. & \ldots. & \ldots. \\ (f_n f_1) & (f_n f_2) & \ldots. & \ldots. & 1-\lambda & g_n(\alpha, \beta) \\ g_1(\alpha, \beta) & g_2(\alpha, \beta) & \ldots. & \ldots. & g_n(\alpha, \beta) & 1-\lambda \end{vmatrix} = 0 \qquad (3)$$

where $g_i(\alpha, \beta)$, defined by

$$g_i(\alpha, \beta) \equiv \int f_i(\alpha_i, \beta_i)\, f_{n+1}(\alpha, \beta)\, dv\,,$$

are explicit functions of α and β. On expanding Eq. (3), one obtains a polynomial equation

$$P(\lambda : \alpha, \beta) \equiv \lambda^{n+1} - (n+1)\,\lambda^n + h_2(\alpha, \beta)\,\lambda^{n-1} + \ldots\ldots + h_{n+1}(\alpha, \beta) = 0\,. \qquad (5)$$

Let us assume a positive constant c to be the acceptable lower limit of $\lambda_{\min}$. That is, the values of α and β, which do not cause the linear dependence problem, satisfy $\lambda_{\min}(\alpha, \beta) \geq c$. One substitutes $\lambda = c$ into Eq. (5) and solves for α and β. Since the λ's are continuous functions of the parameters α and β [8], the solutions of $P(c : \alpha, \beta) = 0$ can always be found. The roots are the values of α and β for which one of the $n+1$ λ's intercepts the line $\lambda = c$. For the case of functions with a single parameter, a typical diagram appears as in Fig. 1.

In a practical application, there are two ways of choosing the functions, f_i. One can take, as f_i, either each term of a CI wave function, or a basis function such as the elliptical orbital or the Slater type orbital. The more profitable choice of f_i is the latter where use is made of the fact that configurations composed of a basis set, which is not linearly dependent, do not give the linear dependence problem.

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* Usually the ratio $\lambda_{\min}/\lambda_{\max}$, or $\lambda_{\max}/\lambda_{\min}$, rather than $\lambda_{\min}$, is used as a test of the linear dependence. If one uses a normalised basis set, $\lambda_{\max} \leq m$, where m is the number of basis functions in the set. Since m is known, one can always use $\lambda_{\min}$ for this purpose. As for the value of $\lambda_{\min}$ which may cause the linear dependence difficulty, there is not a universal opinion. Different criteria are used by different people.

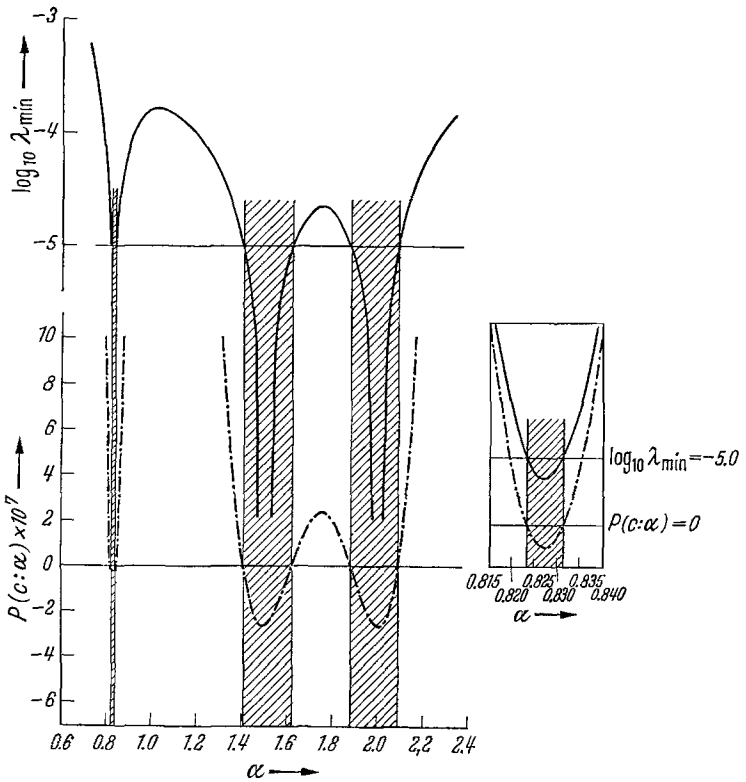

Fig. 1. $\log \lambda_{\min}$ (———) and $P(c:\alpha)$ (—.—.—.) versus α. $c = 10^{-5}$. $f_1 = (4\sqrt{2})e^{-2r}$, $f_2 = (3\sqrt{6/2})e^{-1.5r}$, $f_3 = (2/\sqrt{3})re^{-r}$, $f_4 = (2\,\alpha^{3/2})e^{-\alpha r}$. $\lambda_{\min}$ is included for a comparison. Insets are $\lambda_{\min}$ and $P(c:\alpha)$ in the range: $\alpha = 0.815$—0.840. Intercepts of $P(c:\alpha)$ with the Line $P(c:\alpha) = 0$ correspond to the values of α for which $\lambda_{\min} = c$. If c is the lower limit of $\lambda_{\min}$, the value of α, for f_4, within the shaded regions causes the linear dependence problem when used with f_1, f_2, and f_3 given above

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