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Commentationes

Determination of Molecular Properties by the Method of Moments. I

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The method of moments appears to have some significant advantages over other variational methods of quantum chemistry if complicated molecular systems are investigated and elaborate variational wave functions are applied. The main advantages are (a) the possibility of avoiding the worst difficulties of integration or reducing the number of integrals (b) the possibility of improving the accuracy of the wave function in physically important regions of the configurational space and (c) the possibility of obtaining some "random sampling type" error estimates. The aim of the series of papers starting with the present one is to collect experience in applying the method of moments to problems of quantum chemistry.

Die Methode der Momente scheint gegenüber den üblichen Variationsmethoden in der Quantenchemie einige bedeutende Vorteile zu besitzen, besonders wenn es sich um Untersuchungen komplizierter molekularer Systeme handelt, die nur mit umfangreichen Variationswellenfunktionen behandelt werden können. Die Hauptvorteile der neuen Methode sind: (a) Die bei der Integration auftretenden großen Schwierigkeiten bzw. die Anzahl der zu berechnenden Integrale können erheblich herabgesetzt werden. (b) In den physikalisch besonders wichtigen Bereichen des Konfigurationsraumes besteht die Möglichkeit, die Wellenfunktionen beträchtlich zu verbessern. (c) Es können Fehlerabschätzungen gemacht werden. Ziel dieser Arbeit ist es, erste Erfahrungen in der Anwendung der neuen Rechenmethode auf quantenchemische Probleme zu sammeln.

La méthode des moments parait posséder des avantages nets sur les autres méthodes variationnelles de la chimie quantique si l'on étudie des systèmes moléculaires complexes et si l'on utilise des fonctions d'onde variationnelles perfectionnées. Les avantages principaux sont a) la possibilité d'éviter les difficultés les plus gênantes de l'intégration et de réduire le nombre d'intégrales; b) la possibilité d'améliorer la précision de la fonction d'onde dans les régions de l'espace de configuration les plus importantes pour une observable, et c) la possibilité d'obtenir des évaluations du type «échantillonnage au hasard» des erreurs commises. Le but de la série d'articles qu'inaugure celui-ci est de présenter une information sur l'application de la méthode des moments aux problèmes de la chimie quantique.

1. Introduction

The computation of the necessary integrals is one of the bottlenecks of quantum-chemical ab initio calculations. This difficulty can significantly be reduced if the method of moments is applied to determine the wave function. The aim of the series of papers starting with the present one is to collect some experience in applying the method of moments to problems of quantum chemistry both by theoretical investigations and by testing the method on numerical examples.

The method of moments has two important features which need to be briefly mentionned in advance.

(a) The more complicated systems we investigate and the more elaborate variational wave functions we use the more significant the advantages of the method of moments. It has *e.g.* little reason to determine the wave function of the ground state of an isolated hydrogen molecule by the method of moments. On the other hand the method of moments may have very significant advantages if we investigate *e.g.* an organic molecule adsorbed on a crystal surface, the crystal surface being modelized by a pseudopotential, or if we carry out systematical ab initio or partly ab initio calculations on a series of related molecules in order to predict some practically important property of them. In the following when speaking of molecular systems we shall tacitly think of complicated ones.

(b) If we do not want to loose the computational advantages of the method of moments our results may appear less rigorous than those obtained by certain other variational methods, the method of energy variation, say. The error estimates that are available all have a probability character: we can give an error estimate and at best a probability with which this error estimate is valid. It must, however, always be kept in mind that as soon as we investigate complicated molecular systems the error estimates of any other variational method applicable in practice become meaningless. In such cases the method of moments can prove one of the most reliable methods just because the mentionned "random sampling type" error estimates provided by it are available also in complicated cases.

In the next sections the basic ideas of the method of moments will be summarized with particular emphasis to those which seem important in quantumchemical applications and to those which are useful in comparing the method of moments with other variational methods of quantum chemistry. The next papers of the series mainly present numerical results obtained by applying the method of moments to molecular problems.

Brief historical survey. The first attempt to apply the method of moments to problems of quantum chemistry appears to be due to Montrol [1]. Montrol considered problems of solid state physics and the way he proceeded can hardly be applied to molecular problems as it requires the calculation of integrals involving higher powers of the Hamiltonian operator. Sporadic papers essentially along the same line followed Montrol's paper [2].

The use of the hypervirial relations for determining or improving molecular wave functions has been proposed by Hirschfelder [3], Epstein [4], Coulson [5] *et al.* The hypervirial relations are closely related to the method of moments. The papers dealing with the hypervirial relations called attention to the possibility of using the method of moments for improving molecular wave functions in physically important regions of the configurational space ("guided approximations" cf. also Preuss [6], Schwartz [7], Hall [8] and others [9]).

The possibility of using the method of moments for reducing difficulties of integration has been considered by Szondy [10] and Boys [11].

2. Application of the Method of Moments to Problems of Quantum Chemistry

Let H be the Hamiltonian operator of a molecular system with eigenvalues E_i and eigenfunctions $\psi_i(x)$

$$(H - E_i)\,\psi_i(x) = O\,, \tag{1}$$

$$\langle \psi_i(x) | \psi_j(x) \rangle = \delta_{ij}\,, \tag{2}$$

$$E_i \leqq E_{i+1}\,, \quad (i = 0, 1, 2, \ldots) \tag{3}$$

where x denotes a point of the configurational space. Let $\varphi_k(x, \alpha)$ be a variational wave function depending on the point α of the space of variational parameters $\alpha_1, \alpha_2, \ldots, \alpha_n$. It will be assumed that $\varphi_k(x, \alpha)$ is normalized

$$\langle \varphi_k(x, \alpha) | \varphi_k(x, \alpha) \rangle = 1\,, \tag{4}$$

and that the calculation of the integral

$$\mathscr{E}_k^{(e)}(\alpha) = \langle \varphi_k(x, \alpha) | H | \varphi_k(x, \alpha) \rangle \tag{5}$$

is too tedious to be possible or to pay off. (This is a fortiori true for integrals involving higher powers of H.)

Let

$$w_0(x), w_1(x), \ldots, w_n(x) \tag{6}$$

be a set of linearly independent functions to be referred to as weight functions. It will be assumed that the integrals

$$\langle w_i(x) | \varphi_k(x, \alpha) \rangle\,, \tag{7}$$

$$\langle w_i(x) | H | \varphi_k(x, \alpha) \rangle \tag{8}$$

are finite, and simple enough to be calculated in practice. It will further be assumed that for every value of α at least one of the integrals (7) is non-zero and that none of the integrals (7) and (8) vanishes for every value of α because of trivial symmetry reasons.

Evidently if for some $\alpha = \alpha^{(m)}$ $\varphi_k(x, \alpha^{(m)}) \equiv \psi_k(x)$ and $\mathscr{E}_k^{(m)} = E_k$ then the equations

$$\langle w_i(x) | H - \mathscr{E}_k^{(m)} | \varphi_k(x, \alpha^{(m)}) \rangle = 0 \tag{9}$$

are satisfied for any $w_i(x)$ satisfying the above conditions. If, however, $\varphi_k(x, \alpha^{(m)})$ does not coincide with $\psi_k(x)$ then in general at most $n+1$ equations of the form (9) can be satisfied by proper choice of the variational parameters $\alpha_i^{(m)}$ and $\mathscr{E}_k^{(m)}$. Thus we have in this case a set of equations for the determination of the variational parameters and the energy. The Eqs. (9) will be referred to as basic equations of the method of moments. The integrals

$$m_i(\mathscr{E}, \alpha) = \langle w_i(x) | H - \mathscr{E} | \varphi_k(x, \alpha) \rangle \tag{10}$$

will be referred to as moments of $(H - \mathscr{E})\, \varphi_k(x, \alpha)$ with the weight functions $w_i(x)$.

Evidently the accuracy of $\mathscr{E}_k^{(m)}$ and $\varphi_k(x, \alpha^{(m)})$ is dependent on the proper choice of the weight functions. Before discussing, however, the problem of how to find "good" weight functions attention must be called to a property of the Eqs. (10).

As the moments are linear in the weight functions the results are unchanged if we replace the weight functions by any linearly independent linear combinations made up of them. This possibility can be used to orthogonalize all but one of the weight functions to $\varphi_k(x, \alpha)$ i.e., we can always assume without loss of generality that the orthogonality relations

$$\langle w_i(x) | \varphi_k(x, \alpha) \rangle = 0 \qquad (i = 1, 2, \ldots, n) \tag{11}$$

are satisfied. In this case the set of Eqs. (10) becomes decoupled in the sense that the equations with $i = 1, 2, \ldots, n$ serve for the determination of the variational parameters $\alpha_i^{(m)}$ and they do not make any use of the value of $\mathscr{E}_k^{(m)}$. Having determined $\alpha^{(m)}$ in this way the value of $\mathscr{E}_k^{(m)}$ can be determined from the 0'th equation

$$\mathscr{E}_k^{(m)} = \frac{\langle w_0(x) | H | \varphi_k(x, \alpha^{(m)}) \rangle}{\langle w_0(x) | \varphi_k(x, \alpha^{(m)}) \rangle} . \tag{12}$$

3. The Problem of Constructing "Good" Weight Functions

Let us start from the equation

$$\langle \varphi_k(x, \alpha) | (H - \mathscr{E}_k) \, f(x) \, f^*(x) \, (H - \mathscr{E}_k) | \varphi_k(x, \alpha) \rangle = \min \tag{13}$$

proposed by Preuss [6] for the determination of molecular wave functions. $f(x)$ denotes some weight function (not to be confused with the $w_i(x)$'s) and serves for improving the wave function in physically important regions of the configurational space. If $f(x)$ does not suppress the integrand of (13) in regions which are important for the energy, $\mathscr{E}_k$ may also be determined from (13).

Let $v_i(x)$ $(i = 0, 1, 2, \ldots)$ be a complete orthonormalized set of functions. Making use of the expansion

$$\sum_{i=0}^{\infty} |v_i(x)\rangle \langle v_i(x')| = \delta(x - x') \tag{14}$$

of the Dirac delta function (13) may be written as

$$\sum_{i=0}^{\infty} |\langle f(x) \, v_i(x) | H - \mathscr{E}_k | \varphi_k(x, \alpha) \rangle|^2 = \min . \tag{15}$$

The values of the α_i's and of $\mathscr{E}_k$ determined from (13) will be denoted by $\alpha_i^{(v)}$ and $\mathscr{E}_k^{(v)}$, respectively. It can now be verified that the method of moments is equivalent to approximately solving (15) by truncating the infinite sum at $i = n$ and introducing the notation $w_i(x) = f(x) \, v_i(x)$. The question is: under what conditions will this truncation cause only small changes in the roots $\alpha_i^{(v)}$ and $\mathscr{E}_k^{(v)}$ of (13). (It may be noted that in certain cases advantageous may be to truncate at some $i > n$. It seems unlikely that such a generalization would drastically change the following conclusions.)

Let us define the (finite) partial difference quotient of $\varphi_k(x, \alpha)$ between the points $\alpha^{(1)}$ and $\alpha^{(2)}$ of the space of the parameters by the line integral

$$\frac{D \, \varphi_k(x | \alpha^{(1)}, \alpha^{(2)})}{D \alpha_i} = \frac{1}{\alpha_i^{(2)} - \alpha_i^{(1)}} \int_{\alpha^{(1)}}^{\alpha^{(2)}} \left(d\boldsymbol{\alpha}, \frac{\partial \, \varphi_k(x, \alpha)}{\partial \alpha_i} \, \boldsymbol{i}_i \right) \tag{16}$$

where $\boldsymbol{i}_i$ denotes the unit vector pointing in the direction of the α_i axis and the path of integration is the straight line connecting the points $\alpha^{(1)}$ and $\alpha^{(2)}$. The partial difference quotients defined in this way are generalizations of the respective partial differential quotients and have the property that for finite $\alpha^{(2)} - \alpha^{(1)}$'s

$$\varphi_k(x, \alpha^{(2)}) = \varphi_k(x, \alpha^{(1)}) + \sum_{j=1}^{n} \frac{D\, \varphi_k(x \mid \alpha^{(1)}, \alpha^{(2)})}{D\alpha_j} (\alpha_j^{(2)} - \alpha_j^{(1)}) . \tag{17}$$

Now by (9), (10), and (11) we can write

$$\begin{aligned}\langle w_i(x) \mid H - \mathcal{E}_k^{(v)} \mid \varphi_k(x, \alpha^{(v)})\rangle &= m_i(\mathcal{E}_k^{(v)}, \alpha^{(v)}) \\ &= \sum_{j=1}^{n} \langle w_i(x) \mid H - \mathcal{E}_k^{(v)} \mid D\, \varphi_k(x \mid \alpha^{(m)}, \alpha^{(v)})/D\alpha_j\rangle\, (\alpha_j^{(v)} - \alpha_j^{(m)})\end{aligned} \tag{18}$$

and introducing the abbreviations

$$A_{ij} = \langle w_i(x) \mid H - \mathcal{E}_k^{(v)} \mid D\, \varphi_k(x \mid \alpha^{(m)}, \alpha^{(v)})/D\alpha_j\rangle , \tag{19}$$

$$\Delta\alpha_j = \alpha_j^{(v)} - \alpha_j^{(m)} , \tag{20}$$

$$m_i(\mathcal{E}_k^{(v)}, \alpha^{(v)}) = \delta_i , \tag{21}$$

we obtain

$$\sum_{j=1}^{n} A_{ij} \Delta\alpha_j = \delta_i . \tag{22}$$

Eq. (22) is a set of linear equations for the determination of the $\Delta\alpha_j$. Evidently the exact values of the A_{ij}'s and the δ_i's are not known (this would be equivalent to exactly solving (13)) but we can still draw useful conclusions from (22). First we discuss some qualitative consequences of (22) which are useful in choosing "good" weight functions and then we turn to more quantitative post mortem error estimates.

Loosely speaking: (a) the smaller the $|\delta_i|$'s and (b) the larger $|\mathrm{Det}(A_{ij})|$ the smaller the $|\Delta\alpha_j|$'s.

(a) If the integrals $\langle w_i(x) \mid w_j(x)\rangle$ are finite (this will be assumed in the following) we can – similarly to (11) – assume without loss of generality that the weight functions form an orthonormalized set[1].

Regarding the weight functions as the first $n+1$ functions of an orthonormalized complete set and expanding $(H - \mathcal{E}_k^{(v)})\, \varphi_k(x, \alpha^{(v)})$ in terms of this set we obtain

$$|\delta|^2_{\text{average}} = \frac{1}{n} \sum_{i=1}^{n} |\delta_i|^2 \leqq \frac{1}{n} \langle \varphi_k(x, \alpha^{(v)}) \mid (H - \mathcal{E}_k^{(v)})^2 \mid \varphi_k(x, \alpha^{(v)})\rangle . \tag{23}$$

A qualitative consequence of (23) is that any improvement of the wave function that reduces the integral on the right hand side of (23), and in particular such improvements that are due to an increase in the number of variational parameters reduce the upper limit for the average of the $|\delta_i|^2$'s. This result is obviously very satisfactory.

(b) If we are interested in estimating the order of magnitude of the $|\Delta\alpha_j|$'s we may make use of some approximation to the A_{ij}'s, say,

$$A_{ij} \approx \langle w_i(x) \mid H - \mathcal{E}_k^{(m)} \mid \partial\, \varphi_k(x, \alpha)/\partial\alpha_j\rangle_{\alpha = \alpha^{(m)}} . \tag{24}$$

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[1] The norm of the weight functions does not influence the values of the $\Delta\alpha_j$'s.

It is not easy to give an absolute limit for $|\mathrm{Det}(A_{ij})|$ above which it is "large enough". The value of $|\mathrm{Det}(A_{ij})|$ may be useful, however, in comparing different sets of calculations. Calculating in series using similar weight and wave functions it seems possible to obtain empirical lower limits for $|\mathrm{Det}(A_{ij})|$. In this sense the value of $|\mathrm{Det}(A_{ij})|$ appears to be the most important criterion for accepting or rejecting a set of weight functions.

(c) Let us assume that the weight functions satisfy the orthogonality relations (11) and the usual symmetry, normalizability, continuity and differentiability conditions that must be satisfied by a variational wave function. In this case $\varphi_k(x, \alpha^{(m)})$ has the important property (Hirschfelder [3]) that it can not be improved within the framework of the method of energy variation by adding to it any linear combination of the form $\sum_{i=1}^{n} \beta_i w_i(x)$. Obviously if we want to obtain a wave function which is a good approximation to $\psi_k(x)$ in some domain D of the configurational space, the weight functions must be such that $\sum_{i=1}^{n} \beta_i w_i(x)$ is a highly flexible function in the domain D.

We come now to the problem of post mortem error estimates.

The δ_i's are the overlap integrals between the i'th weight function and the function $(H - \mathscr{E}_k^{(v)})\, \varphi_k(x, \alpha^{(v)})$. $(H - \mathscr{E}_k^{(v)})\, \varphi_k(x, \alpha^{(v)})$ depends on the error in $\varphi_k(x, \alpha^{(v)})$ which we do not know when we construct the weight functions. Both $(H - {}_k^{(v)}) \cdot \varphi_k(x, \alpha^{(v)})$ and the $w_i(x)$'s are, in general, very complicated functions of the coordinates changing their sign at many hypersurfaces of the configurational space. Consequently it has a small probability that δ_i's belonging to different weight functions are approximately equal both in their magnitude and in their sign. In this case, however, it has a small probability that the $\Delta\alpha_i$'s obtained from calculations carried out with different sets of weight functions will, accidentally, be approximately equal both in their magnitude and in their sign. Thus if we calculate the α_i's with two or more different sets of weight functions, it is probable that the differences between the α_i's obtained in the different calculations will be of the same order of magnitude as the $\Delta\alpha_i$'s. The more complicated systems we investigate and the more sets of weight functions we use the higher the probability of obtaining in this way reliable estimates of the $|\Delta\alpha_i|$'s.

Summarizing: The changes of the variational parameter caused by such changes of the weight functions which do not affect the order of magnitude of $|\mathrm{Det}(A_{ij})|$ appear to provide a practical estimate of the order of magnitude of the $|\Delta\alpha_i|$'s.

The calculation of the integrals $m_i(\mathscr{E}_k^{(m)}, \alpha^{(m)})$ with many different normalized $w_i(x)$'s may even provide information about the norm of

$$\langle \varphi_k(x, \alpha^{(m)}) \,|\, (H - \mathscr{E}_k)^2 \,|\, \varphi_k(x, \alpha^{(m)}) \rangle$$

and consequently about the absolute error in $\varphi_k(x, \alpha^{(m)})$. Somewhat oversimplified the problem is to obtain an estimate of the norm of a vector by calculating its scalar products with many random vectors of unit length and estimating the upper limit of the scalar products from their statistical behaviour. This problem is being investigated and will be discussed in a later paper of the series. We only note that even more interesting seems the application of such methods to the estimate (27).

There exists another error estimate which is closely connected with the method of moments. Let us define the error in $\varphi_k(x, \alpha)$ by

$$\eta_k(x, \alpha) = (H - E_k)^{+0} \varphi_k(x, \alpha) \tag{25}$$

and let us consider the integral

$$\langle w(x) | H - E_k | \varphi_k(x, \alpha) \rangle \tag{26}$$

where $w(x)$ is any normalizable function satisfying the same conditions as a variational wave function. Applying the Schwarz inequality to (26) and taking into account (25) we obtain

$$\langle \eta_k(x, \alpha) | \eta_k(x, \alpha) \rangle \geqq \frac{|\langle w(x) | H - E_k | \varphi_k(x, \alpha) \rangle|^2}{\langle w(x) | (H - E_k)^2 | w(x) \rangle} . \tag{27}$$

Thus (27) gives a lower bound for the norm of the error in $\varphi_k(x, \alpha)$. In order to obtain an estimate of the order of magnitude of the error in $\varphi_k(x, \alpha)$ we may introduce some variational parameters into $w(x)$ and maximalize the right hand side of (27). If $\alpha^{(m)}$ is determined by the method of moments and the orthogonality relations (11) are satisfied the wave function $\varphi_k(x, \alpha^{(m)})$ has the property that the error estimate (27) gives the value zero for any $w(x)$ of the form

$$w(x) = \sum_{i=1}^{n} \beta_i w_i(x) . \tag{28}$$

Finally we observe that if $w_0(x)$ is an approximation to $\psi_k(x)$, the value $\mathscr{E}_k^{(m)}$ defined in Eq. (22) is a reasonable approximation to E_k (cf. [11]). Let us namely denote the error in $w_0(x)$ by $\omega_0(x)$

$$\omega_0(x) = (H - E_k)^{+0} w_0(x) \tag{29}$$

and let us consider

$$\mathscr{E}_k^{(m)} - E_k = \frac{\langle w_0(x) | H - E_k | \varphi_k(x, \alpha^{(m)}) \rangle}{\langle w_0(x) | \varphi_k(x, \alpha^{(m)}) \rangle} . \tag{30}$$

Taking into account (25) we obtain

$$\mathscr{E}_k^{(m)} - E_k = \frac{\langle \omega_0(x) | H - E_k | \eta_k(x, \alpha^{(m)}) \rangle}{\langle w_0(x) | \varphi_k(x, \alpha^{(m)}) \rangle} . \tag{31}$$

As both $w_0(x)$ and $\varphi_k(x, \alpha^{(m)})$ are approximations to $\psi_k(x)$ the order of magnitude of the denominator of (31) is 1. On the other hand the numerator contains the small factors $\omega_0(x)$ and $\eta_k(x, \alpha^{(m)})$. It is well known that the good energy values obtained by the method of energy variation are due to a similar effect. In the case of the ground state there is, however, an additional effect which may significantly reduce $|\mathscr{E}_k^{(m)} - E_k|$ as compared with the value obtained by the method of energy variation. Namely in the case of the method of energy variation (*i.e.* in the case $w_0(x) = \varphi_0(x, \alpha^{(m)})$) the numerator of (31) can be written as

$$\langle (H - E_0)^{1/2} \eta_0(x, \alpha^{(m)}) | (H - E_0)^{1/2} \eta_0(x, \alpha^{(m)}) \rangle \tag{32}$$

while in the case of the method of moments we have

$$\langle (H - E_0)^{1/2} \omega_0(x) | (H - E_0)^{1/2} \eta_0(x, \alpha^{(m)}) \rangle . \tag{33}$$

In the later case there is a high probability that the positive and negative contributions to the integral compensate each other to a considerable extent.

The more complicated systems we are investigating the higher the probability of such a compensation.

In the case of the method of energy variation no such compensation can take place.

4. Some Types of Weight Functions

Let us start with a general remark. The method of energy variation determines the values of the variational parameters from the condition

$$\mathscr{E}_k^{(e)}(\alpha) = \langle \varphi_k(x, \alpha) | H | \varphi_k(x, \alpha) \rangle = \text{extremum}\,. \tag{34}$$

(34) and (9) lead to the same values of the parameters if the weight functions are chosen as

$$\begin{aligned} w_0(x) &= \varphi_k(x, \alpha)\,, \\ w_i(x) &= \partial\, \varphi_k(x, \alpha)/\partial \alpha_i \qquad (i = 1, 2, \ldots, n)\,. \end{aligned} \tag{35}$$

Consequently we can expect to obtain an approximation to the wave function determined by the method of energy variation if the weight functions satisfy

$$\begin{aligned} w_0(x) &\approx \varphi_k(x, \alpha)\,, \\ w_i(x) &\approx \partial\, \varphi_k(x, \alpha)/\partial \alpha_i \qquad (i = 1, 2, \ldots, n)\,. \end{aligned} \tag{36}$$

It appears very advantageous to construct such weight functions in the following way. We choose a weight function $w_0(x, \beta)$ which involves the parameters $\beta_1, \beta_2, \ldots, \beta_n$. The parameters β_i should be "similar" to the α_i's in the sense, that within a sufficiently large domain of the space of the α_i's to every point α there should correspond a point $\beta = \beta(\alpha)$ of the space of the β_i's such, that $w_0(x, \beta(\alpha))$ is an approximation to $\varphi_k(x, \alpha)$ [2].

In this case the weight functions

$$\begin{aligned} & w_0(x, \beta)\,, \\ w_i(x, \beta) &= \partial\, w_0(x, \beta)/\partial \beta_i \qquad (i = 1, 2, \ldots, n) \end{aligned} \tag{37}$$

or appropriate linear combinations of them generally automatically satisfy (36).

The wave functions (36) have a number of practical advantages. (a) They make the maximum use of the high amount of numerical experience obtained so far by applying the method of energy variation to molecular problems. (b) By (4) the weight functions (35) automatically satisfy the orthogonality relations (11). Con-

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[2] *E.g.* if $\varphi_k(x, \alpha)$ is a linear combination of some functions $p_i(x)$

$$\varphi_k(x, \alpha) = \sum_{i=1}^{n} p_i(x)\, \alpha_i$$

and if the functions $q_i(x)$ are approximations to the respective $p_i(x)$'s

$$q_i(x) \approx p_i(x)$$

then we can choose $w_0(x, \beta)$ in the form

$$w_0(x, \beta) = \sum_{i=1}^{n} q_i(x)\, \beta_i\,.$$

sequently (11) can easily be fulfilled also by weight functions of the type (36). (c) If both $\varphi_k(x, \alpha)$ and the $w_i(x, \beta)$'s belong to the same irreducible representation of the symmetry group of the molecular system the value of $\mathrm{Det}(A_{ij})$ will in most cases automatically be considerably different from zero. (d) As the order of the integration over x and the differentiation with respect to the β_i's is irrelevant, it is often sufficient to calculate the integrals $\langle w_0(x, \beta)|H|\varphi_k(x, \alpha)\rangle$ and $\langle w_0(x, \beta)|\varphi_k(x, \alpha)\rangle$ the others being obtained by differentiation with respect to the β_i's [3].

Finally we shall give two examples of how can the freedom in the choice of the weight functions be utilized for reducing difficulties of integration (cf. also [11]).

(a) Let us assume that we have a variational wave function $\Phi_k(x, \alpha)$ which is made up of one-electron spin orbitals. If we can not calculate the integrals $\langle \Phi_k(x, \alpha)|H|\Phi_k(x, \alpha)\rangle$ we can attempt to expand the one-electron spin-orbitals in the bras in terms of some simpler functions and calculate the integrals simplified in this way. This means that we solve the problem by the method of moments. In many cases it is necessary to expand the one-electron spin-orbitals in both the bras and the kets. Even in this case we can save much of the accuracy if we use more elaborate expansions in the kets than in the bras. An example for this possibility may be the case in which $\Phi_k(x, \alpha)$ is made up of Slater functions and we expand them both in the bras as in the kets in terms of Boys functions[4], using, however, more terms in the kets than in the bras. In this case the number of integrals can significantly be reduced, and as the results of the next paper of the series indicate, the accuracy of the results is almost unaffected by this simplification.

(b) Let us assume that the wave function $\varphi_k(x, \alpha)$ is made up of spin-geminals which involve terms explicitly depending on the distance of the electrons. In this case the method of energy variation leads to integrals in which all the coordinates of the electrons are coupled inseparably. If, however, the weight functions are made up of one-electron spin-orbitals the most complicated integrals involve the coordinates of 4 electrons. It appears unnecessary to stress the possible gain on computer time. We only want to call attention to some important practical consequences.

The decrease in the number of the coordinates involved in the integrals suggests that on high-speed computers these may be treated by numerical methods independent of the details of the form of the geminals.

Let us denote the geminals comprising $\varphi_k(x, \alpha)$ by $u_i(\boldsymbol{r}, \boldsymbol{r}')$ and the one-electron orbitals comprising $w_0(x)$ by $v_i(\boldsymbol{r})$. By appropriate choice of the one-electron orbitals the "strong orthogonality relations"

$$\int d\boldsymbol{r} \int d\boldsymbol{r}' v_i(\boldsymbol{r})\, v_j(\boldsymbol{r}')\, u_k(\boldsymbol{r}, \boldsymbol{r}') = \delta_{ik}\, \delta_{jk} \tag{38}$$

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[3] The numerical calculations presented in the next paper of this series are all based on weight functions of the form (37).

[4] Throughout the papers of the series we shall refer to the functions

$$N_{n,l,m} \exp(-cr)\, r^{n+l}\, Y_{l,m}(\vartheta, \varphi)$$

as Slater functions and to the functions

$$N_{n,l,m} \exp(-cr^2)\, r^{2n+l}\, Y_{l,m}(\vartheta, \varphi)$$

as Boys functions.

can be satisfied independent of the form of the geminals and the energy expression of the method of moments becomes very similar to that of the Hartree-Fock method (cf. Kapuy [12]). The details of this possibility will be discussed in a later paper of the series.

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