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Determination of Molecular Properties by the Method of Moments. III

M. G. HEGYI, M. MEZEI, and T. SZONDY

Hungarian United Chemical Works, Budapest, and Research Group for Theoretical Physics of the Hungarian Academy of Sciences, Budapest

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The wave functions of the water and the ammonia molecules have been determined for many nuclear configurations by both the method of moments and the method of energy variation. The accuracy of the results obtained by the two methods is similar although the method of moments requires considerably less integrational work. Some technical problems connected with the use of the method of moments are discussed.

Die Wellenfunktionen des Wasser- und Ammoniakmoleküls wurden für mehrere molekulare Konfigurationen nach der Momentenmethode und der Methode der Energievariation bestimmt. Die Genauigkeit beider Methoden ist ungefähr gleich, obwohl bei der Momentenmethode weniger Aufwand an Integration benötigt wird. Einige technische Probleme bei der Verwendung der Momentenmethode werden diskutiert.

Les fonctions d'onde de l'eau et de l'ammoniac ont été déterminées pour de nombreuses configurations nucléaires par la méthode des moments et la méthode variationnelle. Les précisions atteintes par les deux méthodes sont comparables quoique la méthode des moments nécessite un moindre effort sur le plan des intégrations. Discussion de certains problèmes techniques liés à l'emploi de la méthode des moments.

1. Introduction

In previous papers of this series [1][1] the possibility of applying the method of moments for the determination of wave functions of molecular systems has been considered. If the method of moments (or its generalized form, the method of least squares [2]) is used instead of the method of energy variation for the determination of wave functions of molecular systems (a) the difficulties of integration can be significantly reduced (b) bound-state and scattering problems can be treated by a common formalism (c) one has more freedom to take into account different parts of the configurational space with different weights and (d) it is possible to obtain some random-sampling type error estimates.

The main question is naturally: are these advantages of the method of moments not paied by loss of accuracy? One of the aims of this series of papers is to contribute to this problem both theoretically and by numerical calculations. The results obtained so far indicate, that if the parameters of some variational wave function are determined by both the method of moments and the method of energy variation, the difference between the two wave functions is in general small in comparison with the estimated absolute error in the wave functions and it appears accidental which method gives better results in a given case.

The present paper reports the results and analysis of calculations on the H_2O and the H_3N molecules.

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[1] The first and the second paper of the series will be referred to as I and II, respectively.

2. The Results

The wave functions of H_2O and H_3N have been determined in the closed-shell one-determinant Hartree-Fock approximation described in II. The calculations have been carried out for many nuclear configurations.

The simplest way of defining the basis wave and weight functions is to describe them in terms of a set of "starting basis functions". The actual starting basis functions have been the following[2,3]:

H_2O *molecule*

Serial number	Type	α	Center	The axis is directed towards
1	Slater 1*s*	7.700	O	
2	Slater 2*s*	2.275	O	
3–4	Slater 1*s*	1.000	H_a, H_b	
5–6	Slater 2*p*	2.275	O	H_a, H_b
7	Slater 2*p*	2.275	O	a direction vertical to the HOH-plane
8–9	Boys 1*s*	0.370	half way between O and H_a, H_b	

H_3N *molecule*

Serial number	Type	α	Center	The axis is directed towards
1	Slater 1*s*	6.700	N	
2	Slater 2*s*	1.950	N	
3–5	Slater 1*s*	1.000	H_a, H_b, H_c	
6–8	Slater 2*h*	1.950	N	H_a, H_b, H_c
9	Slater 2*p*	1.950	N	a direction vertical to the $H_aH_bH_c$-plane
10–12	Boys 1*s*	0.370	half-way between N and H_a, H_b, H_c	

The actual basis wave and weight functions have been obtained from the starting basis functions by expanding them in terms of a finite number of 1*s* Boys functions as described in II. For both molecules two different expansions

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[2] The H atoms of H_2O and H_3N are denoted by H_a, H_b and H_a, H_b, H_c, respectively.

[3] In accordance with II the following notation is applied (N symbolizes the normalization coefficient):

Slater *ns* function: $N_{ns}r^{n-1}\exp(-\alpha r)\, Y_{00}(\cos\vartheta)$,

Slater *np* function: $N_{np}r^{n-1}\exp(-\alpha r)\, Y_{10}(\cos\vartheta)$,

Boys *ns* function: $N_{nb}r^{2(n-1)}\exp(-\alpha r^2)\, Y_{00}(\cos\vartheta)$.

In addition the

Slater *nh* function: positive half-lobe of the Slater *np* function

has been used.

Table 1. *Number of* 1s *Boys functions making up the basis functions*

H_2O

Serial number	Lower approximation	Higher approximation
1	1	4
2	2	4
3–4	1	4
5–6	2	4
7	2	4
8–9	1	1

H_3N

Serial number	Lower approximation	Higher approximation
1	1	4
2	2	4
3–5	1	4
6–8	1	2
9	2	4
10–12	1	1

have been used which will be referred to as "lower" and "higher" approximations. The details are given in Table 1.

In the calculations specified as "method-of-moments" (MM) calculations, the basis weight and wave functions correspond to the lower and higher approximation, respectively. In the calculations specified as "method-of-energy-variation" (EV) calculations both the basis weight and wave functions correspond to the higher approximation.

The results are summarized in the Tables 2–5. The notation is explained in Figs. 1–2. All quantities are expressed in atomic units. The notation MM, EV and EXP refers to the results calculated by the method of moments, the method of energy variation and the experimental results, respectively.

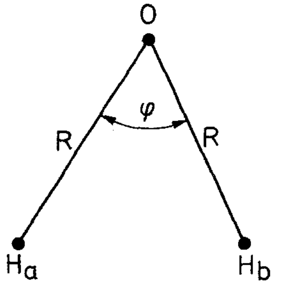

Fig. 1. The nuclei of the H_2O molecule

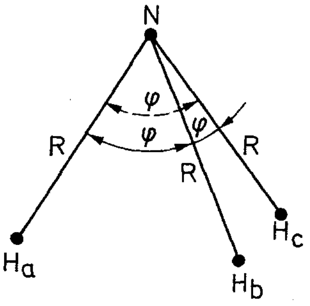

Fig. 2. The nuclei of the H_3N molecule

Table 2. *Energy values of the* H_2O *molecule*

φ \ R		1.60	1.80	1.90	2.00	2.20	2.40
80°	MM	−74.8923	−74.9550	−74.9623	−74.9602	−74.9368	
	EV	−74.9236	−75.0172	−75.0389	−75.0495	−75.0206	−75.0206
90°	MM	−74.9113	−74.9694	−74.9752	−74.9721	−74.9456	
	EV	−74.9438	−75.0305	−75.0499	−75.0584	−75.0522	−75.0256
100°	MM	−74.9195	−74.9738	−74.9790	−75.0571	−74.9469	
	EV	−74.9513	−75.0320	−75.0499	−75.0571	−75.0454	−75.1224
110°	MM	−74.9180	−74.9703	−74.9759	−74.9692	−74.9409	
	EV	−74.9484	−75.0244	−75.0407	−75.0472	−75.0386	−75.0127
120°	MM	−74.9091	−74.9591	−74.9626	−74.9569	−74.9282	
	EV	−74.9376	−75.0096	−75.0244	−75.0298	−75.0209	−74.9946
130°	MM	−74.8938	−74.9414	−74.9442	−74.9376	−74.9088	
	EV	−74.9211	−74.9886	−75.0018	−75.0066	−74.9973	−74.9720

Table 3. *Energy values of the* H_3N *molecule*

φ \ R		1.65	1.85	2.05	2.25	2.45	2.65
80°	MM	−55.0329	−55.2276	−55.3215	−55.3479	−55.3323	−55.2935
	EV	−55.1912	−55.3731	−55.4538	−55.4697	−55.4467	−55.4008
90°	MM	−55.0825	−55.2618	−55.3476	−55.3682	−55.3489	−55.3073
	EV	−55.2540	−55.4183	−55.4885	−55.4981	−55.4716	−55.4240
100°	MM	−55.1056	−55.2771	−55.3540	−55.3707	−55.3482	−55.3051
	EV	−55.2953	−55.4438	−55.5032	−55.5068	−55.4764	−55.4289
110°	MM	−55.0864	−55.2677	−55.3430	−55.3551	−55.3301	−55.2859
	EV	−55.3232	−55.4548	−55.5003	−55.4939	−55.4599	−55.3881
120°	MM	−54.6749	−55.2003	−55.3110	−55.3203	−55.2846	−55.2287
	EV	−55.3452	−55.4560	−55.4819	−55.4584	−55.4086	−55.3474

Table 4. *Equilibrium nuclear configuration* (R_0, φ_0) *and force constants* (F) *of the* H_2O *molecule* [3]

	R_0	φ_0	F_R	F_{R_φ}	F_φ
MM	1.90	101.4	7.96	0.32	1.24
EV	2.04	92.0	8.43	0.51	1.32
EXP	1.81	104.5	8.36	0.35	0.76

Table 5. *Equilibrium nuclear configuration* (R_0, φ_0) *and force constants* (F) *of the* H_3N *molecule* [3]

	R_0	φ_0	F_R	F_{R_φ}	F_φ
MM	2.22	96.7	7.20	0.34	1.00
EV	2.16	101.2	6.42	0.79	0.86
EXP	1.92	106.7	7.08	0.78	0.53

3. Discussion

In accordance with the estimates given in II, the machine times required for the calculation of the method-of-moments wave functions have been shorter by a factor of $1.4-1.8$ than those required for the calculation of the corresponding method-of-energy-variation wave functions (the factor mainly depending on the number of iterations needed to reach self consistence). However significant this gain, it is much smaller than that which can be expected if more elaborate wave functions are applied. (Loosely speaking, a more elaborate wave function can be more drastically simplified to give the corresponding weight function.) The decision to test the method of moments first on the lobe orbital approximation has been based on the recognition, that this approximation made possible a fairly gradual change from the well-tested method of energy variation to the *terra incognita* of the method of moments.

It can immediately be verified from the results presented in the previous section that the accuracy of the results obtained by the method of moments is neither significantly better nor significantly worse than that of the results obtained by the method of energy variation. As, further, the average overlap between the corresponding one-electron wave functions calculated by the two methods is ≈ 0.998 in the case of the water molecule and ≈ 0.990 in the case of the ammonia molecule, it seems justified to expect, that other physical properties which may reasonably be calculated from an approximate wave function of the given type will also not strongly differ.

At this point it may be interesting to investigate, how far it is justified to extrapolate our results to more elaborate and thus more accurate wave functions.

The method of moments determines the variational parameters in the variational wave function φ and the approximation $\mathcal{E}$ to the energy from the equations

$$\langle w_i | \boldsymbol{H} - \mathcal{E} | \varphi \rangle = 0 \qquad (i = 0, 1, \ldots, n), \tag{1}$$

where the w_i's denote the weight functions and n is the number of variational parameters α_i in φ.

We put the question in the following way. It is well known that the method of energy variation is a special case of the method of moments, namely, that case in which $w_0 = \varphi$ and $w_i = \partial\varphi / \partial\alpha_i$. In the usual method-of-moments calculations we replace these weight functions with mathematically more convenient approximations $w_0 \approx \varphi$ and $w_i \approx \partial\varphi / \partial\alpha_i$, which will be denoted by $w_0 + \delta w_0$, and $w_i + \delta w_i$. We are asking: what change $\varphi \rightarrow \varphi + \delta\varphi$ of the wave function results from the small changes $w_0 \rightarrow w_0 + \delta w_0$ and $w_i \rightarrow w_i + \delta w_i$.

It can be assumed without loss of generality (see Section 2 of I) that all the weight functions but one, say w_0, are orthogonal to φ. In this case the variational parameters can be determined from the equations with $i > 0$ while the equation with $i = 0$ serves for the determination of $\mathcal{E}$. Making use of the orthogonality relations

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

we may write in the last n equations of (1) the exact energy value E instead of $\mathcal{E}$ to give

$$\langle w_i | \boldsymbol{H} - E | \varphi \rangle = 0 \qquad (i = 1, 2, \ldots, n). \tag{3}$$

Let us assume now, that we change the weight functions to some $w_i + \delta w_i$ $(i = 0, 1, \ldots, n)$. This will change the variational wave function to some $\varphi + \delta\varphi$. We again may assume without loss of generality that the $w_i + \delta w_i$'s are orthogonal to $\varphi + \delta\varphi$ for $i > 0$, and we obtain

$$\begin{gathered}\langle w_i + \delta w_i | \boldsymbol{H} - E | \varphi + \delta\varphi \rangle = 0 \\ (i = 1, 2, \ldots, n; \langle w_i + \delta w_i | \varphi + \delta\varphi \rangle = 0)\,.\end{gathered} \tag{4}$$

Denoting the exact wave function by ψ and introducing the notation

$$\psi = \varphi + \Delta \tag{5}$$

we obtain from (2) and (5)

$$\langle w_i + \delta w_i | \boldsymbol{H} - E | \delta\varphi \rangle = \langle \delta w_i | \boldsymbol{H} - E | \Delta \rangle\,. \tag{6}$$

It can be verified, that the change in φ due to the change in the w_i's is proportional to Δ, the absolute error in φ. Loosely speaking, it can be expected that the smaller the absolute error in φ, the less φ is changed by small changes in the weight functions.

Thus, if our actual weight functions are mathematically more convenient approximations $w_i + \delta w_i$ to φ and the derivates $\partial\varphi/\partial\alpha_i$ then it can be expected, that the more accurate φ the smaller its change $\delta\varphi$ due to the changes $w_i \to w_i + \delta w_i$.

These considerations suggest that the conclusions drawn from our calculations may be valid also for calculations carried out with more elaborate wave functions.

The results presented in the next paper of the series are obtained by wave functions considerably more accurate than those used in this paper. The results obtained from the more accurate wave functions appear to support uniquely the conclusions of this section.

4. The Problem of Complex Eigenvalues

The method of moments, in contrast to the method of energy variation may lead to complex eigenvalues. Although in a majority of the calculations the eigenvalues remained *de facto* real[4] (in accordance with an interesting remark of Schwartz [4]) but in the case of the ammonia molecule complex eigenvalues appeared in every case even after having reached self-consistence. Consequently it seems necessary to consider this problem in some detail.

In the case of the ammonia molecule, two different types of complex eigenvalues could clearly be distinguished. The first type may be called "real eigenvalue with complex error". These eigenvalues always belonged to degenerate one-electron states, the absolute value of their imaginary part has been small in comparison with the real part (in most cases it has been smaller than 10^{-5} times the real part) and in most cases significantly decreased or vanished as self consistence has been approached. We consider these eigenvalues as "not dangerous" and if they are treated in the way described below they appear to be of a very limited interest.

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[4] In this section we understand by eigenvalue a Hartree-Fock eigenvalue, i.e. a diagonal element of the diagonal Hartree-Fock eigenvalue matrix. If the Hamiltonian matrix is real, the complex eigenvalues are always members of complex conjugate eigenvalue pairs.

It seems probable that in many cases these complex eigenvalues have been due to round-off errors.

The other type of eigenvalues may be called "inherently complex eigenvalues". They are characterized by a large imaginary component which tends to a well defined large value as self-consistence is approached.

In the case of the ammonia molecule the eigenvalues of the two highest (unoccupied) one-electron states have been inherently complex except for the nuclear configuration $R = 1.65$, $\varphi = 120°$.

If such an inherently complex eigenvalue belongs to an unoccupied state, the wave function, which is made up of the one-electron eigenfunctions of the occupied states may be reasonable. (The unoccupied orbitals of a Hartree-Fock approximation are, because of well-known reasons, in general very poor approximations to the corresponding physical orbitals. It seems to be of little importance in what actual way are they inaccurate.) If, however, an inherently complex eigenvalue belongs to an occupied state, the resulting wave function has obviously hardly any physical sense. Such a situation indicates that the actual set of basis wave and weight functions is inadequate for the problem.

In any case there is some indication that the appearence of inherently complex eigenvalues may unfavourably affect the accuracy and may be a sign that the actual basis sets are not very good for the problem. One sign of this is, that for the H_3N molecule in the immediate neighbourhood of $R = 1.65$ and $\varphi = 120°$ the approximation become sensitive to round-off errors.

Let us consider now the treatment of a "real eigenvalue with complex error". If $\boldsymbol{H}$ denotes the (real but non-symmetrical) Hamiltonian matrix, E the (complex) eigenvalue and A the corresponding (complex) eigenvector, the eigenvalue equation has the form

$$\boldsymbol{H}A = EA\,. \tag{7}$$

Writing out the real and imaginary part of (7) we obtain

$$\boldsymbol{H} \cdot \mathrm{Re}(A) = \mathrm{Re}(E) \cdot \mathrm{Re}(A) - \mathrm{Im}(E) \cdot \mathrm{Im}(A)\,, \tag{8}$$

$$\boldsymbol{H} \cdot \mathrm{Im}(A) = \mathrm{Re}(E) \cdot \mathrm{Im}(A) + \mathrm{Im}(E) \cdot \mathrm{Re}(A)\,. \tag{9}$$

It can immediately be verified that if $\mathrm{Im}(E) \to 0$ (8)–(9) becomes the eigenvalue equation of the twice-degenerate eigenvalue $\mathrm{Re}(E)$, the corresponding eigenvectors being $\mathrm{Re}(A)$ and $\mathrm{Im}(A)$.

Thus, if a pair of complex conjugate eigenvalues is considered as a degenerate real eigenvalue with complex error, the corresponding real eigenvectors are $\mathrm{Re}(A)$ and $\mathrm{Im}(A)$.

The program carrying out the calculations treated all the complex eigenvalues (also the "inherent" ones) in this way.

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Dr. Tamás Szondy
Hungarian United Chemical Works
Erzsébet királyné útja 1/c
Budapest, XIV, Hungary