Theoret. chim. Acta (Berl.) 9, 303—311 (1968)

Nonlinear Parameters in the Least-Squares Local Energy Method

I. σ-States of HeH^{++}

Donald K. Harriss* and Ronald K. Roubal**

Department of Chemistry, University of Minnesota, Duluth, Minnesota

Received September 23, 1967

The Least-Squares Local Energy Method is used to calculate energies and wavefunctions for the four lowest σ states of HeH^{++}. An alternative scheme for evaluation of the pertinent matrices is shown which, for exponential-power series wavefunctions, greatly reduces the time necessary for the sum-over-points. The numerical behavior of the variance with changes in the nonlinear parameters is shown for this molecule and an iterative procedure for minimization of variance with respect to nonlinear parameters is proposed.

Mit der Methode lokaler Energie werden Energien und Wellenfunktionen für die vier tiefsten σ Zustände von HeH^{++} berechnet. Dabei wird ein anderes Verfahren zur Berechnung der auftretenden Matrizen aufgezeigt, bei dem für Wellenfunktionen mit $e^{-\alpha r}$-Faktor die Rechenzeit stark verringert wird. Der Einfluß nicht-linearer Parameter auf die Rechnung wird diskutiert und ein iteratives Verfahren zu ihrer Optimalisierung vorgeschlagen.

La méthode des moindre carrés pour l'énergie locale est utilisée pour calculer les énergies et les fonctions d'onde pour les quatre plus bas états σ de HeH. Un autre schéma d'évaluation des matrices nécessaires est proposé; pour des fonctions d'onde séries exponentielles puissances ce schéma réduit considérablement le temps nécessaire à la sommation sur les points. Le comportement numérique de la variance selon les modifications des paramètres non linéaires est exposé pour cette molécule. Un procédé itératif pour la minimisation de la variance par rapport aux paramètres non linéaires est proposé.

Introduction

Due to its conceptual simplicity and the elimination of requirements for evaluation of complicated integrals, Frost's Least-Squares Local Energy Method and related problems [2, 6, 8] continue to be of considerable interest.

Serious doubts as to the extendibility of the Local Energy Method were raised by Gimarc and Frost in describing their results for the lithium atom [3e]. Some of the problems can be summarized as:

1. The excessive amount of computer time required for long wavefunctions and large numbers of points.

2. The treatment of different exponential parameters for different orbitals for three-electron and higher cases.

---

* Present address: The Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin. On leave from the University of Minnesota, Duluth.

** Present and permanent address: Department of Chemistry, Wisconsin State University, Superior, Wisconsin.

3. The choice of nonlinear parameters especially for excited states or for systems for which the experimental energies are not known.

The first of these problems is discussed in the next portion of this work and a procedure is presented which, for exponential-power series wavefunctions, greatly reduces the required computational time. This particular procedure is especially useful in formally considering the question of minimization of the variance with respect to nonlinear parameters and this is discussed in the last section. The HeH^{++} molecule-ion is used as an example and energies and wavefunctions for the four lowest sigma states are determined.

Alternate Computational Scheme

A short review of the Local Energy Method is useful at this point. The variance, V, is defined as the mean-square minus the square-mean local energy,

$$V = \overline{\varepsilon^2} - \bar{\varepsilon}^2 \tag{1}$$

with $\bar{\varepsilon}$ and $\overline{\varepsilon^2}$ defined as weighted averages over a set of points, p,

$$\bar{\varepsilon} = \sum_p g_p\, \varepsilon_p / \sum_p g_p \qquad \overline{\varepsilon^2} = \sum_p g_p\, \varepsilon^2{}_p / \sum_p g_p \tag{2}$$

where

$$\varepsilon_p = \mathscr{H}\, \psi(p)/\psi(p)\,. \tag{3}$$

If g_p is chosen as

$$g_p = w_p\, \psi^2(p) \tag{4}$$

we have

$$\begin{aligned} \bar{\varepsilon} &= \sum_p w_p\, \psi(p)\, \mathscr{H}\, \psi(p) / \sum_p w_p\, \psi^2(p) \\ \overline{\varepsilon^2} &= \sum_p w_p [\mathscr{H}\, \psi(p)]^2 / \sum_p w_p\, \psi^2(p)\,. \end{aligned} \tag{5}$$

For ψ chosen as a linear combination of basis functions, ϕ_i,

$$\psi = \sum_i \phi_i\, c_i\,, \tag{6}$$

requiring V to be a minimum with respect to the linear parameters, $\{c_i\}$, leads to the set of simultaneous equations

$$\sum_j [G_{ij} - 2\bar{\varepsilon}\, H_{ij} + (\bar{\varepsilon}^2 - V)\, S_{ij}]\, c_{ij} = 0 \tag{7}$$

where it has been convenient to define matrices **S**, **H**, and **G** as:

$$\begin{aligned} S_{ij} &= \sum_p w_p\, \phi_i(p)\, \phi_j(p) \\ H_{ij} &= \tfrac{1}{2} \sum_p w_p [\phi_i(p)\, \mathscr{H} \phi_j(p) + \phi_j(p)\, \mathscr{H}\, \phi_i(p)] \\ G_{ij} &= \sum_p w_p [\mathscr{H}\, \phi_i(p)]\, [\mathscr{H}\, \phi_j(p)]\,. \end{aligned} \tag{8}$$

The sequence of steps that have been used in compilation of the **S**, **H**, and **G** matrices can be outlined as:

(a) Choose a point, p, and calculate w_p.

(b) Evaluate $\Phi = \{\phi_i(p)\}$ and $H_\phi = \{\mathscr{H}\, \phi_i(p)\}$.

(c) Add the proper contribution to each matrix element in **S**, **H**, and **G**.

(d) Cycle from (a) through (c) for each point.

Calculations, to date, have involved only rotationless states with trial functions expressible as exponential-power series in either interparticle or mixed interelectronic-confocal elliptic coordinates. For these functions, equations have been given [3f, 4] for $\mathscr{H}\phi_i$ and these have been used in general or explicit form in the second step above. It has been shown [5] for functions of this type that, after multiplication by a suitable function, q, of the coordinates, $q\mathscr{H}\phi_i$ is expressible in the basis set $\{\phi_i\}$ as:

$$q\mathscr{H}\phi_i = \sum_j \phi_j\, h_{ji} \tag{9}$$

where the h_{ji} are determined by inspection.

Definition of

$$\begin{aligned} w'_p &= w_p/q^2 \\ \phi'_i(p) &= (w'_p)^{1/2}\, \phi_i(p) \\ q\phi_i &= \sum_j \phi_j\, s_{ji} \end{aligned} \tag{10}$$

and substitution of (9) and (10) into (8) leads to

$$\begin{aligned} S_{ij} &= \sum_{k,l} s_{ki}\, s_{lj} \sum_p \phi'_k(p)\, \phi'_l(p) \\ H_{ij} &= \tfrac{1}{2} \sum_{k,l} [h_{lj}\, s_{ki} + h_{ki}\, s_{lj}] \sum_p \phi'_k(p)\, \phi'_l(p) \\ G_{ij} &= \sum_{k,l} h_{ki}\, h_{lj} \sum_p \phi'_k(p)\, \phi'_l(p)\,. \end{aligned} \tag{11}$$

An alternate procedure for compilation of $\boldsymbol{S}$, $\boldsymbol{H}$, and $\boldsymbol{G}$ could then be:

(a) Choose point, p, and evaluate w'_p.

(b) Evaluate $\Phi' = \{\phi'_i(p)\}$. Φ' is larger than the Φ from the earlier procedure.

(c) Add the proper contributions to Φ'' where Φ'' is a vector containing the distinct elements of $\Phi'^T\,\Phi'$.

(d) Cycle from (a) through (c) for each point.

(e) Form $\boldsymbol{S}$, $\boldsymbol{H}$, and $\boldsymbol{G}$ using (11).

In this procedure then, only the wavefunction is summed over the points and the matrices are formed later. Eq. (11) may be quite complicated computationally but this is unimportant since they represent a one-time sum.

It is not obvious that the alternate procedure is computationally shorter since, in general, Φ'' can contain a larger number of elements than $\boldsymbol{S}$, $\boldsymbol{H}$, and $\boldsymbol{G}$. The most favorable case is one in which the wavefunction is an exponential-power series, includes all terms up to a given order, and the exponential function is first order in the coordinates. For the case of a vibrating one-electron heteronuclear diatomic, the relative calculational times are; about equal for the sum over points with a four-term function, one-third as great with a twenty-term function, and one-fifth as great with a thirty-five term function.

Sigma States of HeH^{++}

Wave Function

A reasonable trial function for this molecule should recognize its heteronuclear nature and the exponential portion should be relatable to the product of the atomic functions as (using notation similar to that of MATCHA, LYON and HIRSCHFELDER [7])

$$\psi_0 = \exp\,(-\,\alpha\, Z_A\, r_A - \beta\, Z_B\, r_B) \tag{12}$$

where Z_A is the charge on the He nucleus, Z_B the charge on the H nucleus, and α and β are variable parameters. Or, in terms of confocal elliptic coordinates

$$\mu = (r_A + r_B)/R \,, \qquad \nu = (r_A - r_B)/R$$

we have

$$\psi_0 = \exp\,(-\,a\mu - b\nu) \tag{13}$$

where R is the internuclear distance and

$$a = R(\alpha\, Z_A + \beta\, Z_B)/2 \,, \qquad b = R(\alpha\, Z_A - \beta\, Z_B)/2 \,.$$

(Note that $a \geqq b$ if β is to remain positive.)

The complete trial function is chosen as

$$\psi = \sum_i \phi_i\, c_i \tag{14}$$

with

$$\phi_i = \phi(m, n) = \mu^m\, \nu^n \exp\,(-a\mu - b_\nu) \,. \tag{15}$$

A ten-term function was used in this work and it included all terms with total order less than or equal to three.

Points

Gauss-Laguerre [9] points, x_i, and weights, H_μ, were used for the μ coordinate

$$\mu_i = x_{i/2a} + 1 \,. \tag{16}$$

For the ν coordinate, Gauss-Legendre points are appropriate for $b = 0$ while for $b \neq 0$, orthogonal polynomials, their zeros and Gaussian weights were determined for integrals of the form

$$\int\limits_{-1}^{+1} e^{-2by}\, f(y)\, dy = \sum_{j=1} H_j\, f(y_j) \,. \tag{17}$$

Series Expansions

The appropriate expansion and weight factors would be:

$$\begin{aligned} q &= (\mu^2 - \nu^2) \\ w_p &= (R^3/8)\,(\mu^2 - \nu^2)\, H_\mu\, H_\nu \\ w'_p &= R^3\, H_\mu\, H_\nu/8(\mu^2 - \nu^2) \end{aligned} \tag{18}$$

H_μ, H_ν = Gaussian weights for μ and ν.

If we first define

$$\chi(k + n, l + n) = \sum_p w'_p\, \phi(k, l)\, \phi(m, n) \tag{19}$$

and

$$\begin{aligned} p &= k + m \qquad & r &= k - m \\ s &= l + n \qquad & t &= l - n \end{aligned}$$

the expressions for S_{ij} and H_{ij} become, for $b = 0$,

$$\begin{aligned} S_{kl,m,n} &= \chi(p + 4, s) - 2\chi(p + 2, s + 2) + \chi(p, s + 4) \\ -\,2R^2\, H_{kl,m,n} &= 4a^2\, \chi(p + 4, s) - 4\chi\,(pa + 2a - 3R)\, \chi(p + 3, s) \\ &\quad - 4a^2\, \chi(p + 2, s + 2) - 4R\, \chi(p + 2, s + 1) + (p^2 + r^2 \end{aligned} \tag{20}$$

$$\begin{aligned}
&- s^2 - t^2 + 2p - 2s - 4a^2)\,\chi(p + 2, s) \\
&+ (s^2 + t^2 - 2s)\,\chi(p + 2, s - 2) + 4(pa + 2a - 3R)\,\chi(p + 1, s + 2) \\
&+ 4pa\,\chi(p + 1, s) + 4R\,\chi(p, s + 3) - (p^2 + r^2 + s^2 + t^2 \\
&- 2p - 2s)\,\chi(p, s) \qquad\qquad (20) \\
&- (p^2 + r^2 - s^2 - t^2 + 2p - 2s - 4a^2)\,\chi(p, s + 2) \\
&- 4pa\,\chi(p - 1, s + 2) + (p^2 + r^2 - 2p)\,\chi(p - 2, s + 2)\,.
\end{aligned}$$

The equation for G_{ij} will not be shown to save space; it is a 22-term function involving terms of up to fourth order in a.

Numerical Results

For the internuclear distance fixed at 2.0 bohrs, Fig. 1 shows the behavior of the variance with respect to the exponential parameter a when b is fixed at zero. In each case, V is minimized with respect to the coefficients in the wavefunction. V_1 refers to the variance associated with the lowest energy, V_2, the variance associated with the next lowest energy, etc. The curves shown refer to 25-point (5 in μ and 5 in $_{\nu}$) ten-term calculations. These calculations were repeated with 49 points (7 in μ and 7 in $_{\nu}$) and essentially the same curves were found only shifted to higher variances. The 25-point, ten-term calculations should be approximately equivalent to Frost's 12-point nine-term calculation [3c] on H_2^+. The 25 points should be sufficient to exactly evaluate the overlap integrals.

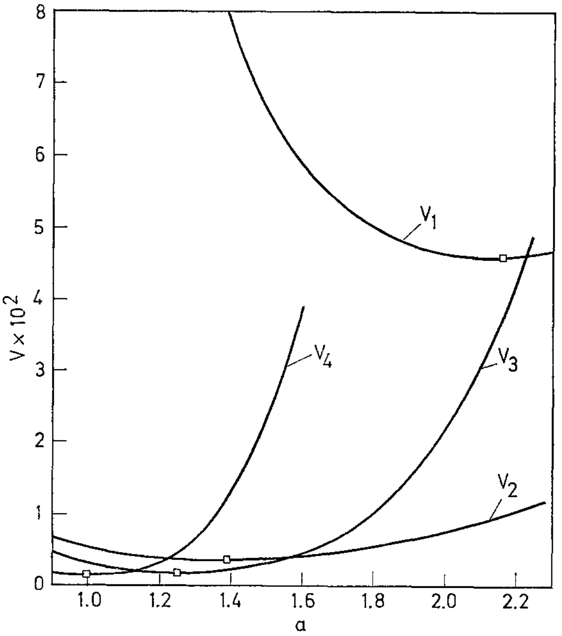

Fig. 1. Variance plotted versus the single exponential parameter (a) for the four lowest sigma states of HeH^{++}. Values refer to 25-point, 10-term calculations for $R = 2.0$ bohrs. Minima calculated from quadratic fits are marked with squares

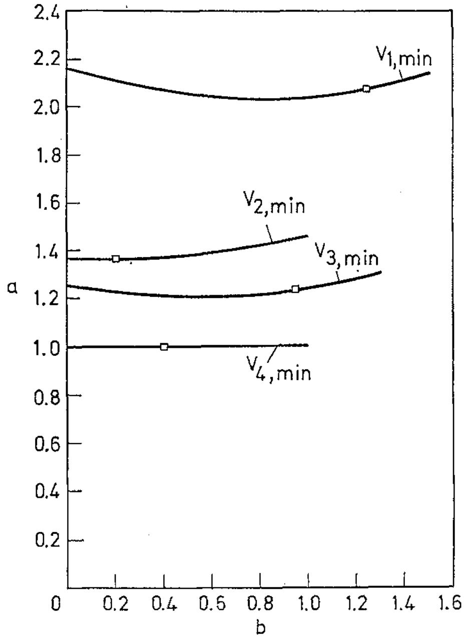

Fig. 2. Values of a corresponding to minima in the variance for fixed b. Absolute minima are marked with squares. Values refer to 25-point, 10-term calculations for $R = 2.0$ bohrs

Of course, when both a and b are allowed to vary ($a \geqq b$) surfaces are generated versus variance. Each surface was found to exhibit a single minimum. The surfaces are not shown here but, in Fig. 2, the minima in V for each value of b are shown (over the range investigated) and the absolute minima are marked with squares.

Optimum values of the exponential parameters and the energies and variances calculated for these values are presented in Tab. 1 for each of the four lowest

Table 1. *Optimum parameters, energies (in hartrees) and variances for* HeH^{++}. *All calculations refer to 25-point, 10-term functions with $R = 2.0$ bohrs*

a	b	$1s\sigma$		$2p\sigma$		$2s\sigma$		$3d\sigma$	
		$-\varepsilon$	$V \times 10^3$	$-\varepsilon$	$V \times 10^3$	$-\varepsilon$	$V \times 10^3$	$-\varepsilon$	$V \times 10^3$
2.163	0	2.50661	46.08	1.34116	9.333	0.720946	37.30		
1.368	0	2.49833	84.58	1.34452	3.383	0.783515	1.822	0.502743	10.40
1.248	0	2.49191	111.8	1.34422	3.556	0.784859	1.668	0.532680	4.334
1.000	0	2.46142	226.7	1.34369	4.977	0.784796	2.402	0.537917	1.527
2.08	1.25	2.51204	0.9225	1.31936	51.36	0.763533	15.18		
1.38	0.25	2.50532	37.54	1.34502	0.3620	0.785777	0.6687	0.509907	13.24
1.25	1.00	2.51056	6.349	1.34000	23.68	0.787064	0.01637	0.527044	9.864
1.00	0.40	2.48445	111.2	1.34408	2.260	0.786603	0.03777	0.535764	0.3408
Exact[a]		2.512195		1.345185		0.78709		0.571255	

[a] See Ref. [1].

Table 2. *Single-exponential parameters for* HeH^{++} *for 10-term functions, 25-point calculations and* $R = 2.0$ *bohrs*

State	Bates and Carson[a]	This work	
		25 points	49 points
$1s\sigma$	2.24151	2.163	2.240
$2p\sigma$	1.64024	1.368	1.389
$2s\sigma$	1.25466	1.248	1.243
$3d\sigma$	1.06888	1.000	0.973

[a] See Ref. [1], these values $= (-2E)^{-1/2}$.

sigma states. Also shown in this table are the optimum single-exponential ($b = 0$) values. These values refer to 25-point calculations. The results for the 3 $d\sigma$ state are poor but this is not surprising with a wavefunction containing no terms higher than third order.

Worth noting is the approximate agreement between the optimum single-exponential values for a and those determined by the exact calculations of Bates and Carson [1]. In Tab. 2, the 25- and 49-point optimized values for a are given along with the values of Bates and Carson [1]. Reasonable agreement is also found with the corresponding values for a and b determined by Matcha, Lyon and Hirschfelder in their perturbation treatment of the ground state [7]. For the ground state at R equal to 2.0 bohrs, they found $a = 2.10$ and $b = 1.82$ versus $a = 2.08$ and $b = 1.25$ determined in this work.

General Treatment of Nonlinear Parameters

Most earlier calculations by the Local Energy Method have used exponential parameters either chosen to facilitate comparison with other methods of calculation or obtained from asymptotic solutions using known energies. In the above work, surfaces were investigated to determine the optimum values of the parameters. Gimarc and Frost have considered the minimization of variance with respect to exponential parameters in calculations involving the helium [3a] and lithium [3e] atoms. In both cases they were treating the lowest state of the particular symmetry involved and in both cases either considered the single exponential case or reduced the problem to one of a single variable through use of asymptotic solutions. (In these calculations, a could have been obtained from the asymptotic solution.) Gimarc and Frost found the energy and variance to be rather insensitive to changes in the exponential parameter for wavefunctions of ten terms or more which is reasonably true for HeH^{++} when dealing with the lower two states and a single exponential parameter. For the higher states greater changes in the variance were found and for some parameter choices we were unable to obtain convergence for the 3 $d\sigma$ state. When two parameters are involved, drastic changes in the variance are observed even for the ground state. In their calculations, the optimum exponential parameter was found to not change smoothly as more terms were added to the wavefunction. This problem was not investigated as we felt that the optimum parameters for a given function were more important at this point.

Clearly, a systematic procedure is needed if several nonlinear parameters are to be used; this would be particularly important for excited states since the ground state seems to be less sensitive to the values of exponential parameters.

Requiring the variance to be a minimum for parameters other than the coefficients $\{c_i\}$,

$$\left(\frac{\partial V}{\partial \alpha}\right)_{\beta,\,\nu,\,\cdots,\,\delta,\,c_1,\,c_2,\,\cdots,\,c_n} = 0$$

leads to a set of simultaneous equations similar to those obtained for linear parameters:

$$\sum_{,ij}\left[\frac{\partial G_{ij}}{\partial \alpha} - 2\,\varepsilon\,\frac{\partial H_{ij}}{\partial \alpha} + (\varepsilon^2 - V)\,\frac{\partial S_{ij}}{\partial \alpha}\right] c_i\,c_j = 0\,. \tag{21}$$

The earlier discussed alternate computational formalism seems particularly suitable for computations involving this set of equations. It can normally be assumed that w_p, q, and the s_{ki} are not functions of the parameters so that

$$\begin{aligned}
\frac{\partial S_{ij}}{\partial \alpha} &= \sum_{k,l} s_{ki}\,s_{lj} \sum_{p} \frac{\partial\,\phi_k'\,\phi_l'}{\partial \alpha}\\
\frac{\partial H_{ij}}{\partial \alpha} &= \tfrac{1}{2}\sum_{k,l}\left[\left(s_{lj}\,\frac{\partial\,h_{kt}}{\partial \alpha} + s_{ki}\,\frac{\partial\,h_{lj}}{\partial \alpha}\right)\sum_{p}\phi_k'\,\phi_l'\right.\\
&\qquad\left. + (s_{lj}\,h_{ki} + h_{lj}\,s_{ki})\,\frac{\partial\,\phi_k'\phi_l'}{\partial \alpha}\right]\\
\frac{\partial G_{ij}}{\partial \alpha} &= \sum_{k,l}\left(\frac{\partial\,h_{ki}\,h_{lj}}{\partial \alpha}\sum_{p}\phi_k'\,\phi_l' + h_{ki}\,h_{lj}\sum_{p}\frac{\partial\,\phi_k'\,\phi_l'}{\partial \alpha}\right).
\end{aligned} \tag{22}$$

In the above expressions for the derivatives, the sums over points are either the same as or are related to those for the variation of linear parameters. In particular, if the nonlinear parameters are exponential and the exponential variables are to first order, the order of functions summed over increases one degree in total order. That is, using the HeH^{++} case with $b = 0$,

$$\begin{aligned}
\frac{\partial S_{kl,mn}}{\partial \alpha} &= -\,p[\chi(p+5,s) - 2\chi(p+3,s+2) + \chi(p+1,s+4)]\\
R^2\,\frac{\partial H_{kl,mn}}{\partial \alpha} &= 4a^2\,\chi(p+5,s) + 4\,(3R - pa - 3a)\,\chi(p+4,s)\\
&\quad - 4a^2\,\chi(p+3,s+2) - 4R\,\chi(p+3,s+1)\\
&\quad + (p^2 + r^2 - s^2 - t^2 + 4p - 4s - 4a^2 + 4)\,\chi(p+3,s)\\
&\quad + (s^2 + t^2 - 2s)\,\chi(p+3,s-2) - [4\,(3R - pa - 3a)\\
&\qquad \chi(p+2,s+2)] + 4a(p+1)\,\chi(p+2,s) + 4R\,\chi(p+1,s+3)\\
&\quad - [(p^2 + r^2 - s^2 - t^2 + 4p - 4s - 4a^2 + 4)\\
&\qquad \chi(p+1,s+2)] - (p^2 + r^2 + s^2 + t^2 - 2s)\,\chi(p+1,s+2)\\
&\quad - (p^2 + r^2 + s^2 + t^2 - 2s)\,\chi(p+1,s+2) - [4a(p+1)\\
&\qquad \chi(p,s+2)] + (p^2 + r^2)\,\chi(p-1,s+2)\,.
\end{aligned} \tag{23}$$

For exponential parameters and variables to the first order, these Eq. (22) will, in general, lead to mixed quartic equations in the parameters.

A suggested iterative procedure that is undergoing numerical investigation is:

(a) Choose initial values for the nonlinear parameters α, β, - - -.

(b) Form the matrices $\boldsymbol{S}$, $\boldsymbol{H}$, $\boldsymbol{G}$.

(c) Solve for ε, V, and $\{c_i\}$ by minimizing V.

(d) Use these ε, V, and $\{c_i\}$ in Eq. (21) to determine new α', β', - - -.

(e) Cycle from (b) to (d) until convergence is obtained.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Partial support was also provided by the Graduate School of the University of Minnesota. In addition to the above I wish to acknowledge use of the computing facilities at the University of Minnesota, Duluth, and to thank Miss Rosemarie Russo for her assistance.

Literatur

1. Bates, D. R., and T. R. Carson: Proc. Roy. Soc. (London) **A234**, 207 (1956).
2. Conroy, H.: J. chem. Physics **41**, 1336 (1964).
3. (a) Frost, A. A.: J. chem. Physics **10**, 240 (1942);
   (b) —, R. E. Kellogg, and E. C. Curtis: Rev. mod. Physics **32**, 313 (1960);
   (c) —, —, B. M. Gimarc, and J. D. Scargle: J. chem. Physics **35**, 827 (1961);
   (d) Gimarc, B. M., and A. A. Frost: Theoret. chim. Acta (Berl.) **1**, 87 (1962);
   (e) — — J. chem. Physics **39**, 1698 (1963);
   (f) Harriss, D. K., and A. A. Frost: J. chem. Physics **40**, 204 (1964).
4. Frost, A. A.: Theoret. chim. Acta (Berl.) **1**, 36 (1962).
5. — J. chem. Physics **41**, 478 (1964).
6. Goodisman, J.: J. chem. Physics **41**, 3889 (1964).
7. Matcha, R. L., W. F. Lyon, and J. O. Hirschfelder: J. chem. Physics **43**, 1101 (1965).
8. Stanton, R. E., and R. L. Taylor: J. chem. Physics **45**, 565 (1966).
9. Stroud, A. H., and D. Secrest: Gaussian Quadrature Formulas. Englewood Cliffs, N. J.: Prentice-Hall Inc. 1966.

Dr. Donald K. Harriss
The Theoretical Chemistry Institute
University of Wisconsin
Madison, Wisconsin, USA