

Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen). Bis zum 10. des Monats bei der Redaktion eingehende Manuskripte können günstigenfalls am 15. des folgenden Monats veröffentlicht werden.

On-line computer determination of rate constants from stopped flow data by a nonlinear least square method*

Andreas D. Zuberbühler and Thomas A. Kaden **

Institut für Anorganische Chemie der Universität Basel

Abstract

The on-line data acquisition from a Durrum D 110 stopped flow spectrophotometer as well as the calculation of rate constants by a nonlinear least square program written for a Hewlett-Packard HP 9820 (or HP 9821) desk top computer is described. Two examples, a first order process and a two step consecutive reaction are used to illustrate the capability of the system. Beside obtaining more precise results and estimates of the corresponding uncertainties there is also a considerable saving of time.

Several methods for on-line data collection in studies of fast chemical reactions have been described in the literature [1-4]. These obviate the tedious conversion of the information mostly displayed on an oscilloscope to the value of rate constants. In general a transient recorder is used to capture the analog signal, to convert it into the digital form, and to store it. The data can then be transferred through an interface to a paper tape puncher or directly to a computer. The setups

described in the literature generally have one or more disadvantages. In some cases the interface is not commercially available, in others the computer is not on-line but must be fed through paper tape, in others again the computer used is an expensive one and finally in most cases the mathematical treatment is not optimal.

We present here a cheap combination of commercially available parts, namely an 8-bit transient recorder (Datalab DL 901, about \$ 2000.-) and an interface (Hewlett-Packard HP 11203 A, about \$ 300.-) [5] with a Hewlett-Packard HP 9820 (or HP 9821) desk computer for which a nonlinear least square program especially designed for the calculation of rate constants has been written.

Even today, rate constants are mostly derived from experimental measurements by linearizing the equation which describes the time dependency of the reactant concentrations. For example, a first order reaction is described by the logarithmic equation (1) which is a

$$\ln c = c_0 - kt \quad (1)$$

* Received September 22, 1977

** Prof. Dr. Th. A. Kaden, Institut für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel

linear function in t with slope k . There are, however, several points to be considered: 1) It is often difficult to obtain an accurate end value, which is needed in order to apply equation (1). 2) The concentration at $t = 0$ is mostly taken from one measurement of the concentration-time-curve, thus giving to it an extreme and undue weight. 3) Generally for the calculation of the best straight line the same statistical weight is taken for all points, although c and not $\ln c$ should be given equal weights.

Having access to a digital computer on-line with a stopped flow instrument it is easy to take these points into account, without any appreciable loss of time.

Method of computation and computer program

The general equation for a first order reaction, for which a physical property y proportional to the concentration is measured, is given by (2) where y_0 and y_∞ are the initial and final values.

$$f(t) = y_\infty + (y_0 - y_\infty) e^{-kt} \quad (2)$$

The "best" fit is obtained by minimizing the square sum of errors (3) for all i measurements.

$$SQ = \sum_i [y_i - f(t)]^2 \rightarrow \text{Min} \quad (3)$$

The nonlinear problem can be solved by the *Newton-Gauss* method [6]. First the function $f(t)$ is expanded into a *Taylor* series, which is truncated after its first term (4). y_0 , y_∞ and k are considered as parameters. In the case of a first order reaction

$$f(t) = f_0 + \frac{\partial f_0}{\partial y_0} \Delta y_0 + \frac{\partial f_0}{\partial y_\infty} \Delta y_\infty + \frac{\partial f_0}{\partial k} \Delta k \quad (4)$$

the partial derivatives can be written in their analytical forms (5).

$$\frac{\partial f_0}{\partial y_0} = e^{-kt}, \quad \frac{\partial f_0}{\partial y_\infty} = 1 - e^{-kt}, \quad \frac{\partial f_0}{\partial k} = -t(y_0 - y_\infty) e^{-kt} \quad (5)$$

For other types of reaction, however, it could be more convenient to obtain the derivatives by numerical methods.

$$\frac{\partial SQ}{\partial y_0} = \frac{\partial SQ}{\partial y_\infty} = \frac{\partial SQ}{\partial k} = 0 \quad (6)$$

For a minimum (6) holds which results in the three equations (7), where $p_1 = y_0$, $p_2 = y_\infty$ and $p_3 = k$.

$$\frac{\partial SQ}{\partial p_j} = \sum_i \left[y_i - \left(f_0 + \frac{\partial f_0}{\partial p_1} \Delta p_1 + \frac{\partial f_0}{\partial p_2} \Delta p_2 + \frac{\partial f_0}{\partial p_3} \Delta p_3 \right) \frac{\partial f_0}{\partial p_j} \right] = 0 \quad (7)$$

with $j = 1, 2, 3$

(7) represents a set of three linear equations in Δp_j , which can be solved by one of the usual methods. The new values of the parameters can thus be calculated (8) and used for a new iteration, until the minimum of SQ is found.

$$p_{j, \text{new}} = p_{j, \text{old}} + \Delta p_j \quad (8)$$

In our system, the initial guess of the parameters is carried out by the program itself. The first measurement y_1 is taken as y_0 . Then from two experimental points at least one half-life time apart [7] k is calculated according to the formula of *Guggenheim* [8]. With y_0 and k the guessed value of y_∞ is determined from the last experimental point using (2).

Results and Discussion

Although the transient recorder used in combination with the stopped flow spectrophotometer is able to store 1024 experimental values only 32 equidistant points are used for the calculation. This is amply sufficient for first order reactions to reduce the standard error in k below the uncertainties introduced by the reproducibility of the experiments. The data transfer from the transient recorder to the computer takes about 30 seconds. The nonlinear fit is generally finished after 3 iterations, which require about 1 minute. A typical printout is shown in Fig. 1.

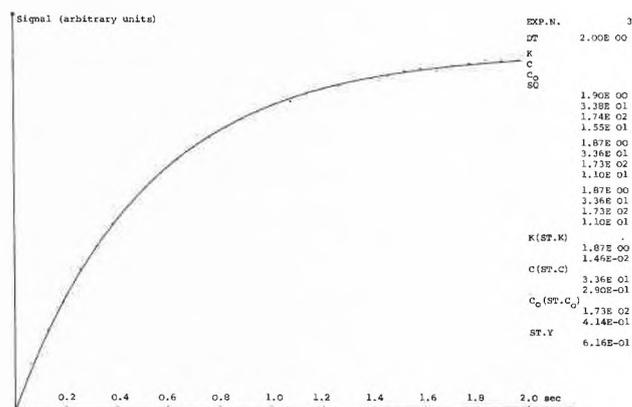


Fig. 1: Example of a first order reaction calculated by the on-line program. experimental points, — best fit with the parameters shown on the computer output.

After each iteration SQ and the parameters are printed out in order to check for convergence. The final values are given with their respective standard errors σ_{y_0} , σ_{y_∞} and σ_k . In addition σ_y , the standard error of y_i , is also calculated. The experimental points and the best fit are also shown in Figure 1.

In Table 1 the results of a series of experiments are collected, illustrating the effectiveness of the on-line calculation. Two reactions [9] with half-life times of 400 ms and 50 ms resp. were followed on a Durrum stopped flow D 110 instrument with a log-amplifier D 131. The total transmission change was 5.4% for the slow and 6.7% for the fast reaction. The standard error σ_y for the measured points is $\frac{0.7}{256} = 0.27\%$ and $\frac{2.6}{256} = 1\%$ of the scale range. Table 1 also shows that k values can be determined with a standard error of 1–3% depending upon the time scale and that the reproducibility is better than 2% even for the faster reactions.

To check the working of the program under nonideal conditions, the slow reaction was followed with different time settings. Changes between 0.5 and 5 seconds (ideal is 2 seconds) do not affect the calculated value of k significantly. However, the errors become somewhat higher. Also shown in Table 1 are the values of k obtained by taking photographs of the curves and comparing them to calculated first order reaction plots.

Table 1: Results obtained with the nonlinear curve fitting program with on-line data on a Durrum stopped flow for the reaction of [Ni DCyclam 13]²⁺ ($5 \cdot 10^{-3}$ M) and CN⁻ ($6 \cdot 10^{-3}$ M and $1.5 \cdot 10^{-1}$ M) at pH 10.40.

Exp. No. (time setting in sec.)	k [s ⁻¹] Photograph	on-line	σ_y
1 (2)	1.67	1.88 ± 0.017	0.73
2 (2)	1.84	1.88 ± 0.017	0.73
3 (2)	1.58	1.87 ± 0.015	0.62
4 (2)	1.63	1.91 ± 0.017	0.73
5 (2)	1.78	1.92 ± 0.015	0.63
Mean*	1.70 ± 0.05	1.89 ± 0.01	
6 (5)	1.67	1.78 ± 0.020	0.84
7 (1)	1.91	1.82 ± 0.046	1.2
8 (1)	2.01	1.96 ± 0.025	0.63
9 (0.5)	—	1.79 ± 0.46	4.5
10 (2)	1.73	1.88 ± 0.017	0.87
Mean*	1.83 ± 0.08	1.85 ± 0.04	
11 (0.2)	12.1	11.9 ± 0.4	2.5
12 (0.2)	14.7	12.7 ± 0.5	2.8
13 (0.2)	14.7	13.1 ± 0.4	2.4
14 (0.2)	15.1	12.8 ± 0.5	2.8
15 (0.2)	14.7	12.9 ± 0.5	2.6
16 (0.2)	14.0	12.1 ± 0.4	2.5
Mean*	14.2 ± 0.4	12.5 ± 0.2	

* The values are weighted means for k on-line, but unweighted for k photograph.

In this case it is not only impossible to estimate the error connected with the rate constant, but also the standard error of the mean is consistently larger, typically by a factor of two to three, compared to that obtained by the on-line calculation.

The on-line calculation with the program described has the following advantages over other techniques used to determine rate constants. 1) All measurements are used with reasonable statistical weights. 2) The initial and final values are considered as parameters. Thus no systematic error from an arbitrary choice of y_0 and y_∞ is introduced. 3) 1.5 minutes after a concentration-time-curve has been recorded, the whole information is available. One can therefore decide whether more measurements are necessary or not. This also represents a substantial saving of time. 4) The accuracy of the k values is increased and there is the possibility of a control between experimental points and the calculated curve. This allows to check whether the reaction is a true first order process or not. 5) The same method can be used for other rate laws (i.e. second order reactions) whereby the numerical calculation of derivatives of the type (5) is to be preferred over the analytical one.

Even more complicated rate laws (parallel or consecutive reactions) can be treated essentially the same way. As an example we report the separation of two rate constants for a consecutive reaction which has been studied before [10]. Fig.2 shows one of the measurements, run on a Durrum stopped flow D 110.

In this case two sets of twenty points with two different time spacings were obtained. The data were then stored on magnetic tape in a file compatible with our general nonlinear least square program [11]. The curve fit was done off-line because of the time required (about 15 minutes). The precision with which the rate constants can be determined is similar to that for single step processes. The mean values $k_1 = 31.8 \pm 0.4$ s⁻¹ and $k_2 = 2.32 \pm 0.2$ s⁻¹ obtained from 6 measurements show how good the reproducibility is.

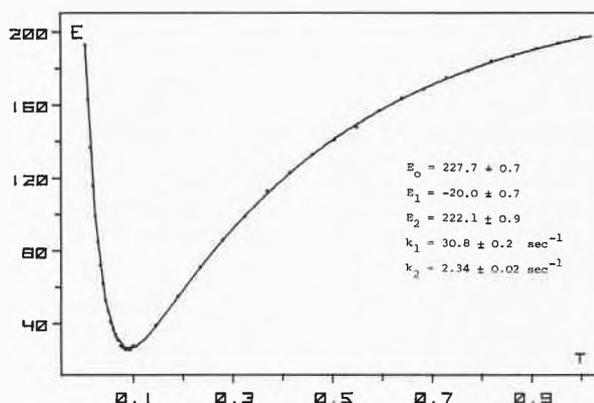


Fig. 2: Example of a two step consecutive reaction ($1.2 \cdot 10^{-3}$ M Cu²⁺, $1.3 \cdot 10^{-3}$ M 3,7-diazanonedioic acid amide, pH = 6.0, α -picoline buffer). experimental points, ——— best fit calculated with the parameters shown on the computer output.

In conclusion the on-line data transfer and computation offer many advantages over the classical way, giving more precise results with a substantial saving of time. Today neither exorbitant costs nor the necessity of being an electronics specialist preclude such procedures in a standard chemical laboratory.

This work was supported by the Swiss National Science Foundation. (Project No. 2.477-0.75)

References

- 1 H. Q. Gibson and R. J. Desa: *Computer Biomed. Res.* 2 (1969) 494.
- 2 B. G. Willis, J. A. Bittikofer, H. L. Pardue and D. W. Margerum: *Anal. Chem.* 42 (1970) 1340.
- 3 A. Queen, J. L. Charlton, E. Dawson and W. Buchannon: *Chem. Instr.* 6 (1975) 153.
- 4 G. Gauglitz and A. Reule: *Z. Anal. Chem.* 276 (1975) 97.
- 5 Before the transient recorder and the interface are connected both must be adjusted either to positive or negative logic.
- 6 P. R. Bevington: *Data reduction and error analysis for the physical sciences.* McGraw Hill, New York, 1969, page 232.
- 7 It is assumed that the time setting for taking up the 32 points corresponds to two to four half-life times of the reaction.
- 8 A. A. Frost and R. G. Pearson: *Kinetics and Mechanism*, John Wiley, New York, 1961, page 49.
- 9 L. Hertli and Th. A. Kaden: to be published.
- 10 A. D. Zuberbühler and Th. A. Kaden: *Helv. Chimia Acta* 57 (1974) 1897.
- 11 A. D. Zuberbühler and Th. A. Kaden: unpublished.

Inadequate Models of Stereochemistry Based on Kimball's Spheres and Pauli's Exclusion Principle*

Christian K. Jørgensen **

Département de Chimie minérale, analytique et appliquée, Université de Genève

Abstract

The confinement of two electrons in each of several non-overlapping spheres is not intended as "Ansatz" for Schrödinger's equation, and the concomitant kinetic energy is studied. The "coexistence integral" of two atomic angular functions is introduced, and the Gillespie description and Pauli exclusion principle are discussed.

Many chemists [1] and certain physicists [2] recommend a model first proposed by Kimball of two electrons occupying a sphere with radius R to explain, to the first approximation, the stereochemistry of molecules by close contact (but no overlap) of spheres each representing a single bond or a lone-pair. The fundamental characteristic of this model is the supposition that each electron possess the kinetic energy T (measured in the atomic unit 1 hartree = 27.2 eV, and distances in bohr units 0.529 Å)

$$T = 9/(8 R^2) \quad (1)$$

Besides arguments derived for the standing waves first suggested by de Broglie [2] it can also be noted that the average value $\langle r \rangle$ for a sphere filled with a constant electronic density is $\frac{3}{4}R$ and $\langle r^{-1} \rangle = 3/(2R)$.

If the sum of the potential energy $-\langle r^{-1} \rangle$ and T is minimized as a function of R for a hydrogen atom, the groundstate has the correct energy $-1/2$ hartree (= -1 rydberg) and shows $R = \frac{3}{2}$ bohr, the same value as $\langle r \rangle$ for the 1s orbital obtained as solution to Schrödinger's equation. The identification of a higher limit of r with its average value weakens the former justification for the numerical constant (9/8). Actually, as previously discussed in a Danish journal [3], the lowest eigen-value for an electron confined in a sphere rather is

$$T = \pi^2/(2 R^2) \quad (2)$$

with the constant 4.38... times larger than in eq. (1). Said in other words, the Kimball model does not constitute a legitimate «Ansatz» for solving the Schrödinger equation, and the pairs of electrons are not strictly confined to their spheres, but overlap in some indefinite way. It may be noted that the product $\langle r \rangle \langle r^{-1} \rangle$ is a kind of shape factor for atomic orbitals, between 1.27 and 1.30 for most Hartree-Fock functions of many-electron atoms [4], and $(2l+3)/(2l+2)$ for hydrogenic radial functions without nodes (1s, 2p, 3d, 4f, 5g, ...) and hence this quantity is (9/8) both for the constant density inside a sphere and for 4f in the one-electron atoms. In general, $\langle r^k \rangle = 3R^k/(k+3)$ for the sphere.

* Received 27 September 1977

** Prof. Dr. C. K. Jørgensen, 30 Quai Ansermet, CH-1211 Geneva 4

Seen from the point of view of a spectroscopist, the most serious weakness of the Kimball model is the neglect of l -values, and some authors have gone as far as to apply geometrical arguments to packing of spherical electron pairs, proposing tetrahedral clusters in molecules obeying the octet rule, and octahedral clusters in hexafluoro complexes of aluminium(III), silicon(IV), phosphorus(V), sulphur(VI) and the recently prepared ClF_6^+ . Before rejecting the Kimball model as incommensurable with quantum mechanics, it must be realized that Gillespie [5, 6] successfully described the equilibrium positions of the nuclei in the groundstate (shortly, the "Stereochemistry" as far goes bond angles) by the working hypothesis that lone-pairs need more angular space than bonding electron pairs, and that bonds to highly electronegative atoms (such as fluorine) need the least space in spite of the frequent opinion that the covalent radius of hydrogen is smaller than of fluorine. In many ways, this could be explained by a virial theorem making the potential energy $-2I$ and the kinetic energy $T=I$ (proportional to R^{-2}) where I is the ionization energy determined from photo-electron spectra [7] if it was not for the difficulty that the angular part of the kinetic energy in spherical symmetry:

$$T_{\text{ang}} = \frac{l(l+1)}{2} \langle r^{-2} \rangle \quad (3)$$

is 200 to 300 eV in typical 3d group central atoms (some 20 times I) and twice as much in 4f group compounds. It has been analyzed [4] why the Gillespie description is much more appropriate for post-transition group compounds than for the d groups, and also why fluoride-containing complexes such as TeF_6^- , IF_5 and XeF_5^+ look like octahedra having one ligand replaced by a lone-pair, whereas the time-average picture of TeCl_6^{2-} and TeBr_6^{2-} is regular octahedral in cubic crystals (but the absorption spectra suggest deviations on an instantaneous picture, rather similar to Jahn-Teller distortion except for the lack of inversion symmetry). This question of the characteristic time-scale of an experimental technique (at a given temperature) has many ramifications [4] and many apparent discrepancies can now be understood.

Gillespie argues that the stereochemistry (qualitatively explained by the Kimball model) is based mainly on Pauli's exclusion principle. It is true that the repetition in the Periodic Table is connected with the maximum number $(4l+2)$ of electrons in a given shell, and with the symmetry types of the closed shell constituting the neutral element of Hund vector coupling [8]. However, it is likely that the local contributions [4] to the kinetic

energy are more fundamental than the exclusion principle, because they prevent the implosion of all atoms, molecules and solids, even of the hydrogen atom, where the exclusion principle does not act. We would like to show quantitatively why it is not a satisfactory model of the three orthogonal p orbitals to consider [1] three inflated balloons, squeezed in the middle, and held together in the center by a piece of wire. As a measure of spatial coexistence, we may define the integral over the spherical surface (at a given distance from the nucleus) of the product $(A_1)^2(A_2)^2$ of two squared angular functions each having a definite value of l . Obviously, this integral is zero for spatially excluded entities. If the two angular functions A_1 and A_2 are orthogonal (this means vanishing integral of A_1A_2 on the spherical surface because of compensating, positive and negative contributions) and have the same l , the product $(A_1)^2(A_2)^2$ represents the square of an angular function $A_3 = A_1A_2$ having twice as large l . A comparison of the normalization constants [4, 9]

$$\begin{array}{ll} p\pi c & \sqrt{3} (x/r) \quad d\delta c \quad \sqrt{15} (x^2 - y^2)/2r^2 \\ p\pi s & \sqrt{3} (y/r) \quad g\gamma s \quad \sqrt{315} (x^2y - xy^2)/2r^4 \\ d\delta s & \sqrt{15} (xy/r^2) \end{array} \quad (4)$$

clearly shows that $p\pi c$ and $p\pi s$ forming the product $(A_1)^2(A_2)^2$ has the integral $(9/15) = 0.6$ times as large as the square of the $d\delta s$ orbital, and $d\delta s$ and $d\delta c$ the integral $(225/315) = 5/7$ times as large as the square of the $g\gamma s$ orbital. These values indicating spatial coexistence of two orthogonal orbitals (the other obtained by turning one 90° in the xy -plane) are higher than a half, and actually $(2l+1)/(2l+3)$.

This result can be obtained from the average value of w^k (k even integer, w one of the Cartesian coordinates) on a spherical surface being $1/(k+1)$ and the more general result eq. (78) of *Harnung* and *Schäffer* [9] that the average value of $x^{2p}y^{2q}z^{2r}$ (if one of the exponents is odd, the average vanishes) is

$$\frac{(2p)! (2q)! (2r)! (p+q+r)!}{p! q! r! (2p+2q+2r+1)!} \quad (5)$$

Thus, the coexistence integral of two different among the $d\delta c$ functions can be shown to be $5/7$. It must be added in all fairness that the orbitals with positive l have a coexistence integral with themselves ($A_1 = A_2$) higher than 1, and actually $9/5$ for any p orbital and $15/7$ for any of the five d orbitals. It is noted that in spite of the different shape and orientation, these values are exactly 3 times the coexistence integral of two different orbitals of the same l . This is likely to be a general result, because *Unsöld's* theorem that the sum of the $(2l+1)$ different A^2 is $(2l+1)$ in all directions can be extended to the square of the sum being the sum of $(2l+1)$ different A^4 then each being $3(2l+1)/(2l+3)$, and $(4l^2 + 2l)$ different $(A_1)^2(A_2)^2$ each a-third as large, on the average.

We have spoken about *Pauli's* exclusion principle in its original form [10] of electrons all having differing sets

of quantum numbers, which was incorporated in the *Slater-Condon-Shortley* treatment and in the *Hartree-Fock* functions as the requirement of mutually orthogonal orbitals, each containing at most two electrons (with opposite spin-direction). Recent text-books sometimes restrict the exclusion principle to the requirement of anti-symmetrized many-fermion wave-functions. Thus, the determinant $|1s\alpha 1s\beta 2s\alpha 2s\beta|$ with orthogonal 1s and 2s orbitals (and opposite spin direction α and β) is proportional (with a normalization constant dependent on κ) to $|1s\alpha 1s\beta k\alpha k\beta|$ where $k\alpha = (2s + \kappa 1s)$ is not orthogonal on 1s. This might be interpreted as the exclusion principle not demanding orthogonality, but it must be noted that the observable quantities, and in particular the electronic density, behave as if 2s cannot become closer adjacent to 1s than by being orthogonal, and further on, that the normalization constant diverges if κ is chosen very large in an attempt to accommodate all four electrons in the same (1s) orbital. This compensates the apparently more negative one-electron energy of (the normalized) $|k\alpha > (1 + \kappa^2)^{-1/2}$ compared with 2s.

It may very well be that eq. (1) is heuristically useful, though a large (perhaps half) part of the electronic density occurs outside the sphere with radius R , for reasons similar to the extensive coexistence of orbitals eq. (4) belonging to the same l , corresponding to some kind of mutual adaptation of the extruding electronic densities from different orbitals. Quite independently of the recognized situation that photo-electron spectra [7] indicate l of delocalized M.O. being, to a certain approximation, the eigen-states of an effective one-electron operator (and only the inner shells remain localized) the writer would like to warn chemists that the *Kimball* model should not be construed to denote pairs of electrons confined in the spheres, and that the factor $(9/8)$ in eq. (1) is a "Stellschraubenparameter" fitted to the hydrogen atom.

Acknowledgement

I am grateful to Professor *Ernst Schumacher*, University of Berne, for continued helpful discussions about this subject since December 1976, and in particular for him pointing out that the discrepancy between eqs. (1) and (2) is the distinction between a heuristic model and a valid Ansatz.

References

- 1 *R. M. Roberts* and *J. G. Traynham*: *J. Chem. Educ.* 53 (1976) 233.
- 2 *F. Rioux* and *P. Kroger*: *Amer. J. Phys.* 44 (1976) 56.
- 3 *C. K. Jørgensen*: *Dansk Kemi* (Copenhagen) 48 (1967) 33.
- 4 *C. K. Jørgensen*: *Modern Aspects of Ligand Field Theory*, North-Holland Publishing Co., Amsterdam 1971.
- 5 *R. J. Gillespie*: *Molecular Geometry*, Van Nostrand-Reinhold, New-York 1972.
- 6 *R. J. Gillespie*: *J. Chem. Educ.* 51 (1974) 367.
- 7 *C. K. Jørgensen*: *Structure and Bonding* 24 (1975) 1 and 30 (1976) 141.
- 8 *C. K. Jørgensen*: *Adv. Quantum Chem.* 11.
- 9 *S. E. Harnung* and *C. E. Schäffer*: *Structure and Bonding* 2 (1972) 201.
- 10 *W. Pauli*: *Z. Physik* 31 (1925) 765.