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Calculation of Adiabatic Energy Surfaces for Molecules Using the Method of Atomic Associations

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1. INTRODUCTION

IN applying the principles of quantum mechanics to chemistry we must deal with large numbers of electrons located in the fields of many positive charges distributed arbitrarily in space. The multicentered character of chemical electron systems allows only limited applicability of the symmetry considerations of atomic structural physics and the orthodox methods of many-particle theory. Thus, quantum chemistry has been able to gain access to purely chemical questions only when such treatments are chosen, as, for example, the Hückel treatment, the resonance concept, the method of hybridization of atomic states, or the "atoms in molecules" treatment.

This paper involves calculating the energy states of molecules, as well as atomic systems, where we mean atoms which cannot enter into mutual bonding relationships. The basic idea of this work, which we will call the concept of "atomic associations," is to reduce the multicentered problem to a series of conveniently solved single-center systems. Thus, we may deal with an arbitrary molecule using a formulation free from factors involved in using a finite number of fictitious atoms. This method of "building" to larger molecules distinguishes it from most conventional treatments, which always begin with a multielectron and multicenter system. Thus, the large errors obtained in deriving excitation, dissociation, or resonance energy of molecules or parts of molecules, which are always small when compared to total energy, are removed because the absolute values often can be determined rather exactly as a percentage.

The semiempirical frame of this method includes the "atoms in molecules"[1] and "united atom"[2] treatments and the method of a single-center expansion[3] as a special case. The general formulation of the atomic associations method shows how "activation energy" can be determined and thus permits a relationship to earlier calculations whose goal was the approximate determination of "activation energy" using the three-atom process.[4]

Examples calculated thus far (Sec. 6) give results agreeing more closely with empirical values than those from conventional treatments. The information from energy surfaces does not always agree with the magnitude of the chemist's activation energy, but the approximate course of the energy surfaces permits general conclusions about the order of magnitude of activation energy, and the information from energy surfaces is absolutely necessary for further study of all the steps of a reaction.

The basis in quantum mechanics (quantum chemistry) for calculating the physical and chemical properties of molecules and atomic systems is the time-independent Schrödinger equation

$$(\mathcal{H} - \mathcal{E})\Psi = 0 \qquad (1)$$

for relatively slow atoms, where the solution Ψ of this partial differential equation will be assumed as

$$\int \psi^* \psi d\tau = 1 \,. \qquad (1a)$$

This leads to an eigenvalue problem for Eq. (1) with eigenfunction $\psi_s (s = 1, 2 \cdots)$ and corresponding energy eigenvalue $\mathcal{E}_s$. The Pauli principle also applies independently to Eq. (1) and requires of the solution of ψ_s (which depends on all electron coordinates) that it be antisymmetric in these coordinates. Thus,

$$T_{ij}\psi_s = -\psi_s \quad (T_{ij} \text{ is an interchange operator}) \qquad (2)$$

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[1] W. Moffitt, Proc. Roy. Soc. (London) **A210**, 245 (1951).

[2] P. M. Morse and E. C. G. Stueckelnberg, Phys. Rev. **33**, 932 (1929); W. Bingel, Z. Naturforsch. **12a**, 59 (1957); J. Chem. Phys. **30**, 1250, 1254 (1959).

[3] For example: H. Hartmann, Z. Naturforsch. **2a**, 489 (1947); Tien Chi Chen, J. Chem. Phys. **23**, 2200 (1955); R. G. Parr, J. Chem. Phys. **26**, 428 (1957); K. M. Howell and H. Shull, J. Chem. Phys. **30**, 627 (1959); H. Hartmann and G. Gliemann, Z. Phys. Chem. **15**, 108 (1958); **19**, 29 (1959); and J. R. Hoyland and F. W. Lampe, J. Chem. Phys. **37**, 1066 (1962).

[4] R. A. Ogg and M. Polanyi, Trans. Faraday Soc. **31**, 604 (1935); M. G. Evans and M. Polanyi, Trans. Faraday Soc. **31**, 875 (1935).

must be valid when the electron coordinates are interchanged. The coordinates of an ith electron can be described, for example, by the space coordinates $(x_i,y_i,z_i) = \mathfrak{r}_i$ and a spin coordinate σ_i.

For a system of n electrons, ψ_s is written in detail as

$$\psi_s = \psi_s(\mathfrak{r}_1,\mathfrak{r}_2\cdots\mathfrak{r}_n,\sigma_1,\sigma_2\cdots\sigma_n)\ . \tag{3}$$

Neglecting relativistic effects and the spin-orbit coupling, the Hamiltonian operator $\mathcal{H}$ in Eq. (1) becomes

$$\mathcal{H} = \sum_{i=1}^{n} h(i) + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{1}{r_{ij}} + \sum_{\lambda=1}^{N-1}\sum_{\mu=\lambda+1}^{N}\frac{Z_\lambda Z_\mu}{R_{\lambda\mu}}\ , \tag{4}$$

where

$$h(i) = -\tfrac{1}{2}\Delta_i - \sum_{\lambda=1}^{N}\frac{Z_\lambda}{r_{\lambda i}}\ ;\ \Delta_i = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \tag{4a}$$

(in Cartesian coordinates) when N atoms have the nucleus charge $Z_\lambda (\lambda = 1,2,3\cdots N)$ and atomic units are used. If the vector of atom λ (charge Z_λ) is defined as $\mathfrak{R}_\lambda = (R_{\lambda x},R_{\lambda y},R_{\lambda z})$, then

$$\begin{aligned} |\mathfrak{R}_\lambda - \mathfrak{R}_\mu| &= R_{\lambda\mu}\ , \\ |\mathfrak{r}_i - \mathfrak{r}_j| &= r_{ij}\ , \\ |\mathfrak{r}_i - \mathfrak{R}_\lambda| &= r_{\lambda i}\ . \end{aligned} \tag{5}$$

And all of the properties of the system can be derived from ψ_s and $\mathcal{E}_s$.

We want particularly to discuss the total energy $\mathcal{E}_s$, where

$$\mathcal{E}_s = \mathcal{E}_s(Z_\lambda,\mathfrak{R}_\lambda;n)\ . \tag{6}$$

ψ_s is also a function of these parameters. This means, then, that if one knows the number of electrons and the arrangement of the nuclei with their charges, all of the physical and chemical properties of the system can be determined uniquely by Eqs. (1) and (2).

$\mathcal{E}_s$, as functions of the parameter $\mathfrak{R}_\lambda$, are called "energy surfaces." To every arrangement of nuclei belongs a completely orthogonal system of ψ_s functions. In the case of two atoms $a,b (N = 2)$, $\mathcal{E}_s$ is dependent only upon R_{ab} and in the bonding case can be represented approximately by a Morse curve, for example (see Sec. 5).

If $\mathcal{E}_s$ is dependent on two parameters, one obtains a family of surfaces representing the series for all atomic arrangements, such as for three atoms which interact with one another in a linear process of the form

$$a + bc \rightleftarrows ab + c\ . \tag{7}$$

The Schrödinger equation (1) gives an exact solution in only a few cases, so approximation treatments are used, often proceeding from the fact that

$$\mathcal{E}_s \leq \tilde{\mathcal{E}}_s \tag{8}$$

is always valid if $\tilde{\mathcal{E}}_s$ is the minimum of

$$\mathcal{E}_s = \int \tilde{\psi}_s^* \mathcal{H} \tilde{\psi}_s d\tau\ , \tag{9}$$

where the approximation functions $\tilde{\psi}_s$ are varied and are linear combinations of definite functions χ_r

$$\tilde{\psi}_s = \sum\nolimits_r c_{rs}\chi_r\ . \tag{9a}$$

From Eqs. (9) and (9a) it follows that

$$\tilde{\mathcal{E}}_s = \int \tilde{\psi}_s^* H \tilde{\psi}_s d\tau + \sum_{\lambda=1}^{N-1}\sum_{\mu=\lambda+1}^{N}\frac{Z_\lambda Z_\mu}{R_{\lambda\mu}}\ , \tag{10}$$

where

$$H = \sum_{i=1}^{n} h(i) + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{1}{r_{ij}} \tag{10a}$$

and where $h(i)$ is determined by Eq. (4a), so that it is then convenient to consider only the so-called "electron energy"

$$E_s = \mathcal{E}_s - \sum_{\lambda=1}^{N-1}\sum_{\mu=\lambda+1}^{N}\frac{Z_\lambda Z_\mu}{R_{\lambda\mu}}\ , \tag{11}$$

because this always remains finite for the difference between nucleus interaction and total energy. So in the following we will use the expression "energy surfaces" only for E_s.

2. THE CONCEPT OF ATOMIC ASSOCIATIONS

The point of departure of this concept is the assumption that one may expect good results in multicenter problems, if one can assume a sufficient number of exactly solved single-center problems. That means for energy calculations, which are calculated from a zero level, that it contains the largest part of the total energy. Thus the energy, which arises from the multicentered character of the system (as does the bonding energy or activation energy), is obtained with greater exactness and reliability. So it is valid to develop a formulation that contains the atom problem as a basis and describes the molecules with the aid of "structures" which are constructed from the different atom arrangements.

These structures, which we will call "atomic associations" $[K]$ are obtained by the transitions $R_{\lambda\mu} \rightarrow 0$ (unions) and $R_{\lambda\mu} \rightarrow \infty$ (separations) which actually receive nuclear charges in the molecule.[5] For

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[5] H. Preuss; Z. Naturforsch. **12a**, 599 (1957); **13a**, 364 (1958); Naturwiss. **47**, 241 (1960), Theoret. Chim. Acta **1**, 42 (1962) Z. Naturforsch. **18a**, 489 (1963).

example, if there are three atoms—a, b, and c—then one of the five associations obtained can be written in the form

$$[K] = [a|bc] \tag{12}$$

and has the transition

$$R_{ab} \rightarrow \infty \;;\quad R_{ac} \rightarrow \infty \;;\quad R_{bc} \rightarrow 0\,. \tag{12a}$$

Another association is

$$[L] = [a|b|c]\,, \tag{13}$$

which comes from the transition

$$R_{ab} \rightarrow \infty \;;\quad R_{ac} \rightarrow \infty \;;\quad R_{bc} \rightarrow \infty\,. \tag{13a}$$

We designate the single-center system as (bc) in Eq. (12), and (a) or (b) as "partial unions" in Eq. (13).

In general, we determine that every atomic association $[K]$ (number $\overline{A}_N$) contains the partial unions (K_j) $(j = 1 \cdots A_K)$,

$$[K] \equiv [K_1|K_2|\cdots|K_{A_K}]\,, \tag{14}$$

where

$$1 \leq A_K \leq N\,. \tag{14a}$$

If the number of atoms in (K_j) is further defined as N_{Kj}, then

$$\sum_{j=1}^{A_K} N_{K_j} = N \tag{15}$$

must be valid, as is

$$\sum_{j=1}^{A_K} n_{K_j} = n\,, \tag{16}$$

if N_{Kj} is the number of electrons in the partial union (K_j). As an abbreviation for transitions (12a) or (13a) we write $\lim_{[K]}$ or $\lim_{[L]}$, respectively.

In the sense of the concept of atomic associations, the Hamiltonian operator can be partitioned:

$$H = H(K) + V(K)\,, \tag{17}$$

whereby the anticipated values of the remainder $V(K)$ disappear with the transition to $[K]$:

$$\lim_{[K]} \langle|V(K)|\rangle = 0\,, \tag{18a}$$

$$\lim_{[K]} \langle|H|\rangle = \langle|H(K)|\rangle\,. \tag{18b}$$

The eigenfunctions of the operator $H(K)$

$$\{H(K) - \mathcal{E}_s(K)\}\Phi_s(K) = 0 \tag{19}$$

are then obtained from the solution of H from the transition

$$\lim_{[K]} \psi_s = \Phi_s(K)\,, \tag{20}$$

where we note that due to Eqs. (1), (4), (10), and (11),

$$(\mathcal{H} - \mathcal{E}_s)\psi_s \equiv (H - E_s)\psi_s \equiv 0 \tag{21}$$

is valid. Corresponding to Eq. (20), the eigenvalue of Eq. (19) also follows from the passage to the limit

$$\lim_{[K]} E_s = \mathcal{E}_s(K)\,. \tag{22}$$

Similar equations can also be written for the partial unions. $H(K)$ consists of a series of single-center systems whose interactions disappear due to the passage to the limit of $\lim_{[K]}$. Thus

$$\langle|H(K)|\rangle = \sum_{j=1}^{A_K} \langle|\mathcal{H}(K_j)|\rangle \tag{23}$$

is valid, and the electron energy of the association $[K]$ results from the sum of each individual energy of the single-center systems (K_j):

$$\mathcal{E}_s(K) = \sum_{j=1}^{A_K} \mathcal{E}_s(K_j)\,. \tag{24}$$

The solution of the Schrödinger equation for the partial union (K_j) is defined as φ_{Kj}, so we have

$$\{\mathcal{H}(K_j) - \mathcal{E}_s(K_j)\}\varphi_{K_j} = 0 \tag{25}$$

and $\Phi_s(K)$ follows from Eq. (20) as the antisymmetrical product (P_m is a permutation operator) of all φ_{Kj}

$$\Phi_s(K) = D' \sum_m (-1)^{P_m} P_m \prod_{j=1}^{A_K} \varphi_{K_j}(n_{K_j})\,, \tag{26}$$

where $(-1)^{P_m} = 1$ or -1, depending on whether P_m contains an even or odd number of transpositions. (D' is a normalization constant.) The eigensolutions of Eq. (25) are thus already antisymmetrical, but it will be possible generally to apply the operator

$$\mathcal{A} = D' \sum_m (-1)^{P_m} P_m \tag{27}$$

based on running through all permutations obtained in the numerical value of D'. This is essentially the basis of the concept of atomic associations.

The index s of ψ_s that we carried along in the equations distinguishes the different eigenstates of the system. In this sense Eq. (26) means that such $\varphi_{Kj}(N_{Kj})$ are used, as always follow from the passage to the limit of $\lim_{[K]}$ of Eq. (21) for Eq. (19) according to Eq. (25), i.e., s numbers the different energy surfaces, and every passage to the limit for an atomic association is a definite surface. Thus, in addition to excited states of (K_j), they also appear under circumstances in which the fictitious partial unions no longer represent neutral atoms. This is expressed by

$$\sum_{\lambda=1}^{(Nj)} Z_\lambda \lesseqgtr n_{Kj} \,, \tag{28}$$

if the sum runs over all nucleus charges of the partial union (K_j). In any event, the association $\Phi_s(K)$ belonging to it can appear for energy surfaces in which the total system

$$\sum_{\lambda=1}^{N} Z_\lambda = n \tag{29}$$

is neutral.

The partitioning of H in Eqs. (17) and (23) can be done in many ways due to the indistinguishability of the electrons relative to their numbering. This fact leads to the so-called exchange-degeneration of the solutions of Eq. (1), which was reduced by requirement (1a) and the Pauli principle (2) and leads to unique antisymmetrical solutions, because

$$T_{ij}H = H \tag{30}$$

is valid for H, and this leads directly to the previously mentioned ambiguous numbering that is not equivalent to any physical ambiguity. We can decide about this later only on the basis of suitability in relation to a simple calculation of this or that reduction of H.

In this connection another difference in the appearance of $\Phi_s(K)$ must be pointed out. According to Eq. (20), $\Phi_s(K)$ is obtained as a limiting function of ψ_s if certain $R_{\lambda\mu}$'s go to zero or infinity corresponding to associations of $[K]$. The representation (26) for $\Phi_s(K)$ is also to be understood in this sense. These functions represent an orthogonal function system when passed to the limit[6]

$$\lim_{[K]} \int \Phi_s^*(K)\phi_t(K)d\tau = \delta_{st} \,. \tag{20a}$$

For fixed $H(K)$ in Eq. (19) the $\Phi_s(K)$ are, in contrast, originally pure products of $\varphi_{Kj}(N_{Kj})$ and for this, Eq. (20a) is always valid. But because we always want to view the Eq. (26) representation of $\Phi_s(K)$ as a point of departure, Eq. (19) is to be understood as a relationship that can be applied to every product of Eq. (26), depending on how H is partitioned by Eq. (17).

Thus, here we obtain the same conditions as in the Heitler–London method for H_2 molecules, i.e., there the Hamiltonian operator was differentially partitioned relative to the electron numbering on the nuclei to make use in every case of the fact that the single particle functions are solutions for hydrogen atoms.

Through the concept of atomic associations certain *points* are distinguished on the energy surfaces whose corresponding energy values are represented by Eqs. (22) and (24) as energy *sums* originating from free atoms. An N-atom molecule can be set in relation to systems which possess the same quantity of electrons, but it exhibits a smaller number of atoms. Due to Eq. (11), this relationship can always be produced. The possibility of distinguishing specific *curves* on the energy surfaces will be handled in Sec. 4.

The number of associations $(\bar{A}_N)$ increases rapidly with N. If for two atoms, a and b, there are only two $[a|b]$, $[ab]$, then for $N = 3$ there are the following five association possibilities: $[a|b|c]$, $[a|bc]$, $[ab|c]$, $[b|ac]$, $[abc]$. For four atoms—a, b, c, and d—one obtains 15 possibilities $[a|b|c|d]$, $[a|bcd]$, $[b|acd]$, $[c|abd]$, $[d|abc]$, $[ab|cd]$, $[ad|bc]$, $[ac|bd]$, $[a|b|cd]$, $[c|d|ab]$, $[a|c|bd]$, $[a|d|bc]$, $[b|d|ac]$, $[c|b|ad]$, $[abcd]$, some of which, however, need not always be considered as taking place physically.

As an approximate illustration, $H(K)$ can be given for $K = [a|c|bd]$, in atomic units, as

$$H(K) = \mathcal{H}(a) + \mathcal{H}(c) + \mathcal{H}(bd) \tag{31}$$

with

$$\begin{aligned} \mathcal{H}(a) &= -\tfrac{1}{2}\sum_{i=1}^{n_a} \Delta_i - \sum_{i=1}^{n_a} \frac{Z_a}{r_{ai}} + \sum_{i=1}^{n_a-1} \sum_{j=i+1}^{n_a} \frac{1}{r_{ij}} \,, \\ \mathcal{H}(c) &= -\tfrac{1}{2}\sum_{i=1}^{n_c} \Delta i - \sum_{i=1}^{n_c} \frac{Z_c}{r_{ci}} + \sum_{i=1}^{n_c-1} \sum_{j=i+1}^{n_c} \frac{1}{r_{ij}} \,, \\ \mathcal{H}(bd) &= -\tfrac{1}{2}\sum_{i=1}^{n_b+n_d} \Delta i - \sum_{i=1}^{n_b+n_d} \frac{Z_b + Z_d}{r_{bd,i}} \\ &\quad + \sum_{i=1}^{n_b+n_d-1} \sum_{j=i+1}^{n_b+n_d} \frac{1}{r_{ij}} \,, \end{aligned} \tag{31a}$$

where, from Eq. (16), n_λ $(\lambda = a,c,bd)$ represents the number of electrons which, in the passage to the limit of

$$\begin{aligned} &R_{ac} \to \infty \,, \quad R_{ab} \to \infty \,, \quad R_{ad} \to \infty \,, \\ &R_{cb} \to \infty \,, \quad R_{cd} \to \infty \,, \quad R_{bd} \to 0 \,, \end{aligned} \tag{31b}$$

"belong" to atom λ.

Then from Eq. (24)

$$\mathcal{E}_s(a|c|bd) = \mathcal{E}_s(a) + \mathcal{E}_s(c) + \mathcal{E}_s(bd) \,. \tag{32}$$

The concept of atomic associations joins the bases of two known methods. On the one hand it deals with the method of "atoms in molecules,"[2] derived only from the association

$$[K] = [a|b|c|\cdots|N] \,, \tag{33}$$

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[6] For the foregoing degeneration, one applies the proper linear combinations, constructed according to representation (26), in $\Phi_s(K)$.

which started from the completely separated atoms, and on the other hand, deals with the "united atoms"[3] treatment in which the point of departure is

$$[L] = [abc\cdots N]\,. \tag{34}$$

In the first case, the $\varphi_{Kj}(N_{Kj})$ of Eq. (25) are the total atomic functions of the atoms that are actually in the molecule, while Eq. (34) gives only a single total atomic function.

Because so far we know the φ_{Kj} in many cases either not at all or only for some roughly approximated atoms, Eq. (34) as a point of departure assists in comprehending a common single-center representation.[3] In the other case, one must apply both treatment (33) and (34) in a semiempirical form, by which the $\mathcal{E}_s(K_j)$ have been determined from spectroscopic data and the matrix elements of $V(K)$ for the determination of the total energy were calculated with approximation functions.

Thereby, an approximate calculation of the energy surfaces is possible, which is Eq. (33), produces very poor results when $R_{\lambda\mu} \rightarrow 0$ because the application of Eq. (34) when $R_{\lambda\mu} \rightarrow \infty$ does not produce the energy expected from Eq. (22) for $\mathcal{E}_s(a|b|c|\cdots N)$.

From a purely theoretical standpoint this semiempirical conception does not permit further conclusions for the applied approximation function from Eq. (9), and so far we do not know if one unconditionally exists in this case (for details see Sec. 5). Nevertheless, this semiempirical form is of great practical value and has in the last few years pointed up new possibilities for molecular calculations. As this treatment is not at all exhausted, there are many important and interesting problems here for the future.

3. THE MATHEMATICAL MODEL OF THE METHOD OF ATOMIC ASSOCIATIONS.

a. In the Form of a Variation Treatment.

A form of the variation treatment that is used quite often is the representation of the approximation solutions of Eq. (1) as linear combinations of a function set $\chi_r = \chi_r(\mathrm{r}_1\cdots;\sigma_1\cdots)$ [compare with Eq. (9a)]

$$\tilde{\psi}_s = \sum_{r=1}^{M} C_{sr}\chi_r\,. \tag{35}$$

If the set χ_r is complete, then in principle it allows, by means of an infinite sum in Eq. (35), all solutions of Eq. (1) to be represented exactly:

$$\psi_s = \sum_{r}^{\infty} C_{sr}\chi_r\,. \tag{35a}$$

If one substitutes Eq. (35) in Eq. (9) and makes $\tilde{\mathcal{E}}$ a minimum in the coefficient c_r, one obtains M secular equations

$$\sum C_r\{H_{rt} - \tilde{\mathcal{E}}S_{rt}\} = 0\,;\quad (t = 1\cdots M) \tag{36}$$

from which, if the eigenvalue $\mathcal{E}_s$ of

$$\det\{H_{rt} - \tilde{\mathcal{E}}S_{rt}\} = 0 \tag{37}$$

is substituted in Eq. (36), the coefficients C_{sr} for $\tilde{\mathcal{E}}$ = minimum are determined. The elements of the secular determinant (31) are defined as follows:

$$H_{rt} = \int \chi_r^* H \chi_t d\tau\,;\quad S_{rt} = \int \chi_r^* \chi_t d\tau\,. \tag{37a}$$

If one designates the vector of the coefficients C_r with $\mathfrak{C}$, every equation of (36) gives in matrix fashion

$$(\mathfrak{H} - \tilde{\mathcal{E}}\mathfrak{S})\,\mathfrak{C} = 0\,. \tag{38}$$

If, in contrast, all eigenvectors $\mathfrak{C}$ of Eq. (36) are put together in a matrix $\mathfrak{C}$, it can be written in the form

$$(\mathfrak{H} - \mathfrak{E}\mathfrak{S})\,\mathfrak{C} = 0\,, \tag{38a}$$

where $\mathfrak{H}$ and $\mathfrak{S}$ are the matrices of the elements of Eq. (37a) and $\mathfrak{E}$ is a diagonal matrix

$$\mathfrak{E} = \begin{bmatrix} \tilde{\mathcal{E}}_1\cdot & 0 \\ 0 & \cdot\tilde{\mathcal{E}}_M \end{bmatrix}, \tag{39}$$

whose elements satisfy the inequality Eq. (8).

To combine this form of the variation treatment with the concept of atomic associations, we first consider only the electron energy in Eq. (11) and replace $\mathcal{H}$ with H [after Eq. (10)] in Eqs. (36) to (38). Likewise, we must substitute the approximation values $\tilde{E}_s$ of Eq. (11) in Eq. (39) in the place of $\tilde{\mathcal{E}}_s$.

Next, due to Eq. (20), we require of the approximation solution (35) that

$$\lim_{[K]} \tilde{\psi}_s = \Phi_s(K) \tag{40}$$

be valid. In order also to allow for excited states, as the case was in Eq. (39), we reduce the freedom in the choice of the function sets χ_r in Eq. (35) so far that, in addition, the limiting condition

$$\lim_{[K]} \chi_r = \phi_r(K) \tag{41}$$

shall also be satisfied for every association $[K]$ $(K = 1\cdots\bar{A}_N)$. Requirement (41) includes Eq. (40) because according to Eqs. (41) and (20a), the $\Phi_s(K)$ represents an orthogonal system according to a passage to the limit. Thus,

$$\lim_{[K]} \mathfrak{S} = \vartheta = \begin{bmatrix} 1\cdot & 0 \\ 0 & \cdot 1 \end{bmatrix} \tag{42}$$

is valid if the $\Phi_r(K)$ is still assumed as normalized. Because of Eqs. (17) and (18), as well as the application of Eqs. (19) and (21), one further obtains

$$\lim_{[K]} \mathfrak{H} = \mathfrak{W}(K) \tag{43}$$

with

$$\mathfrak{W}(K) = \begin{bmatrix} \tilde{E}_1(K) \cdot & 0 \\ 0 & \cdot \tilde{E}_M(K) \end{bmatrix}, \tag{43a}$$

so that the elements of the normalized vector $\mathfrak{C}_s$ from Eq. (38) give

$$\lim_{[K]} C_{rs} = \delta_{sr} \tag{44}$$

and so that the matrix $\mathfrak{C}$ of Eq. (38a) becomes a unit matrix, which is equivalent to Eq. (40) because of Eq. (35).

Because the requirements of Eq. (41) are thus imposed on χ_r, we also obtain the correct behavior of the energy surfaces in the passages to the limit from the association $[K]$, all within the frame of the variations treatment [Eqs. (35), (36), and (37)].

We now pass on to constructing the function χ_r, with allowances for Eq. (41), with the help of the atomic associations $[K]$.

For finite $R_{\lambda\mu}$, it is natural to describe the χ_r as linear combinations of all $\Phi_r(K)$ [the LCAA = linear combination of atomic associations]:

$$\chi_r(n,N) = \sum_K^{\bar{A}_N} B_{Kr}(N)\Phi_r(K), \tag{45}$$

whereby $\Phi_r(K)$ is also valid for *finite* internucleus distances. These $\Phi(K)$ then describe systems of atoms as they are defined in the atomic association $[K]$, between which no interactions are forthcoming. The B_K are functions of all $R_{\lambda\mu}$ and

$$\lim_{[L]} B_K = \delta_{KL} \tag{46}$$

must be satisfied from the first because of Eq. (41). Again the index r numbers the individual energy states and in Eq. (45) includes such $\Phi(K)$ as belong to equal energy surfaces r. In contrast, we also want to set

$$B_{Kr} \equiv B_{Kt}(t \neq r), \tag{47}$$

which has no influence on the fulfillment of condition (41).[7]

But still further demands can be made on B_K. If one of the N atoms (for example atom λ_0) is brought to infinity, it must be required in this case [due to Eqs. (26) and (27)] that Eq. (45) go over to the form

$$\lim_{R\lambda_0\mu\to\infty} \chi_r(n,N) = \mathfrak{A}\{\chi_r(n - n_{\lambda_0},N - 1)\varphi_{\lambda_0}(n_{\lambda_0})\}, \tag{48}$$

where $\chi_r(N-1)$ is again constructed according to Eq. (45) and no longer contains the atom λ_0. That is, with this transition all the B_K belonging to associations in which atom λ_0 is united with other atoms must disappear. Therefore we can also write Eq. (48) in the following fashion:

$$\lim_{R\lambda_0\mu\to\infty} \chi_r(n,N) = \sum_K^{\bar{A}_{N-1}} {}^{(\lambda_0)} B_K(N-1)\Phi_r(K), \tag{48a}$$

in which the symbol (λ_0) indicates that definite associations have been omitted.

On the other hand, it must be required further that all associations in Eq. (45) disappear for a definite $R_{\lambda_0\mu_0} \to 0$, where the atoms λ_0, μ_0 are separated. We want to describe this in the following way

$$\lim_{R\lambda_0\mu_0\to 0} \chi_r(n,N) = \sum_K^{\bar{A}_{N-1}} {}^{(\lambda_0\mu_0)} B_K(N-1)\phi_r(K). \tag{49}$$

It may be seen that in Eq. (48) $\chi_r(N-1)$ is already antisymmetrical and that this representation makes the energy expression interesting in the way the amount $\mathcal{E}_r(\lambda_0)$ for the total electron energy of $N-1$ atoms standing in interaction increases additively. If λ_0 remains at infinity, the calculation also can be made from the beginning with $\chi_r(N-1)$ without φ_{λ_0} entering.

Manifold applications of Eqs. (48a) and (49) lead to a single association in every case. In Eq. (48), after further transitions, the association (33) results, while in Eq. (49) the association (34) of the united atoms finally results. Thereby it is shown that in Eq. (45) the methods mentioned in Sec. 2 are obtained as a special case.

Now, in order to construct B_K to satisfy the above conditions, we introduce definite functions $P_{\lambda\mu}$ between every two atoms λ and μ that are dependent only on the separation of the two atoms and which will satisfy the following conditions:

$$1.\ \lim_{R_{\lambda\mu}\to 0} P_{\lambda\mu}(R_{\lambda\mu}) = 0, \tag{50a}$$

$$2.\ P_{\lambda\mu}(R_{\lambda\mu}) \geqslant 0, \tag{50b}$$

$$3.\ \lim_{R_{\lambda\mu}\to\infty} P_{\lambda\mu}(R_{\lambda\mu}) = \infty. \tag{50c}$$

Then we define

$$\Pi_K = \prod_{\lambda,\mu}^{[K]} P_{\lambda\mu}(R_{\lambda\mu}), \tag{51}$$

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[7] The counting of the energy surfaces in s [compare with Eq. (35)] represents the same as results from the interaction of the original states $E_r(\mathfrak{R}_\lambda)$.

where only the $P_{\lambda\mu}$ are multiplied with one another in the product whose separations (in the association of $[K]$) belong to the separated atoms. Π_K shall be set equal to unity for the association of the united atoms. Thus every association is associated with a function Π_K.

Table I contains some examples for the atomic numbers $N = 2$, 3, and 4.

TABLE I. Atomic associations for $N = 2$, 3, and 4.

$N = 2$		$N = 3$	
$[K]$	Π_K	$[K]$	Π_K
(1) $[ab]$	1	(1) $[abc]$	1
(2) $[a\|b]$	P_{ab}	(2) $[a\|bc]$	$P_{ab}P_{ac}$
		(3) $[b\|ac]$	$P_{ab}P_{bc}$
		(4) $[c\|ab]$	$P_{ac}P_{bc}$
		(5) $[a\|b\|c]$	$P_{ab}P_{bc}P_{ac}$
		$N = 4$	
$[K]$	Π_K	$[K]$	Π_K
(1) $[abcd]$	1	(8) $[ad\|cb]$	$P_{ac}P_{ab}P_{cd}P_{bd}$
(2) $[a\|bcd]$	$P_{ab}P_{ac}P_{ad}$	(9) $[a\|bc\|d]$	$P_{ab}P_{ac}P_{bd}P_{cd}P_{ad}$
(3) $[b\|acd]$	$P_{ab}P_{bc}P_{bd}$	(10) $[c\|ab\|d]$	$P_{ac}P_{bc}P_{ad}P_{bd}P_{cd}$
(4) $[c\|abd]$	$P_{ac}P_{bc}P_{cd}$	(11) $[b\|ad\|c]$	$P_{ab}P_{bd}P_{ac}P_{cd}P_{bc}$
(5) $[d\|abc]$	$P_{ad}P_{bd}P_{cd}$	(12) $[a\|bd\|c]$	$P_{ab}P_{ad}P_{bc}P_{cd}P_{ac}$
(6) $[ab\|cd]$	$P_{ac}P_{ad}P_{bc}P_{bd}$	(13) $[a\|cd\|b]$	$P_{ac}P_{ad}P_{bc}P_{bd}P_{ab}$
(7) $[ac\|bd]$	$P_{ab}P_{ad}P_{bc}P_{cd}$	(14) $[b\|ac\|d]$	$P_{ab}P_{bc}P_{ad}P_{cd}P_{bd}$
		(15) $[a\|b\|c\|d]$	$P_{ab}P_{ac}P_{ad}P_{bc}P_{bd}P_{cd}$

Further, if we set

$$B_K = \Pi_K \left\{ \sum_{L}^{\bar{A}_N} \Pi_L \right\}^{-1} , \tag{52}$$

B_K thus defined then fulfills all conditions stated above, as we now show in detail.

The resulting normalized χ_r function becomes

$$\chi_r = \left\{ \sum_{K,L} \Pi_K \Pi_L S_{rr}(K|L) \right\}^{-\frac{1}{2}} \sum_{K} \Pi_K \phi_r(K) , \tag{53}$$

where

$$S_{rr}(K|L) = \int \Phi_r^*(K) \Phi_r(L) d\tau . \tag{53a}$$

With Eq. (53) the matrix elements of the matrices $\mathfrak{H}$ and $\mathfrak{S}$ then can be calculated with Eq. (37a), and from Eq. (37) we are able to determine the energy surfaces by approximations, where for $M \to \infty$ in Eq. (35) (due to the completeness of χ_r) the approximation values converge with the exact values.

Because Eq. (52) satisfies our given conditions, we now demonstrate a simple example and from that, go into a possible determination of the $P_{\lambda\mu}$ functions. Assume four centers—a, b, c, and d—if in Eq. (53) we allow center d to go to c ($R_{cd} \to 0$) and call this uniting c', from Table I we will obtain the following representation for χ:

$$\begin{aligned} \chi(n,3) = D'\{ & \Phi(abc') + P_{ac'}P_{bc'}\Phi(c'|ab) \\ & + P_{ab}P_{c'b}\Phi(b|ac') + P_{ab}P_{ac'}\Phi(a|bc') \\ & + P_{ab}P_{bc'}P_{ac'}\Phi(a|b|c')\}, \end{aligned} \tag{54}$$

if D' is the normalization constant. One easily recognizes that for $R_{\lambda\mu} \to 0$, and, respectively, $R_{\lambda\mu} \to \infty$, the association $\Phi(abc)$, and, respectively, $\Phi(a|b|c)$, remains. If in Eq. (54) $c \equiv c'$ goes to infinity ($R_{ac} \to \infty$, $R_{bc} \to \infty$), Eq. (54) takes the form

$$\lim \chi(n,3) = \frac{\Phi(ab|c) + P_{ab}\Phi(a|b|c)}{\{1 + 2P_{ab}S(4|5) + P_{ab}^2\}^{\frac{1}{2}}} = \omega(ab|c) , \tag{55}$$

if the numbering of the associations from Table I are applied in the overlap integral $S(4|5)$ from Eq. (53a). But the representation (55) is identical with Eq. (48) for $N = 3$ and $\lambda_0 = c$, as will be shown. Likewise one obtains from Eq. (54) the functions $\omega(bc|a)$ or $\omega(ac|b)$ for $a \to \infty$ or $b \to \infty$.

On the other hand, if in $\chi(n,4)$ the atoms a, b, c, and d are so separated that only the separations R_{ab} and R_{cd} stay finite, the following expression results:

$$\begin{aligned} \lim \chi(n,4) = D''\{ & \Phi(ab|cd) + P_{cd}\Phi(ab|c|d) \\ & + P_{ab}\Phi(a|b|cd) + P_{ab}P_{cd}\Phi(a|b|c|d)\} , \end{aligned} \tag{56}$$

which can be written as an antisymmetrical product of two functions $\eta(a-b)$ and $\eta(c-d)$:

$$\lim \chi(n,4) = \mathfrak{A}\eta(a-b)\eta(c-d) , \tag{57}$$

where

$$\eta(a-b) = D^{\mathrm{III}}\{\Phi(ab) + P_{ab}\Phi(a|b)\} , \tag{58a}$$

$$\eta(c-d) = D^{\mathrm{IV}}\{\Phi(cd) + P_{cd}\Phi(c|d)\} . \tag{58b}$$

With this, a process is described which, if, for example, the systems a–b and c–d are stable, exists in two molecules (ab) and (cd) in the separation of the system a, b, c, d, just as in Eq. (55) the separation of the atom c from the system a, b, c was forthcoming. Corresponding to Eq. (57), Eq. (55) can be written in the form

$$\lim \chi(n,3) = \mathfrak{A}\varphi_c\eta(a-b) . \tag{55a}$$

The transitions (55a) and (37) are completely valid in general if partial systems of $\chi(n,N)$ are removed from one another. Thus

$$\lim \chi(n,N) = \mathfrak{A}\eta(a-b)\eta(c-d)\eta(e-f)\cdots , \tag{59a}$$

or

$$\lim \chi(n,N) = \mathfrak{A}\chi(n_\sigma,N_\sigma)\chi(n-n_\sigma,N-N_\sigma) , \tag{59b}$$

if N_σ atoms having together n_σ electrons are split apart from the total N atoms.

The case where a definite $R_{\lambda\mu} \to 0$ in $\chi(n,N)$ must be considered still more closely. If, for example $R_{ac} \to 0$,

$$\lim \chi(n,3) = D\{\Phi(abc) + P_{ab}(R_{b,ac})P_{bc}(R_{b,ac})\Phi(ac|b)\} \qquad (60)$$

follows from Eq. (54) and $R_{ab} = R_{bc} = R_{b,ac}$ is understood as the distance between b and the united atom (ca), which, for example, lies at the center of gravity of a and c. According to Eq. (50), $P_{\lambda\mu}(R_{\lambda\mu})$ is defined only for two atoms λ and μ actually arising in the molecule and resulting from $R_{\lambda\mu} \to \infty$. If we require of Eq. (60) that it again assume the structure of $\eta(a' - b)$ if $a' = (ac)$, we can determine $P_{b,ac}(R_{b,ac})$ because it must then be generally true that

$$P_{\lambda\mu}(R_{\lambda,\mu\sigma})P_{\lambda\sigma}(R_{\lambda,\mu\sigma}) \equiv P_{\lambda,\mu\sigma}(R_{\lambda,\mu\sigma}) \,. \qquad (61)$$

With this definition we also get an invariance of the structure of Eq. (35) for the transition $R_{\mu\sigma} \to 0$.

According to Eqs. (55a) and (58), $\eta(\lambda - \mu)$ is identical with $\chi(n,2)$. That we choose another symbol for $\chi(n,2)$ is based on the fact that it allows a convenient determination of $P_{\lambda\mu}$ for $\eta(\lambda - \mu)$, in addition to other reasons discussed in Sec. 4.

If we write in the place of Eq. (58)

$$\eta(\lambda - \mu) = C_{\mathrm{I}}\Phi(\lambda\mu) + C_{\mathrm{II}}\Phi(\lambda|\mu) \,, \qquad (62)$$

and determine the energy (as well as the coefficients C_{I} and C_{II}) from a secular problem according to Eqs. (36) and (37) and H according to Eq. (10a), we obtain two energy curves $\tilde{E}_I$ and $\tilde{E}_{\mathrm{II}}(\tilde{E}_{\mathrm{I}} < \tilde{E}_{\mathrm{II}})$. $\tilde{E}_{\mathrm{I}}$ for $R_{\lambda\mu} \to 0$, and, respectively, $R_{\lambda\mu} \to \infty$, goes to the exact eigenvalues $\mathcal{E}(\lambda\mu)$ and $\mathcal{E}(\lambda|\mu)$, respectively. Thus $\tilde{E}_{\mathrm{I}}$ can be considered as an approximation for the eigenvalue of the electron energy of the system $\lambda - \mu$, which coincides with this for $R_{\lambda\mu} \to 0$ and $\to \infty$. From comparison with Eq. (58) it follows that we must set

$$C_{\mathrm{II}}/C_{\mathrm{I}} = P_{\lambda\mu}(R_{\lambda\mu}) \,. \qquad (63)$$

Equation (63) shows the correct behavior for $P_{\lambda\mu}$, which is

$$C_{\mathrm{I}} = 0 \,, \qquad \text{if} \qquad R_{\lambda\mu} = \infty$$

and

$$C_{\mathrm{II}} = 0 \,, \qquad \text{if} \qquad R_{\lambda\mu} = 0 \,. \qquad (63a)$$

With this, a possible determination of $P_{\lambda\mu}$ is stated. The product formulation for Π_K from Eq. (51) can then be interpreted approximately so that the $P_{\lambda\mu}$, which are determined on the unperturbed bond $\lambda - \mu$, cannot be changed by an approximation of the other atoms. This assumption is related to the experience that in most cases the bonding energy between two atoms in molecules remains unchanged in the first approximation.

Also one can proceed in the same way for excited states with Eq. (62) and obtain again a $P_{\lambda\mu}$ function for the next lowest of the two eigenvalues. Thus had we applied the same $P_{\lambda\mu}$ functions for all states [see Eq. (47)], the possibility of an improvement of the formulation (53) would exist, i.e., corresponding to the excited states, which are determined in χ_r, the associated $P_{\lambda\mu}$ would find application. In the case where $N = 2$, it then appears that from

$$\tilde{\psi}_s = \sum_{r=1}^{M} C_{sr}\eta_r(\lambda - \mu) \qquad (64)$$

that the η_r are built with the $P_{\lambda\mu}$ constructed from Eq. (62) for the rth state [Eq. (58)].

In Eq. (64) M states are determined by approximations. If for $R_{\lambda\mu} \to \infty$ some of the terms of the united atoms split up, it means that some of the functions $\Phi_r(\lambda\mu)$, according to the degree of splitting up, must arise manifoldly in some η_r. For $N > 2$ the behavior is such, for example, that "excited" $P_{\lambda_0\mu}$ are applied if the excited electron has its greatest density on atom λ_0. In general, it may be said that through the use of excited states the inexactnesses in the Π_K due to the variation of C_{sr} in Eq. (35) are partly corrected. In so far as that happens, the terms in Eq. (35) depend on the quantity M. The use of an χ_r from Eq. (53) for the calculation of the ground states might give only a rough approximation, particularly if the number of centers is large. In this case it is useful to construct the functions

$$\chi = \sum_{K}^{\bar{A}_N} B_K\Phi(K) \qquad (65)$$

[corresponding to Eq. (45)] and to determine the coefficient B_K from a secular problem. Here, only an eigenvalue will give the proper behavior in the ground state, while the other solutions are not usable physically. This is because only for a Kth column and row of the determinant (37) in the equation

$$\begin{aligned} H_{LK} &= \int \Phi^*(L)H\Phi(K)d\tau \\ &= \int \Phi^*(L)\{H(K) + V(K)\}\Phi(K)d\tau \\ &= \mathcal{E}(K)S_{LK} + \int \Phi^*(L)V(K)\Phi(K)d\tau \,, \end{aligned} \qquad (66)$$

where

$$S_{LK} = \int \Phi^*(L)\Phi(K)d\tau \qquad (L = 1\cdots\bar{A}_N)$$

does the expression $\langle | V(K) | \rangle$ disappear [compare with Eq. (18a)]. The matrix $\mathfrak{H}$ does not transform to a diagonal matrix for other states. From that we may expect relation (46) only for a state. That is, there is, for example,

$$\lim_{[K]} \chi_0 = \Phi_0(K) \tag{67}$$

if the index 0 denotes the ground state.[8] With B_{K0} determined thusly we could have done the calculation in formulation (45) in place of (52), if one assumes Eq. (47), which in the case of $P_{\lambda\mu}$ basically was not necessary, as remarked above.

Formulation (45) may be considered as a good approximation, by which the B_{K0} from Eq. (65), and the remaining $B_{Kr}(r \neq 0)$ from Eq. (52), find application. Although B_{K0} satisfies all conditions from Eqs. (48) and (49), it might be difficult to comprehend the many-dimensioned $B_{K0}(R_{\lambda\mu})$ analytically in total space. There it can be thought of, particularly if N is large, only over the partial range where formulation (65) can find application. In this sense the introduction of the one-dimensional $P_{\lambda\mu}$ possesses great advantages. But the B_{K0} from Eq. (65) presents a possibility for proving the usefulness of Eq. (52) in some $R_{\lambda\mu}$ fields.

b. A Perturbations Theory Representation

The perturbations theory representation[9] proceeds from the fact that the solutions of the atomic problem (24) exist and that with these $\varphi_{Kj}(n_{Kj})$, a $\Phi_r(K)$ is constructed according to Eq. (19) if a fixed partition of H is adopted in relation to the electron enumeration. That is, $\Phi_r(K)$ still is not antisymmetrical in this approximation, rather it must be written as the simple product

$$\Phi_r(K) = \prod_{j=1}^{A_K} \varphi_{Kj}(n_{Kj}) \, . \tag{68}$$

As already pointed out in Sec. 2, the single $\Phi_r(K)$ in this case build an orthogonal system without a passage to the limit because the φ_{Kj} themselves can be made orthogonal. Thus, we have

$$\int \varphi_{Kj}^{*(n)}(n_{Kj}) \varphi_{Kj}^{(m)}(n_{Kj}) d\tau_{nKj} = \delta_{nm} \tag{69}$$

if the (m) and (n) differentiate the different states (including degeneration) of the single-center system (K_j). Therefore,

$$\int \Phi_r^* \Phi_s(K) d\tau = \delta_{rs} \tag{70}$$

is also valid because in the states r and s, if these differ, at least two states of a φ_{Kj} are different. If continuous functions exist, the eigendifferentials in Eq. (69) are written with this thought in mind.

That we write a pure product in Eq. (68) shows a certain relationship to the Hartree treatment or to the shortened method of molecular states, where in the first step a formulation is used for the wave function that is not antisymmetrical. In the sense of the perturbation calculation, whose formulation has been written out so far only for orthogonal function sets, we write the total wave function of Eq. (1) as a development

$$\psi_s = \phi_s(K) + \sum_{i=1}^{\infty} \mu_K^i \psi_s^{(i)}(K) \, , \tag{71}$$

where it is to be expected that ψ_s gives an antisymmetrical result for the completion of the series development. Simple examples, which have been calculated through for similar cases, confirm this.[10] The μ_K are parameters which we will now go into further, and $\psi_s^{(i)}(K)$ will be determined more closely in the frame of perturbation theory.

Corresponding to Eq. (71) we also can write for the electron energy of the system

$$E_s = \mathcal{E}_s(K) + \sum_{i=1}^{\infty} \mu_K^i \mathcal{E}_s^{(i)}(K) \, . \tag{71a}$$

With Eq. (19) the Hamiltonian operator can now be represented, for a formal expansion of Eq. (17), in the form

$$H = H(K) + \mu_K V(K) \, . \tag{71b}$$

In the Eqs. (19), (70), (71), (71a), and (71b) we have the basic equations of the perturbation theory. With them we can consider the results from the substitution of Eq. (71) in the energy expression E_s of Eq. (10), and compare the resulting single expressions with equal powers of μ_K [together with Eq. (71)]. That gives defining equations for the $\psi_s^{(i)}(K)$ and the corresponding $\mathcal{E}_s^{(i)}$.

If further $\psi_s^{(i)}$ is developed similarly according to the complete system of the $\Phi_s(K)$ and Eqs. (19) and (71b) are again heeded, one finally obtains the following equations for the first $\mathcal{E}_s^{(i)}$:

$$\mathcal{E}_s^{(1)}(K) = \int \Phi^*(K) V(K) \Phi(K) d\tau = V_{ss}(K) \, , \tag{72a}$$

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[8] If in Eq. (65) all $\Phi_r(K)$ of the rth energy surfaces were collected together, their determination would be valid only for the rth state.

[9] H. Preuss, technical note, April 20, 1959, University of Uppsala, Uppsala, Sweden.

[10] P.-O. Löwdin and J. O. Hirschfelder, technical report, August 20, 1957, University of Uppsala, Uppsala, Sweden.

$$\mathcal{E}_s^{(2)}(K) = \sum_{m\neq s} \frac{V_{sm}(K)V_{ms}(K)}{\mathcal{E}_s(K) - \mathcal{E}_m(K)}\,, \qquad (72b)$$

$$\vdots \qquad \vdots$$

as well as for the $\psi_s^{(i)}$

$$\psi_s^{(1)}(K) = \sum_{m\neq s} \Phi_m(K)\frac{V_{sm}(K)}{\mathcal{E}_s(K) - \mathcal{E}_m(K)} \qquad (73a)$$

$$\psi_s^{(2)}(K) = \sum_{m\neq s}\left[\sum_{k\neq s}\frac{V_{mk}(K)V_{ks}(K)}{[\mathcal{E}_s(K)-\mathcal{E}_k(K)][\mathcal{E}_s(K)-\mathcal{E}_m(K)]} - \frac{V_{ss}(K)V_{sm}(K)}{[\mathcal{E}_s(K)-\mathcal{E}_m(K)]}\right]\Phi_m(K)\,. \qquad (73b)$$

$$\vdots \qquad \vdots$$

Higher approximations of the perturbations theory result in rather complicated expressions. Eqs. (72) and (73) suffice for a determination of ψ_s and E_s if the "perturbation" $V(K)$ is small enough, whereby the products of the integral V_{sk} disappear rapidly enough if the order (i) of the development increases. But V_{sk} is only small if we remain in the vicinity of an association $[K]$ for the arrangement of the atomic nucleus. Otherwise, we must proceed from another association which gives sufficiently small V_{sk}.

We want to distinguish between the single developments (71) and (71a), which proceed from a definite association $[K]$, by means of $\psi_s^{(K)}$ snd $E_s^{(K)}$, which are mutually equal if all approximations are allowed, all μ_K are mutually equal, and the treatment converges.

Hence, we can simultaneously link up all $\psi_s^{(K)}$ and $E_s^{(K)}$

$$\psi_s = \sum_K^{\bar{A}_N} \lambda(K)\psi_s^{(K)}, \qquad (74)$$

$$E_s = \sum_K^{\bar{A}_N} \lambda(K)E_s(K)\,, \qquad (75)$$

if only

$$\sum_K^{\bar{A}_N} \lambda(K) = 1 \qquad (76)$$

is valid. In order to agree again with Eq. (17), we also want the above requirement on the μ_K to be limited by

$$\mu_K \equiv \mu_L \equiv 1\,, \qquad (K \neq L)\,. \qquad (77)$$

Thus, because of Eq. (76), in Eqs. (74) and (75) it is done by taking the means from the $\psi_s^{(K)}$ and $E_s^{(K)}$, which still depend on all $R_{\lambda\mu}$.

Because of Eqs. (20) and (22) it is required of the $\lambda(K)$, along with Eq. (76), that the following relation is satisfied

$$\lim_{[K]} \lambda(L) = \delta_{KL}\,. \qquad (78)$$

Now if we link up the ith approximations of Eqs. (71) and (71a) we obtain the developments

$$\psi_s = \bar{\psi}_s^{(0)} + \bar{\psi}_s^{(1)} + \cdots \bar{\psi}_s^{(L)} + \cdots\,, \qquad (79a)$$

$$E_s = \bar{E}_s^{(0)} + \bar{E}_s^{(1)} + \cdots \bar{E}_s^{(L)} + \cdots\,, \qquad (79b)$$

where individually we get

$$\bar{\psi}_s^{(0)} = \sum_K^{\bar{A}_N} \lambda(K)\Phi_s(K)\,, \qquad (80a)$$

$$\bar{\psi}_s^{(1)} = \sum_K^{\bar{A}_N} \lambda(K)\sum_{m\neq s}\frac{V_{sm}(K)}{\mathcal{E}_s(K) - \mathcal{E}_m(K)}\,\Phi_m(K)\,, \qquad (80b)$$

$$\vdots \qquad \vdots$$

as well as

$$\bar{E}_s^{(0)} = \sum_K^{\bar{A}_N} \lambda(K)\mathcal{E}_s(K)\,, \qquad (81a)$$

$$\bar{E}_s^{(1)} = \sum_K^{\bar{A}_N} \lambda(K)V_{ss}(K)\,, \qquad (81b)$$

$$\bar{E}_s^{(2)} = \sum_K^{\bar{A}_N} \lambda(K)\sum_{m\neq s}\frac{V_{sm}(K)V_{ms}(K)}{\mathcal{E}_s(K) - \mathcal{E}_m(K)}\,. \qquad (81c)$$

$$\vdots \qquad \vdots$$

Due to Eqs. (78) and (18a), the approximations for $i \geqslant 1$ in Eq. (79) disappear for every transition into an atomic association.

An important circumstance is that by means of the coupling of the single $\psi_s^{(K)}$ and $E_s^{(K)}$ in Eqs. (74) and (75) the relationship, as it existed in the original form of the perturbation calculation, between the single approximations $\psi_s^{(i)}(K)$ and $\mathcal{E}_s^{(i)}(K)$ of Eqs. (71) and (71a) is lost. That is, that we thus still have included from Eq. (79) the approximation of the ith order, but that we can no longer assume any definition of an order for the perturbations calculation in Eq. (79). It can thus arise, for example, that a definite choice of the $\lambda(K)$ gives good $\bar{E}_s^{(0)}$-values ($|\bar{E}_s^{(i)}| < |\bar{E}_s^{(0)}|$, for $i \geqslant 1$), but that $\bar{\psi}_s^{(0)}$ still represents a rough approximation with this $\lambda(K)$.

If we assume at first that the development (71a) converges, then

$$E_s^{(K)} = \mathcal{E}_s(K) + \sum_{i=1}^{m} \mathcal{E}_s^{(L)}(K) + R_m^{(s)}(K) \qquad (82)$$

is valid, with

$$|R_{m+1}^{(s)}(K)| < |R_m^{(s)}(K)|\,. \qquad (82a)$$

From this it follows from Eq. (79b) that

$$E_s = \bar{E}_s^{(0)} + \sum_{i=1}^{m} \bar{E}_s^{(i)} + \bar{R}_m^{(s)}(\lambda) \tag{83}$$

$$\bar{R}_m^{(s)}(\lambda) = \sum_{K}^{\bar{A}_N} \lambda(K) R_m^{(s)}(K) \, . \tag{83a}$$

Due to Eq. (76) $|\bar{R}_m(\lambda)|$ is always smaller than (or at most, equal to) the largest $|R_m(K)|$.

If now we set $m = \bar{A}_N - 1$, $\lambda(K)$, for example, can be uniquely determined from the requirements of Eq. (76) and

$$\bar{E}_s^{(i)} = 0 \qquad (i = 1 \cdots m) \, , \tag{84}$$

one obtains

$$\lambda(K) = D_m(K)/D_m \, , \tag{85}$$

where $D_m(K)$ represents the minor of

$$D_m = \begin{vmatrix} 1 & 1 & 1 \cdots 1 \\ \mathcal{E}_s^{(1)}(K) & \cdots & \mathcal{E}_s^{(1)}(\bar{A}_N) \\ \cdot & & \cdot \\ \vdots & & \vdots \\ \mathcal{E}_s^{(m)}(K) & \cdots & \mathcal{E}_s^{(m)}(\bar{A}_N) \end{vmatrix} \, , \tag{86}$$

if the first row and the Kth column are struck out and are multiplied by $(-1)^{K+1}$.

Due to Eq. (18a) one recognizes with Eqs. (72), (85), and (86) that Eq. (78) is also satisfied for $\lambda(K)$. Equation (83) transforms from there in

$$E_s = \frac{1}{D_m} \sum_{K}^{\bar{A}_N} \mathcal{E}_s(K) D_m(K) + \bar{R}_m(\lambda) \, , \tag{87}$$

if the $\lambda(K)$ of Eq. (85) is substituted in $\bar{R}_m(\lambda)$ from Eq. (83a). The first sum of Eq. (87) has the form of $\bar{E}_s^{(0)}$ from Eq. (81a). That means that λ functions have been found from Eq. (85) [already substituted in $\bar{E}_s^{(0)}$ of Eq. (81a)] that approximate energy surfaces up to the error $|\bar{R}_m(\lambda)|$. From Eq. (87) it also follows that

$$E_s = D_m^{(E)}/D_m + \bar{R}_m(\lambda) \tag{88}$$

with

$$D_m^{(E)} = \begin{vmatrix} \mathcal{E}_s(K)\mathcal{E}_s(L) & \cdots & \mathcal{E}_s(\bar{A}_N) \\ \mathcal{E}_s^{(1)}(K) & \cdots & \mathcal{E}_s^{(1)}(\bar{A}_N) \\ \cdot & & \cdot \\ \vdots & & \vdots \\ \mathcal{E}_s^{(m)}(K) & \cdots & \mathcal{E}_s^{(m)}(\bar{A}_N) \end{vmatrix} \, . \tag{88a}$$

For diatomic molecules ($\bar{A}_N = 2$) one obtains from Eqs. (85) and (86) the λ functions

$$\lambda(K) = \frac{\mathcal{E}_s^{(1)}(L)}{\mathcal{E}_s^{(1)}(L) - \mathcal{E}_s^{(1)}(K)} \tag{89}$$

and

$$\lambda(L) = \frac{\mathcal{E}_s^{(1)}(K)}{\mathcal{E}_s^{(1)}(K) - \mathcal{E}_s^{(1)}(L)} \, , \tag{89}$$

which due to Eq. (72a) assume the form

$$\lambda(K) = \frac{V_{ss}(L)}{V_{ss}(L) - V_{ss}(K)} \, ; \lambda(L) = \frac{V_{ss}(K)}{V_{ss}(K) - V_{ss}(L)} \, . \tag{89a}$$

From Eq. (89a) we then get the expression

$$E_s \approx \bar{E}_s^{(0)} = \frac{\mathcal{E}_s(K) - [V_{ss}(K)/V_{ss}(L)]\mathcal{E}_s(L)}{1 - V_{ss}(K)/V_{ss}(L)} \, , \tag{90}$$

as an approximation of the energy and from which is thus produced a relationship with the $P_{\lambda\mu}$ functions of Eq. (50). The requirements (76) and (78) on $\lambda(K)$ are also satisfied by B_K of Eqs. (46) and (52) so that a further possibility for $\lambda(K)$ exists in the equality

$$\lambda(K) \equiv B_K \, . \tag{91}$$

For $\bar{A}_N \geqslant 3$ the B_K of Eq. (52) and the $\lambda(K)$ of Eq. (85) are different, but for $\bar{A}_N = 2$, Eq. (91) can be used in agreement with both cases if we set

$$P_{\lambda\mu} = -V_{ss}(K)/V_{ss}(L) \tag{92}$$

and $[K]$ represents the association of the united atoms. Definition (92) consequently gives a $P_{\lambda\mu}$ which can be used in Eq. (64) for the state s.

In principle, there is for every s a set of $\lambda(K)$ functions for which

$$\sum_{i=1}^{\infty} \bar{E}_s^{(i)} = 0 \tag{93}$$

is valid so that the exact energy can be described in the form of (81a):

$$E_s = \bar{E}_s^{(0)} \, . \tag{94}$$

Also these $\lambda(K)$ exist if series (87) no longer converges. From this, one sees that the $\lambda(K)$ in Eq. (83) can alter the convergence behavior in that they have an influence on the contributions of $\bar{E}_s^{(i)}$ to the total energy in Eq. (81b) and further approximations for $i = 2, \cdots$.

The behavior of $\bar{E}_s^{(0)}$ may be studied still further if the $\lambda(K)$ of Eq. (91) are used. If there are three atoms—a, b, and c—and the last is removed, one obtains the expression

$$\bar{E}_s^{(0)} = \frac{\mathcal{E}_s(c|ab) + P_{ab}\mathcal{E}_s(a|b|c)}{1 + P_{ab}} \tag{95}$$

which, due to Eq. (24), must also be written in the form

$$\bar{E}_s^{(0)} = \mathcal{E}_s(c) + \frac{\mathcal{E}_s(ab) + P_{ab}\{\mathcal{E}_s(a) + \mathcal{E}_s(b)\}}{1 + P_{ab}} \, . \tag{95a}$$

The quotient (95a) will likewise be obtained for $N = 2$.

If four atoms—a, b, c, and d—are thus removed (the separations a, b and c, d remaining finite), the $\bar{E}_s^{(0)}$, corresponding to Eq. (56), transforms to

$$\bar{E}_s^{(0)} = \frac{\mathcal{E}_s(ab|cd) + P_{ab}\mathcal{E}_s(cd|a|b) + P_{cd}\mathcal{E}_s(ab|c|d) + P_{ab}P_{cd}\mathcal{E}_s(a|b|c|d)}{1 + P_{ab} + P_{cd} + P_{ab}P_{cd}}, \tag{96}$$

which may also be written as a sum of two expression for $N = 2$ [compare with Eq. (57)]:

$$E_s^{(0)} = \frac{\mathcal{E}_s(ab) + P_{ab}\mathcal{E}_s(a|b)}{1 + P_{ab}} + \frac{\mathcal{E}_s(cd) + P_{cd}\mathcal{E}_s(c|d)}{1 + P_{cd}}. \tag{96a}$$

Equation (93) means for the diatomic molecule that a P_{ab} from Eq. (95a) exists which gives the proper curve of the energy with

$$P_{ab} = \frac{\mathcal{E}(ab) - E(\text{measured})}{E(\text{measured}) - \mathcal{E}(a|b)}. \tag{97}$$

The difference between the P_{ab} of Eqs. (92) and (97), if the latter is known, gives information in so far as the assumption (84) of the atomic association treatment already describes the relations in the diatomic molecule.

4. GENERAL FORMULATION OF THE TREATMENT

In Sec. 3a, we obtained Eq. (55) for the case of three atoms—a, b, and c—and the transition $R_{bc} \to \infty$ and $R_{ac} \to \infty$. According to Eq. (55a) the system

$$a - b \cdots c \tag{98}$$

can thus be described with

$$\omega(ab|c) = \mathcal{A}\varphi_c\eta(a - b). \tag{98a}$$

If atom a is removed

$$a \cdots b - c, \tag{99}$$

one obtains in the place of Eq. (98a) the function

$$\omega(a|bc) = \mathcal{A}\varphi_a\eta(b - c). \tag{99a}$$

Now if the system

$$a \cdots b \cdots c \tag{100}$$

is not stable, in contrast to the molecules a-b and b-c, the representations (98a) and (99a) can be comprehended as stable ground states (substitution)

$$a + b - c \rightleftarrows a - b + c \tag{101}$$

for whose accomplishment a certain energy is necessary and which one defines as the activation energy (101) (with definite corrections).

If we also include excited atoms (*) or atoms with free valences (x) or ions (±), the following types of substitution reactions can be described with the limiting conditions (98a) and (99a)

$$\begin{aligned}
&(\alpha)\ c + b - a \rightleftarrows \begin{cases}(c - b)^- + a^+\\ (c - b)^+ + a^-\end{cases}\\
&c^+ + b - a \rightleftarrows \begin{cases}(c - b)^+ + a\\ c - b + a^+\end{cases}\\
&(\beta)\ c^* + b - a \rightleftarrows \begin{cases}(c - b)^* + a\\ c - b + a^*\end{cases}\\
&(\gamma)\ c^x + b - a \rightleftarrows \begin{cases}(c - b)^x + a\\ c - b + a^x\end{cases}
\end{aligned} \tag{102}$$

which, among other things, one defines as nucleophillic, electrophillic (α), or radial (γ) substitution mechanisms. In all cases, one assumes that a more or less loose transition state is formed and then decays. With Eq. (57) the limiting states of the reaction

$$\begin{array}{c} a \\ | \\ b \end{array} + \begin{array}{c} c \\ | \\ d \end{array} \rightleftarrows \begin{array}{c} a - c \\ b - d \end{array} \tag{103}$$

can be represented by means of

$$\omega(ab|cd) = \mathcal{A}\eta(a - b)\eta(c - d), \tag{104a}$$

$$\omega(ac|bd) = \mathcal{A}\eta(a - c)\eta(b - d), \tag{104b}$$

if on both sides of Eq. (103) the separations between unbonded atoms go to infinity.

Within the concept of the atomic associations both processes can be described by an expansion of Eq. (62) if the following formulations are applied for the reactions (102) and (103):

$$\bar{\chi} = C_{\text{I}}\omega(ab|c) + C_{\text{II}}\omega(a|bc), \tag{105}$$

$$\bar{\chi} = C_{\text{I}}\omega(ab|cd) + C_{\text{II}}\omega(ac|bd). \tag{106}$$

As in Eq. (62),

$$C_{\text{I}} = 0 \quad \text{if} \quad R_{ab} \to \infty, \quad R_{ac} \to \infty$$

and

$$C_{\text{II}} = 0 \quad \text{if} \quad R_{ac} \to \infty, \quad R_{bc} \to \infty, \tag{105a}$$

are now valid for (105) and the same for (106) if the molecules a–b and c–d or a–c and b–d are separated from one another.

After the C_{I} and C_{II} of Eqs. (105) and (106) have been calculated from a secular problem we can proceed as in Eq. (64), i.e., the total wave function is written as a linear combination of all $\bar{\chi}$:

$$\tilde{\psi}_s = \sum_r C_{sr}\bar{\chi}_r \, . \tag{107}$$

The formulation of this method can now be made more generalized. We remarked in Sec. 2 that by means of atomic associations the *points* are distinguished on the energy surfaces whose corresponding energy values can be represented as sums of energy coming from the single-center systems. This energy enters into the theory as exact values in that the wave function is constructed with the eigensolutions of this particular atomic configuration, and use is made in the calculation of the partitioning of H in Eq. (17). Corresponding to the representations (105) and (106) only one partitioning of H in this way can be assumed:

$$\begin{aligned} H &= H(a-b,c) + V(a-b,c) \, , \\ H &= H(b-c,a) + V(b-c,a) \, , \end{aligned} \tag{108}$$

that the $\omega(\lambda\mu,\nu)$ are now eigensolutions of

$$\{H(\lambda-\mu,\nu) - E(\lambda-\mu,\nu)\}\omega(\lambda\mu,\nu) = 0 \tag{109}$$

and the energy is

$$E(\lambda-\mu,\nu) = \mathcal{E}(\nu) + \mathcal{E}(\lambda-\mu) \, , \tag{109a}$$

if $\mathcal{E}(\lambda-\mu)$ is the electron energy of the molecule $\lambda-\mu$ and $\mathcal{E}(\nu)$ is explained according to Eq. (25). Corresponding to Eq. (18)

$$\lim \langle|V(\lambda-\mu,\nu)|\rangle = 0 \tag{110}$$

is now valid if

$$R_{\lambda\mu} \to \infty \, , \qquad R_{\mu\nu} \to \infty \, . \tag{111}$$

That means, then, that we have distinguished definite *curves* on the energy surfaces which are given by $\mathcal{E}(\lambda-\mu)$. The last step consequently represents a logical extension of the concept developed in Sec. 2.

If H were to be partitioned as

$$H = H(\lambda-\mu,\nu-\sigma) + V(\lambda-\mu,\nu-\sigma) \tag{112}$$

for $\omega(\lambda\mu|\nu\sigma)$ of Eq. (106), then the ω are now solutions of

$$\{H(\lambda-\mu,\nu-\sigma) - E(\lambda-\mu,\nu-\sigma)\}\omega(\lambda\mu|\nu\sigma) = 0 \, , \tag{113}$$

where

$$E(\lambda-\mu,\nu-\sigma) = \mathcal{E}(\lambda-\mu) + \mathcal{E}(\nu-\sigma) \, , \tag{113a}$$

and $\langle|V(\lambda-\mu,\nu-\sigma)|\rangle$ in Eq. (112) disappears if the two molecules are separated from one another.

It would be possible to say the same about the Eqs. (109) and (113) in relation to the partitioning in Eqs. (108) and (112), as was noticed about Eq. (19) relative to Eq. (17). In the place of Eq. (26) we now have Eqs. (98a) and (103).

It is also possible to begin with a partitioning of the Hamiltonian operator according to the general representation (59), but processes (101) and (103) might be of greater chemical interest.

The equations used so far assume the *exact solutions* of Eqs. (19), (25), (109), or (113) in all cases, with which the total wave functions were constructed, whereby definite functions $P_{\lambda\mu}(R_{\lambda\mu})$ of Eqs. (50) and (52) or coefficients of Eq. (65) were determined so that the electron energy of the total system transforms to the *exact energy values* of the above solutions for certain configurations of the atomic nuclei.

It may be assumed that the center of a partial union, consisting of N_{Kj} atoms, lies in the center of the nuclear charges $\mathfrak{R}_{Kj}$ of the shared nucleus charges[2]

$$\sum_{\lambda=1}^{NKj} Z_\lambda \mathfrak{R}_{\lambda Kj} = 0 \, , \tag{114}$$

where the distance of the atom λ from the center $\mathfrak{R}_{Kj}$ is

$$\mathfrak{R}_{\lambda Kj} = \mathfrak{R}_\lambda - \mathfrak{R}_{Kj} \quad [\mathfrak{R}_\lambda \text{ of Eq. (5)}] \, . \tag{114a}$$

Requirement (114) also applies to the association of a molecule united to an atom.

If we consider a definite association $[K]$,

$$[K] = [K_1|K_2|\cdots|K_{A_K}] \, , \tag{115}$$

the case can arise that for a fixed atomic arrangement in the molecule definite centers of nuclear charges $\mathfrak{R}_{Kj}$ coincide or are identical with some $\mathfrak{R}_\lambda$. This means, therefore, that the association (115) must be arranged in direct reference with other similarly related associations through definite atomic arrangements, as obtained from Eq. (115), through the combining of partial unions, to produce the aforementioned result. For example, if $\mathfrak{R}_{K1} = \mathfrak{R}_{K2}$ it follows from (115) that

$$[K] \to [K'] = [K_1'|\lambda|\mu|K_3|\cdots|K_{A_K}{}'] \, , \tag{115a}$$

where

$$(K_1') = (K_1K_2) \, , \tag{115b}$$

and consequently

$$A_{K'} < A_K \, . \tag{115c}$$

The associations derived in this way from an association $[K]$ always possess a smaller number of partial unions. We want to designate them as *transition associations* belonging to $[K]$ and write $K[K'$.

From Eqs. (35) and (45) we constructed the total wave function from the eigenfunctions of different associations (no interactions existing between the partial unions). Due to Eq. (35) we require of the coefficients B_K in Eq. (45) that

$$\lim_{[L]} B_K = \delta_{KL} \tag{116}$$

shall be valid. A possible representation of B_K as a function of the nucleus distances $R_{\lambda\mu}$, which also satisfies a number of requirements stated in Sec. 3, was given with Eq. (52) by the Π_K of Eqs. (50) and (51). From Eq. (115a) it must now be required of the B_K in Eq. (45) that they also retain with greater weight the multitude of atomic associations appearing through $\mathfrak{R}_{Ki} = \mathfrak{R}_{Kj}$. That is, that the B_K also must depend on the coordinates of the center of nuclear charge in such a way that a replacement of the atomic associations of Eq. (115a) is assumed for definite arrangements in the molecule, without thereby influencing the earlier stipulations on B_K.

An extension of the definition of B_K of Eq. (52) is possible in this sense as follows:

$$\hat{B}_K = \Gamma_K / \textstyle\sum_L \Gamma_L \, . \tag{117}$$

If the Γ_K are constructed as linear combinations of the Π_K of Eq. (51), then

$$\Gamma_L = \textstyle\sum_K \Pi_K \sigma_L^K \, . \tag{117a}$$

The Π_K are dependent on the nucleus distances of the $P_{\lambda\mu}$ of Eq. (50). Hence, the σ_L^K are to be understood as functions of the separations of the centers of nuclear charge where, corresponding to Eq. (5),

$$|\mathfrak{R}_{Ki} - \mathfrak{R}_{Kj}| = R_{KiKj} \equiv R_{ij} \, . \tag{118}$$

There are many constructions of σ_L^K which agree with requirement (116). We want to choose those that include process (115a), where an association $[K]$ coincides with a minimum of two centers of nuclear charge essentially by taking its place by means of the corresponding transition associations.

In order to show the structure of σ_L^K in detail, we again introduce [as in Eq. (50)] functions $q_{KiKj} \equiv q_{ij}$ between every two centers of nuclear charge $\mathfrak{R}_{Ki}$ and $\mathfrak{R}_{Kj}$ which depend only on R_{ij} [Eq. (118)] and satisfy the following condition

$$\lim_{R_{ij} \to \infty} |q_{ij}(R_{ij})| = \infty \, . \tag{119}$$

Then we define [again analogous to Eq. (51)] the product

$$\gamma_L^K = \prod_{i,j}^{[L]} q_{ij}(R_{ij}) \qquad , \quad K[L \tag{120}$$

wherein only the transition associations of $[K]$ are admitted for $[L]$. Otherwise we set

$$\gamma_L^K \equiv 0 \, . \tag{120a}$$

In Eq. (120) only those q_{ij} are multiplied together whose separations R_{ij} in $[L]$ belong to different partial associations or to separations between a partial association and an atom (when the latter are understood as partial associations). For the association $[L]$ of the united atoms, which is a transition association for every association, we write

$$\gamma_L^L \equiv \gamma_L^K \equiv 1 \, . \tag{120b}$$

Equation (120b) is also valid for an $[L]$ corresponding to separated atoms.

For association $[K] = [K_1|K_2|K_3]$ there exists, for example, four transition associations

$$\begin{aligned} [L] &= [K_1K_2|K_3] \, , \quad [M] = [K_1K_3|K_2] \, , \\ [S] &= [K_1|K_2K_3] \, , \quad [T] = [K_1K_2K_3] \, , \end{aligned} \tag{121}$$

with the γ_X^K functions

$$\begin{aligned} &\gamma_K^K = q_{12}q_{13}q_{23} \, , \quad \gamma_L^K = q_{13}q_{23} \, , \quad \gamma_M^K = q_{12}q_{23} \, , \\ &q_S^K = q_{12}q_{13} \, , \qquad \gamma_T^K = 1 \, . \end{aligned} \tag{121a}$$

If, for example, $(K_1) = a$, $(K_2) = (bc)$ and $(K_3) = (d)$, then $(U) = [ab|c|d]$ is not a transition association of $[K]$, and hence $\gamma_U^K = 0$.

To every association $[K]$ having A_K partial unions there belong $\overline{A}_{A_K} - 1$ transition associations if $\overline{A}_N$, according to Sec. 2, represents the number of associations by N atoms.

Next we set

$$\sigma_L^K = \gamma_L^K / \textstyle\sum_M \gamma_M^K \qquad K[M \, , \tag{122}$$

and, hence, define σ_L^K as a function of the R_{ij}. Due to Eq. (120a), the sum in Eq. (122) runs over the transition associations of $[K]$, which we again denote by the symbol $K[M$. From Eq. (122) it follows that

$$\textstyle\sum_L \sigma_L^K = 1 \quad , \text{ if } \quad K[L \, . \tag{122a}$$

Before we state an interpretation of the σ_L^K as defined in Eqs. (117) and (117a), we want to show that, with σ_L^K [Eq. (122)], the requirements (116) on the $\hat{B}_K$ that were constructed in Eq. (117) are satisfied. For that purpose we must first examine the treatment of σ_L^K for the transition to the different associations. From Eqs. (119), (120), and (122) it follows that

$$\lim_{[K]} \sigma_M^K = \delta_{KM} \tag{123}$$

is valid. For all further transitions it is enough to require that the σ_L^K always remain limited

$$\lim_{[X]} \sigma_L^K < \infty \; . \tag{123a}$$

If Eq. (117a) is substituted in Eq. (117)

$$\hat{B}_K = \frac{\sum_S \Pi_S \, \sigma_K^S}{\sum_L \sum_S \Pi_S \, \sigma_L^S} \tag{124}$$

and if Eq. (122) is heeded, one obtains

$$\hat{B}_K = \frac{\sum_S \Pi_S \, \sigma_K^S}{\sum_S \Pi_S} \tag{124a}$$

and further [due to Eq. (52)]

$$\hat{B}_K = \sum_S B_S \sigma_K^S \qquad S[K \; . \tag{125}$$

As the conditions (46) and (116) are already satisfied for B_s in Eq. (52), it follows with Eqs. (123) and (123a) that for the $\hat{B}_K$

$$\lim_{[L]} \hat{B}_K = \delta_{KL} \; . \tag{126}$$

The efficacy of the σ_L^K is seen best in the frame of the perturbation method (Sec. 3b). From Eq. (91) we can set

$$\lambda(K) = \hat{B}_K \tag{127}$$

and obtain from Eq. (81a) for the first term of the development (79b)

$$\overline{E}^{(0)} = \sum_K^{\bar{A}_N} \hat{B}_K \hat{\mathcal{E}}(K) \; . \tag{128}$$

After introducing Eq. (125) this again transforms to form (81a)

$$\overline{E}^{(0)} = \sum_S B_S \hat{\mathcal{E}}(S) \; , \tag{128a}$$

if in place of $\mathcal{E}(K)$ we set

$$\hat{\mathcal{E}}(S) = \sum_K \sigma_K^S \hat{\mathcal{E}}(K) \qquad S[K \; . \tag{128b}$$

Now if we assume that in the association $[S]$ no center of nuclear charge coincides with another ($\mathfrak{R}_{ij} \neq 0, i \neq j$) and then take relation (119) in the rough form

$$|q_{ij}(R_{ij})| = \infty \quad \text{for} \quad R_{ij} > 0 \; , \tag{119a}$$

it follows from Eq. (128a), due to Eqs. (120) and (122), that

$$\hat{\mathcal{E}}(S) = \mathcal{E}(S) \; . \tag{129}$$

Consequently we again obtain relation (128) for $\overline{E}^{(0)}$. If conversely some of the $\mathfrak{R}_{Kj}$ in $[S]$ are equal, it thus follows from Eq. (119a) that

$$\hat{\mathcal{E}}(S) \approx \mathcal{E}(L) \quad , \quad S[L \tag{130}$$

if the association $[L]$ is the same as that resulting from $[S]$ through the equality of some $\mathfrak{R}_{Kj}$ in the sense of Eq. (115a,b). From these examples, one recognizes that the σ_L^K in Eq. (128b), due to Eq. (122a), assume an average value construction of all energy of atomic association $\mathcal{E}(K)$ whose associations are transition associations to $[S]$, and that the momentary position of the centers of nuclear charge has an influence on which association $[K]$ in Eq. (128b) has the greatest importance.

Finally, the Γ_K functions for three atoms, a, b, and c, can be stated (for later use) whereby the different partial unions and associations are abbreviated in the following manner:

$$(1) = (a), (2) = (b), (3) = (c), (4) = (ab), (5) = (ac), (6) = (bc); [\mathrm{I}] = [abc], [\mathrm{II}] = [a|bc], [\mathrm{III}] = [b|ac], [\mathrm{IV}] = [c|ab], [\mathrm{V}] = [a|b|c] = [1|2|3]. \tag{131}$$

There then results

$$\begin{aligned} \Gamma_{\mathrm{V}} &= P_{12}P_{13}P_{23} \; , & \Gamma_{\mathrm{IV}} &= \frac{P_{13}P_{23}q_{34}}{1 + q_{34}} \; , \\ \Gamma_{\mathrm{III}} &= \frac{P_{12}P_{23}q_{25}}{1 + q_{25}} \; , & \Gamma_{\mathrm{II}} &= \frac{P_{12}P_{13}q_{16}}{1 + q_{16}} \; , \\ \Gamma_{\mathrm{I}} &= 1 + \frac{P_{13}P_{23}}{1 + q_{34}} + \frac{P_{12}P_{23}}{1 + q_{25}} + \frac{P_{12}P_{13}}{1 + q_{16}} \; . \end{aligned} \tag{132}$$

While a convenient connection for the $P_{\lambda\mu}$ functions from Eq. (97) to the potential curves is produced, it is not so easy to find a corresponding relation to the energy surfaces for the q_{ij} functions.

In any event, we will become acquainted with a possibility in Sec. 6 of making use of the behavior of σ_L^K without knowing the q_{ij} functions explicitly.

After the introduction of the q_{ij} functions, the definition (61) of the $P_{\lambda\mu}$ between the centers of nuclear charge is modified. For definite $R_{\lambda\mu} \to 0$ some of the Π_K in Γ_L [Eq. 117a)] disappear as, of course, do those $[K]$ which are not transition associations of the associations indicated by the transition $R_{\lambda\mu} \to 0$, which we can call $[M]$.[11] From Eqs. (117), (117a), and (124a) it then follows for the energy [Eq. (128)] that

$$\overline{E}^{(0)} \; \frac{\sum_K \sum_S \Pi_S \, \sigma_K^S \mathcal{E}(K)}{\sum_S \Pi_S} \; , M[S \tag{133}$$

whereby S runs over only all transition associations of $[M]$. From Eq. (120a) the condition $S[K$ must also be valid for the $[K]$ in Eq. (133), so that in Eq. (133) only transition associations of $[M]$ and their energy

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[11] It should be pointed out here that the association $[M]$ is first represented when all remaining $R_{\lambda\nu}$ go to infinity.

$\mathcal{E}(K)$ enter in. The $P_{\lambda\mu}$ of the remaining Π_S in Eq. (133) are now functions of the center of nuclear charge distances, whose attending partial unions are given by the association $[M]$. Due to the transition $R_{\lambda\mu} \to \infty$, expressions in the form of the left side of Eq. (61) appear in the Π_S [Eq. (51)] in Eq. (133). We designate these Π_S with Π_S', in contrast to the Π_S with which the energy [Eq. (128)] in Eq. (133) likewise can be represented if the partial unions are again understood as atoms, because the transition $R_{\lambda\mu} \to 0$ can be thought of as a reduction in the number of atoms of the system. More general than in Eq. (60), we must require that both representations for $\bar{E}^{(0)}$ be the same. This, then, again leads to a definition of the $P_{KiKj}(R_{ij})$, which appear for $R_{\lambda\mu} \to 0$ and are contained in the Π_K.

A comparison of the two representations for the energy gives for every $[M]$ a number of relationships between Π_S' and Π_S:

$$\frac{\sum_S \Pi_S' \sigma_K^S}{\sum_S \Pi_S'} = \frac{\sum_L \Pi_L \sigma_K^L}{\sum_L \Pi_L}, \quad \begin{matrix} M[S \\ M[K \end{matrix} \quad [K] = 1,2\cdots \tag{134}$$

or, from Eq. (124a), the shorter

$$\hat{B}_K' = \hat{B}_K\,, \tag{134a}$$

from which can be derived the $P_{\lambda\mu}$ between partial unions, which originally were not defined [Eq. (50)].

In the case of three atoms, a, b, and c, the relation for $P_{a,bc}$ follows from Eq. (134)

$$P_{a,bc}(R_{a,bc}) = \frac{P_{ac}(R_{a,bc})P_{ab}(R_{a,bc})q_{a,bc}(R_{a,bc})}{1 + q_{a,bc}(R_{a,bc}) + P_{ab}(R_{a,bc})P_{ac}(R_{a,bc})}\,. \tag{135}$$

Equation (135), when solved for q, gives a q which automatically satisfies Eq. (119) (also compare Eq. (161)]. Similarly, Eq. (123a) is satisfied in the Eq. (132) representations if Eq. (135) is utilized.

5. THE SEMIEMPIRICAL CONCEPTION AND SOME APPROXIMATIONS

Once the formulation has been developed for handling every molecule as an assumed collection of solved single-center problems, the question now arises of how useful the developed equations are in light of our knowledge of the *exact* functions $\varphi_{Kj}(n_{Kj})$ whose eigenvalues give only the approximation solutions $\tilde{\varphi}_{Kj}(n_{Kj})$ and $\tilde{\mathcal{E}}(K_j)$.

In the frame of his method, Moffitt[1] has pointed out in which ways the calculations can be carried out with approximation functions. Later, Bingel[21] and Artman,[12] in particular, did this in another respect.

Applied to the method of atomic associations, this means that the calculation is made formally with the exact solutions $\Phi(K)$ of Eq. (19) as long as possible, and only at the conclusion of the calculation is $\Phi(K)$ replaced by $\tilde{\Phi}(K)$. In this way, the correlations of the electrons of the fictitious single atoms (partial unions) are mutually taken into consideration. An important result is that the limiting behavior of the matrix $\mathfrak{H}$, which is now transformed to $\tilde{\mathfrak{H}}$, still holds because it is valid that

$$\lim_{[K]} \tilde{\mathfrak{H}} = \mathfrak{w}(K)\,, \tag{136}$$

if $\mathfrak{w}(K)$ represents the diagonal matrix of the eigenvalues of Eq. (19) according to Eq. (43a). The longest possible retention of $\Phi(K)$ in the calculations means that the elements of the matrix $\tilde{\mathfrak{H}}$ of Eq. (37a) can be written as

$$\tilde{H}_{rt} = \int \tilde{\chi}_r^* H \tilde{\chi}_t d\tau\,, \tag{137}$$

and further, due to Eq. (53),

$$\tilde{H}_{rt} = \frac{\sum_K \sum_L \Pi_K \Pi_L \tilde{H}_{rt}(K|L)}{\{[\sum_K \sum_L \Pi_K \Pi_L \tilde{S}_{rr}(K|L)][\sum_K \sum_L \Pi_K \Pi_L \tilde{S}_{tt}(K|L)]\}^{\frac{1}{2}}}\,. \tag{138}$$

The individual $\tilde{H}$ and $\tilde{S}$ resulting are

$$\tilde{S}_{rt}(K|L) = \int \tilde{\Phi}_r^*(K)\tilde{\Phi}_t(L)d\tau \tag{139a}$$

and

$$\tilde{H}_{rt}(K|L) = \int \tilde{\Phi}_r^*(K)H\tilde{\Phi}_t(L)d\tau = \mathcal{E}_t(L)\tilde{S}_{rt}(K|L) + \tilde{V}_{rt}^{(L)}(K|L)\,,$$

$$\tilde{V}_{rt}^{(L)}(K|L) = \int \tilde{\Phi}_r^*(K)V(L)\tilde{\Phi}_t(L)d\tau\,, \tag{139b}$$

if Eqs. (17) and (19) find application in (139b) [compare with Eq. (66)].

From Eq. (18a)

$$\lim_{[L]} V_{rt}^{(L)}(K|L) = 0 \tag{140}$$

is still valid, as is [Eq. (20a)]

$$\lim_{[K]} \tilde{S}_{rt}(K|K) = \delta_{rt} \tag{141}$$

for the $\tilde{S}$ integral, which survives due to the limiting conditions for the Π_K of Eq. (52), so that from this

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[12] K. Artmann, Z. Physik **149**, 299 (1957).

the relation (136) results as before for the elements (138) of $\tilde{\mathfrak{H}}$.[13]

That is the semiempirical conception of the variation treatment, which consists of gathering the elements of the matrix $\mathfrak{w}(K)$ from experiments and calculating the integrals of (139) with approximation functions.

There are still three facts to be pointed out, which are characteristic of this form of the method:

1. Through the empirical setting of the "zero levels" $\mathfrak{w}(K)$ of Eq. (133), the molecular energy calculated from Eqs. (36) and (37) is essentially more exact because only the interaction energy of the different associations is handled with approximation functions $\tilde{\Phi}(K)$. Through $\mathfrak{w}(K)$ the largest parts of the energy are determined, so that it can be assumed that the coefficients C_{sr} in Eq. (35) also are a good approximation of those obtained from Eqs. (138) and (139).

2. We are not concerned with a Ritz treatment for the energy variations, which lead to Eq. (36) and (37), because the energy values obtained are beyond the boundaries of the actual ones [compare (8)]. In principle it happens much more often that these energy values lie a bit lower than the exact ones.

3. Because the matrix $\tilde{\mathfrak{H}}$ is usually not Hermitian, in place of $\tilde{\mathfrak{H}}$ we write

$$\tilde{\tilde{\mathfrak{H}}} = \tfrac{1}{2}\,[\tilde{\mathfrak{H}} + \tilde{\mathfrak{H}}^{+}]\,, \tag{142}$$

if $\tilde{\mathfrak{H}}^{+}$ is the matrix adjuncted to $\tilde{\mathfrak{H}}$. Because of the Π_K in Eqs. (138) and (140), the boundary results of $\tilde{\tilde{\mathfrak{H}}}$ remain as obtained by Eq. (136).

Concerning Point 2, notice that we can no longer say which set of functions χ_r of Eq. (35) actually have been used, or whether one even exists. Conversely, we can establish that a more consequential and sensible formulation exists [refering to a calculation of the energy surfaces of molecules with assumptions (137)–(139) as before], which also permits a calculation of the energy of larger molecules because the concept of atomic associations has remained unchanged in basic structure for the semiempirical conception. Together with the Π_K respective to Γ_K, which guarantees the correct behavior of the energy surfaces in definite limiting states, the empirical information emerging in the determination of $\mathfrak{w}(K)$ has been applied in a far-reaching manner.

The chosen approximation functions $\tilde{\Phi}(K)$ can be constructed from either Eqs. (26) or (68), and the approximated total atomic function $\tilde{\varphi}_{Kj}(n_{Kj})$ can be, for example, a Hartree or a Hartree–Fock function. The calculation of the matrix elements of Eq. (139) is also applicable for the case in Eq. (62), from which a $P_{\lambda\mu}$ similarly can be determined.

Consequential behavior likewise is obtained by application of formulations (105) and (106) according to Eq. (139). Together with Eqs. (108) and (109) there now results

$$\begin{aligned}\int \tilde{\omega}^*(\lambda\mu|\nu)H\tilde{\omega}(\lambda\mu|\nu)d\tau &= E(\lambda-\mu,\nu)\\ &\quad+\int \tilde{\omega}^*(\lambda\mu|\nu)V(\lambda-\mu,\nu)\tilde{\omega}(\lambda\mu|\nu)d\tau\,,\\ \int \tilde{\omega}^*(\lambda|\mu\nu)H\tilde{\omega}(\lambda|\mu\nu)d\tau &= E(\mu-\nu,\lambda)\\ &\quad+\int \tilde{\omega}^*(\lambda|\mu\nu)V(\mu-\nu,\lambda)\tilde{\omega}(\lambda|\mu\nu)d\tau\,,\end{aligned} \tag{143}$$

and, for example

$$\begin{aligned}&\int \tilde{\omega}^*(\lambda\mu|\nu)H\tilde{\omega}(\lambda|\mu\nu)d\tau\\ &\quad= E(\lambda,\mu-\nu)\int \tilde{\omega}^*(\lambda\mu|\nu)\tilde{\omega}(\lambda|\mu\nu)d\tau\\ &\qquad+\int \tilde{\omega}^*(\lambda\mu|\nu)V(\mu-\nu,\lambda)\tilde{\omega}(\lambda|\mu\nu)d\tau\,,\end{aligned} \tag{143a}$$

if $\tilde{\omega}$ is assumed to be normalized. Here also the potential energy of the atoms λ and μ are experimentally determined from Eq. (109a). The same is true for $\omega(\lambda\mu|\nu\sigma)$ in Eq. (106).

We will consider more closely the calculation of the energy of the system—a, b, and c—with the aid of a secular problem (37) whose matrix elements result from Eq. (143). This procedure shows certain similarities to an earlier method which in special cases drew on the approximation determination of activation energy.[4] Due to Eqs. (110) and (143) one sees from Eq. (37) that for $c \to \infty$, and, respectively, $a \to \infty$, that we obtain the exact energy of the molecules a–b, and, respectively, b–c, plus the energy of the free atoms. In the work named above the two energy curves of the reaction

$$a^- + b-c \to a-b + c^- \tag{144}$$

had been considered in a simple manner for a fixed separation R_{ab} and which results in R_{bc} as a variable. In this case we are concerned with the potential energy curve W_{bc} on the left side of Eq. (144), which is displaced a bit vertically through the ion a^-. On the right side of Eq. (144) the energy curve of the interaction W_c of the ion c^- corresponds to the completed molecule a–b. Because the two curves do not intersect, a rough conclusion can be made about the ex-

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[13] H. Preuss, "Acta Vålådalensis, Part I", 1958, University of Uppsala, Uppsala, Sweden, technical report.

pected "adiabatic activation energy" of Eq. (144) from the course of the lower energy curve.

This simplification of the example (144) is contained in Eq. (31) with Eq. (143), if one interprets the integral in the following way for the rough approximation (R_{ab} = const)

$$E(a,b-c)+\int \tilde{\omega}^*(a|bc)V(a|b-c)\tilde{\omega}(a|bc)d\tau \approx W_{bc}(R_{bc})-W\,,$$
$$E(a-b,c)+\int \tilde{\omega}^*(c|ab)V(c,a-b)\tilde{\omega}(c|ab)d\tau \approx W_c(R_{bc})-W\,, \qquad (145)$$

where W represents the nucleus interation. The overlapping of the two $\tilde{\omega}$ functions may be neglected. Further, it may be assumed that

$$\int \tilde{\omega}^*(a|bc)V(a,b-c)\tilde{\omega}(c|ab)d\tau \approx \int \tilde{\omega}^*(a|bc)V(c,a-b)\tilde{\omega}(c|ab)d\tau = \alpha\,, \qquad (145a)$$

where α may be assumed to be small compared to W_c or W_{bc}.

From Eq. (37) both solutions for (145) are (including W)

$$\mathcal{E} \approx \tfrac{1}{2}[W_{bc}+W_c] \pm (\alpha^2+\tfrac{1}{2}[W_{bc}-W_c]^2)^{\frac{1}{2}}\,, \qquad (146)$$

which for $\alpha = 0$ represent the energy curves mentioned above. If α is shifted slightly from zero the intersection will be raised and the two curves split off at "point of intersection" ($W_{bc} = W_c$) by the amount $|2\alpha|$. The energy trough of the two curves in Eq. (146) is identical with that given above, from which the "activation energy" may be estimated. Thus the calculation of the total energy with the aid of Eq. (143) already includes a known, more simple estimation method.

What has been said so far is essentially an outline of the semiempirical conception of the method of atomic associations. In principle, the $P_{\lambda\mu}$ and q_{ij} functions can be chosen arbitrarily if they satisfy only conditions (50) and (119). Approximations for $P_{\lambda\mu}$ are stated in the Eqs. (63) and (92). The approximation functions $\tilde{\Phi}(K)$ find application in every case. The choice of the $P_{\lambda\mu}$ and the q_{ij} decides how many functions χ_r must be carried along in Eq. (35) and to which approximation the perturbation calculation (79) must be carried through in order to obtain the energy well enough. In the first case the secular problem (36) and (37) can be held to a minimum through an apt choice of the $P_{\lambda\mu}$ and q_{ij} functions, and in the frame of the perturbation calculation we know that there are definite $P_{\lambda\mu}$ and q_{ij} with which the exact electron energy of a system can be described already, through $\overline{E}^{(0)}$ of Eqs. (79b) and (81a).

Thus the $P_{\lambda\mu}$ and q_{ij} functions have an influence on the amount of calculation, hence one should try to go a step farther than we have so far in the application of empirical values because one also uses the measured data for $P_{\lambda\mu}$ and q_{ij} for the determination. In this case the relation (97) can be applied, if one still subtracts from E (measured) the energy of the separated atoms

$$\hat{U}(R) = E(\text{measured}) - \mathcal{E}(a|b)\,, \qquad (147)$$

and which must be written in the form[14]

$$P(R) = \frac{\{\mathcal{E}(ab)-\mathcal{E}(a|b)\}-\hat{U}(R)}{\hat{U}(R)} \quad (\hat{U} \leqslant 0)\,. \qquad (148)$$

According to

$$U = \hat{U} + Z_aZ_b/R_{ab}\,, \qquad (149)$$

$\hat{U}(R)$ goes further together with the potential curve U of the diatomic molecule, whose atoms have the nucleus charges Z_a and Z_b. $U(R)$ can be represented by approximations by means of the known Morse curve[15]

$$U(R) = D\{e^{-2a(R-R_0)} - 2e^{-a(R-R_0)}\} \qquad (150)$$

in which R_0 stands for the equilibrium separation of the atoms and $-D$ is the value of the potential belonging to R_0. The parameter a is determined from the curvature k of Eq. (150), which is connected with the eigenfrequency of the molecule. The D, a, and R_c values for a number of molecules are stated in the literature.[16] Unfortunately, the Morse curves describe the actual potential rather poorly for small and large R, so that with Eqs. (150) and (148) a sufficient approximation for $P(R)$ can be expected only for average R. Conversely, $P(0) = 0$ is not fulfilled with (148) or (149).

It is still valid from Eq. (50) that

$$\lim_{R\to 0} \hat{U}(R) = \mathcal{E}(ab) - \mathcal{E}(a|b) \qquad (151)$$

and

$$\lim_{R\to\infty} \hat{U}(R) = 0\,.$$

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[14] If $\mathcal{E}(ab) - \mathcal{E}(a|b) < \hat{U}$, which usually is satisfied, then $P \geq 0$, as required in Eq. (50b).

[15] M. P. Morse, Phys. Rev. **34**, 57 (1929).

[16] H. Sponer, *Molekülspektren und ihre Anwendungen auf chemische Probleme* (Springer-Verlag, Berlin, 1936). G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., New York, 1950).

When solved for U, it follows from Eqs. (148) and (149) that

$$U = \frac{\mathcal{E}(ab) - \mathcal{E}(a|b)}{1 + P(R)} + \frac{Z_a Z_b}{R}, \qquad (152)$$

so that, for example, with an analytically stated $P(R)$, which still contains free parameters, the condition can be satisfied that

$$\begin{aligned} &(1)\ P(0) = 0 &&(3)\ U(R_0) = -D \\ &(2)\ P(\infty) = \infty &&(4)\ \partial U/\partial R|_{R=R_0} = 0 \\ &&&(5)\ \partial^2 U/\partial R^2|_{R=R_0} = k\,. \end{aligned} \qquad (153)$$

With that, a potential course could be found which should represent a good approximation of all ranges of R.[17]

With the $P_{\lambda\mu}$ values from Eqs. (150) or (152) and (153) we can now consider the treatments of Secs. 3a and 3b. And from Eqs. (134) and (135) we can find the q_{ij} functions if the $P_{\lambda\mu}$ functions are known. Thus we conclude that the determination of the energy surfaces for systems with more than two atoms goes back to diatomic systems and to the atomic energy appearing in the concept of atomic associations. In particular, the method in Sec. 3b (perturbation method) allows an explicit statement of the energy surfaces for $N \geqslant 3$, for which the $P_{\lambda\mu}$ and q_{ij} functions from Eqs. (148), (152), and (134) can serve.

We will carry this out in more detail for the example of a triatomic system a, b, c. The Γ_K functions in this case have been stated already in Eq. (132). With the assistance of Eq. (148) the total energy can be represented by the potential curves $\hat{U}(R)$ between the atoms if we initially ignore the influence of the q_{ij} functions. (In this case we set $q_{ij} = \infty$.) One then obtains

$$\mathcal{E} = \frac{P}{Q} + \frac{Z_a Z_b}{R_{ab}} + \frac{Z_b Z_c}{R_{bc}} + \frac{Z_a Z_c}{R_{ac}} = \frac{P}{Q} + W \qquad (154)$$

with

$$\begin{aligned} P = {} & \Delta' \hat{U}_{ab} \hat{U}_{bc} \hat{U}_{ac} + \Delta^{a}_{bc}[\Delta_{ab} - \hat{U}_{ab}][\Delta_{ac} - \hat{U}_{ac}]\hat{U}_{bc} \\ & + \Delta^{b}_{ac}[\Delta_{ab} - \hat{U}_{ab}][\Delta_{bc} - \hat{U}_{bc}]\hat{U}_{ac} \\ & + \Delta^{c}_{ab}[\Delta_{ac} - \hat{U}_{ac}][\Delta_{bc} - \hat{U}_{bc}]\hat{U}_{ab}\,, \\ Q = {} & \hat{U}_{ab} \hat{U}_{bc} \hat{U}_{ac} + [\Delta_{ab} - \hat{U}_{ab}][\Delta_{ac} - \hat{U}_{ac}]\hat{U}_{bc} \\ & + [\Delta_{ab} - \hat{U}_{ab}][\Delta_{bc} - \hat{U}_{bc}]\hat{U}_{ac} \\ & + [\Delta_{ac} - \hat{U}_{ac}][\Delta_{bc} - \hat{U}_{bc}]\hat{U}_{ab}\,, \end{aligned} \qquad (155)$$

and the abbreviations

$$\hat{U}_{\lambda\mu} \equiv \hat{U}_{\lambda\mu}(R_{\lambda\mu})\,, \qquad (156)$$

as well as

$$\begin{aligned} \Delta' &= \mathcal{E}(abc) - \mathcal{E}(a) - \mathcal{E}(b) - \mathcal{E}(c)\,, \\ \Delta^{\sigma}_{\mu\nu} &= \mathcal{E}(\sigma|\mu\nu) - \mathcal{E}(\sigma|\mu|\nu)\,, \end{aligned} \qquad (156a)$$

and

$$\Delta_{\lambda\mu} = \mathcal{E}(\lambda\mu) - \mathcal{E}(\lambda) - \mathcal{E}(\mu)\,, \qquad (156b)$$

if the zero level of Eq. (154) is the energy of the three separated atoms.

Due to Eq. (24) $\Delta^{b}_{\mu\nu}$ and $\Delta_{\mu\nu}$ are equal in this form. That we distinguish between these two, however, is due to a subsequent adoption of the q_{ij} functions.

With Eq. (154) we found an approximation for the energy surfaces of the triatomic system. It is worth remarking that a development of $\mathcal{E}$ from the $\hat{U}$ functions occurs in the following way:

$$\begin{aligned} \mathcal{E} \approx W & + \left(\frac{\Delta^{c}_{ab}}{\Delta_{ab}}\right)\hat{U}_{ab} + \left(\frac{\Delta^{a}_{bc}}{\Delta_{bc}}\right)\hat{U}_{bc} + \left(\frac{\Delta^{b}_{ac}}{\Delta_{ac}}\right)\hat{U}_{ac} \\ & - \frac{1}{2}\left(\frac{\Delta^{c}_{ab} + \Delta^{a}_{bc}}{\Delta_{ab}\Delta_{bc}}\right)\hat{U}_{ab}\hat{U}_{bc} \\ & - \frac{1}{2}\left(\frac{\Delta^{c}_{ab} + \Delta^{b}_{ac}}{\Delta_{ab}\Delta_{ac}}\right)\hat{U}_{ab}\hat{U}_{ac} \\ & - \frac{1}{2}\left(\frac{\Delta^{a}_{bc} + \Delta^{b}_{ac}}{\Delta_{bc}\Delta_{ac}}\right)\hat{U}_{bc}\hat{U}_{ac} + \cdots\,. \end{aligned} \qquad (157)$$

So for $\Delta^{b}_{\mu\nu} \equiv \Delta_{\mu\nu}$ the initial forms of Eq. (157) give the rough approximation

$$\mathcal{E} \approx W + \hat{U}_{ab} + \hat{U}_{bc} + \hat{U}_{ac} + \cdots \qquad (158)$$

whose interpretation lies at hand.

The passage to the consideration of the q_{ij} functions is easily made with the assistance of Eqs. (124), (125), and (128b). In this case, the structure of Eq. (154) remains, and in place of Eqs. (156a) and (156b) there now enters

$$\begin{aligned} \Delta^{\sigma}_{\mu\nu} &= \hat{\mathcal{E}}(\sigma|\mu\nu) - \hat{\mathcal{E}}(\sigma|\mu|\nu)\,, \\ \Delta_{\mu\nu} &= \mathcal{E}(\mu\nu) - \mathcal{E}(\mu|\nu)\,, \end{aligned} \qquad (159)$$

whereby from Eqs. (128) and (132) we obtain the individual results

$$\begin{aligned} \hat{\mathcal{E}}(\sigma|\mu\nu) &= \frac{\mathcal{E}(\sigma\mu\nu) + q(\sigma|\mu\nu)\mathcal{E}(\sigma|\mu\nu)}{1 + q(\sigma|\mu\nu)}\,, \\ q(\sigma|\mu\nu) &\equiv q_{\sigma,\mu\nu}\,, \end{aligned} \qquad (160)$$

as well as

$$\hat{\mathcal{E}}(\sigma|\mu|\nu) = \mathcal{E}(\sigma|\mu|\nu)\,.$$

The function q can then be determined from Eq. (135)

$$q(\sigma|\mu\nu) = \frac{P_{\sigma,\mu\nu}(1 + P_{\sigma\mu}P_{\sigma\nu})}{P_{\sigma\mu}P_{\sigma\nu} - P_{\sigma,\mu\nu}}\,, \qquad (161)$$

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[17] A paper on this subject is in preparation by the author.

if the $P_{b,\mu\nu}$ is known from Eq. (148). Because $P_{b,\mu\nu}$ and $P_{b\nu}P_{b\mu}$ have about the same course and the numerical values increase rapidly, one can expect that $q(\sigma_1|\mu\nu)$ goes rapidly to infinity with increasing distance. The case where $R_{\sigma,\mu\nu} \rightarrow 0$ should be investigated particularly, although we will not discuss it here.

The formulas are remarkably simplified if the three atoms are on a line. Then we have

$$a \text{ —— } b \text{ —— } c$$

$$R_{ac} = R_{ab} + R_{bc}\,, \qquad R_{b,ac} = \left| R_{bc} - R_{ac}\frac{Z_a}{Z_a + Z_c} \right|,$$

$$R_{c,ab} = R_{bc} + R_{ab}\frac{Z_a}{Z_a + Z_b}\,, R_{a,bc} = R_{ab} + R_{bc}\frac{Z_c}{Z_b + Z_c}. \tag{162}$$

If three of the same a atoms exist and if the $P_{\lambda\mu}$ is brought in again and $R_{ab} = R_{bc} = R$ still holds, it follows from Eqs. (154) and (155) that

$$\overline{E}^{(0)} = \frac{\Delta'\{1 + P^2(R)\} + 2P(R)P(2R)\Delta_{aa}}{1 + 2P(R)P(2R) + P^2(R)\{1 + P(2R)\}} + \frac{5}{2R}\,, \tag{163}$$

where $q(b|ac) = 0$ is set by approximations and the remaining q's are assumed to have been very large; moreover, R cannot be very small, all of which must be left out of Eq. (163).[18] So individually we have

$$\begin{aligned} \Delta' &= \mathcal{E}(aaa) - 3\mathcal{E}(a)\,, \\ \Delta aa &= \mathcal{E}(aa) - 2\mathcal{E}(a)\,. \end{aligned} \tag{163a}$$

With the aid of the $P_{\lambda\mu}$ and q_{ij} functions of Eqs. (148) and (161), one may conveniently make an approximate determination of the energy surfaces of arbitrary atomic systems in complete generality with $\overline{E}^{(0)}$ in Eq. (88a). In the next step there is an improvement because the matrix elements (72a) are calculated with approximation functions and the energy resulting from Eq. (79b) is

$$\tilde{\mathcal{E}}_s \approx \tilde{\mathcal{E}}_s^{(0)} + \tilde{\mathcal{E}}_s^{(1)} \tag{164}$$

if the nearest approximation of Eq. (81b)

$$\tilde{\mathcal{E}}_s^{(1)} = \overline{E}_s^{(1)} = \sum_K^{\bar{A}_N} \lambda(K)\tilde{V}_{ss}(K) \tag{165}$$

is utilized.

Conclusions can be obtained from energy surfaces acquired in this way using approximations for the order of magnitude of the activation energy to be expected. For a detailed statement about the reaction process there are further circumstances to be taken into consideration that arise from the application of the time-dependent perturbation calculation.[19] For that purpose, the knowledge of the energy surfaces is necessary above all else. Only in the pure adiabatic case (very slow nucleus movement) can the ground state of an energy be derived from energy surfaces alone, which essentially represent the activation energy.

6. SOME NUMERICAL CALCULATIONS

The semiempirical conception of the variation treatment (Sec. 3a) may be applied to a simple H_2^+ molecule. For Eq. (62) the applied approximation functions give

$$\begin{aligned} &\tilde{\Phi}_0(a|b) \equiv [2\pi(1 + S)]^{-\frac{1}{2}}(e^{-ra} + e^{-rb}) = \Phi_0(a|b) \\ &\tilde{\Phi}_0(ab) = (8/\pi)^{\frac{1}{2}}e^{-2r_c} = \Phi_0(ab)\,, \text{ (united atom, He}^+\text{)}\,. \end{aligned} \tag{166}$$

From Eq. (109) the operator of the total electron energy has the form

$$H = -\tfrac{1}{2}\,\Delta - \frac{1}{r_a} - \frac{1}{r_b} \qquad \begin{array}{ccc} & R & \\ & \longleftrightarrow & \\ \cdot & \text{——}\cdot\text{——} & \cdot \\ a & c & b\,. \\ \mathrm{H} & & \mathrm{H} \end{array} \tag{167}$$

The integral S in Eq. (166) is

$$S = \frac{1}{\pi}\int e^{-(r_a+r_b)}d\tau\,. \tag{168}$$

The two eigenvalues $\mathcal{E}_0(K)$ in Eq. (19) yield

$$\mathcal{E}_0(a|b) = -0{,}5 \text{ a.u.}\,, \qquad \mathcal{E}_0(ab) = -2{,}0 \text{ a.u.} \tag{169}$$

and the partitioning of the operator H of Eq. (17) is begun in the following way

$$\begin{aligned} &H(a|b) = \begin{cases} -\tfrac{1}{2}\,\Delta - 1/r_a\,, \\ -\tfrac{1}{2}\,\Delta - 1/r_b\,, \end{cases} \quad V(a|b) = \begin{cases} -1/r_b\,, \\ -1/r_a\,, \end{cases} \\ &H(ab) = -\tfrac{1}{2}\,\Delta - 2/r_c\,, \\ &\qquad\qquad V(ab) = 2/r_c - 1/r_a - 1/r_b\,. \end{aligned} \tag{170}$$

Here $H(ab)$ is identical with $\mathcal{H}(c)$ according to Eqs. (24) and (25). $H(a|b)$ likewise can be shown with $\mathcal{H}(b)$ or $\mathcal{H}(a)$.

Available integral tables[20] can be used with success

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[18] The assumption $q(b|ac) = 0$ gives the same sign in Eq. (130), so $\hat{\mathcal{E}}(ac|b) = \mathcal{E}(abc)$.

[19] H. Hellmann, *Einführung in die Quantenchemie* (Franz Deuticke, Wien, 1937).

[20] J. Miller, J. M. Gerhauser, and F. A. Matsen, *Quantum Chemistry Integrals and Tables* (University of Texas Press, Austin, 1959); M. Kotani, A. Amemiya; E. Ishiguro; T. Kimura, *Tables of Molecular Integrals* (Mamzen, Tokyo, 1955); R. C. Sahni and J. W. Cooley, NASA, Washington, D. C., technical note D-146, I, II, 1959; H. Preuss, *Integraltafeln zur Quantenchemie* (Julius Springer-Verlag, Berlin, 1956/61) Vols. I–IV.

for the calculation of the matrix elements of H with the functions (166), which are used in the secular problem (37) [compare Eq. (66)]. Only the three-center integral that occurs

$$[a^{-1}|\overset{1}{b}\,\overset{2}{c}\,] = \frac{1}{\pi}\int\frac{1}{r_a}\,e^{-(r_b+2r_c)}d\tau \qquad (171)$$

has not yet been collected in a table, so by means of the approximations

$$a^{-1}|\overset{1}{b}\,\overset{2}{c}] \approx \begin{cases} \left\{\dfrac{[\overset{1}{a}\,\overset{2}{c}\,]([a^{-1}|\overset{1}{b}\,\overset{2}{b}\,] + [a^{-1}|\overset{1}{c}\,\overset{2}{c}\,])}{[\overset{1}{a}\,\overset{1}{c}\,]([a^{-1}|\overset{1}{b}\,\overset{1}{b}\,] + [a^{-1}|\overset{1}{c}\,\overset{1}{c}\,])}\right\} \lfloor a^{-1}|\overset{1}{b}\,\overset{1}{c}\,] \\[2ex] \left\{\dfrac{[\overset{1}{a}\,\overset{2}{c}\,]([a^{-1}|\overset{1}{b}\,\overset{2}{b}\,] + [a^{-1}|]\overset{1}{c}\,\overset{2}{c}\,)}{[\overset{2}{a}\,\overset{2}{c}\,]([a^{-1}|\overset{2}{b}\,\overset{2}{b}\,] + [a^{-1}|\overset{2}{c}\,\overset{2}{c}\,])}\right\} [a^{-1}|\overset{2}{b}\,\overset{2}{c}\,] \end{cases} \qquad (172)$$

it must be refered back to the known integral $[a^{-1}|\overset{\alpha\alpha}{bc}]$; $(\alpha = 1{,}2)$. The definition of the integral when applied to Eq. (172) is

$$[\overset{\alpha}{\lambda}\,\overset{\beta}{\mu}\,] \equiv \frac{(\alpha\beta)^{\frac{3}{2}}}{\pi}\int e^{-(\alpha r_\lambda+\beta r_\mu)}d\tau\;;$$

$$[\sigma^{-1}|\overset{\alpha}{\lambda}\,\overset{\beta}{\mu}\,] \equiv \frac{(\alpha\beta)^{\frac{3}{2}}}{\pi}\int\frac{1}{r_\sigma}\,e^{-(\alpha r_\lambda+\beta r_\mu)}d\tau\,. \qquad (173)$$

Due to computation (172) one obtains two energy curves for the electron energy $\tilde{E}_0$, as shown in Table II.

TABLE II. Energy values for H_2^+.

R	$\tilde{E}_0$	
0.0	−2.000	−2.000
1.0	−1.479	−1.465
2.0	−1.099	−1.090
3.0	−0.908	−0.904
∞	−0.500	−0.500

The characteristic of the method of atomic associations is that $\tilde{E}_0$ exactly transforms into the eigenvalues of Eq. (169) for $R_{ab} \rightarrow 0$ or $R_{ab} \rightarrow \infty$.

The potential energy curve $\tilde{\mathcal{E}}_0$, with Eqs. (11) and (169) is

$$\tilde{\mathcal{E}}_0 = \tilde{E}_0 + 1/R + 0.5 \qquad (174)$$

from which we get a bonding energy of about −2.60 ± 0.08 eV for a nucleus distance of 2.0 a.u., using the values from Table II. This result is in good agreement with the exact values of 2.78 eV for $R = 2.0$ a.u.

For the H_2 *molecule* there results in place of Eq. (166)

$$\Phi_0(a|b) = \frac{1}{\pi}\,[2(1+S^2)]^{-\frac{1}{2}}(e^{-(r_{a_1}+r_{b_2})} + e^{-(r_{a_2}+r_{b_1})})$$

$$\Phi_0(ab) = \frac{\lambda^3}{\pi}\,e^{-\lambda(r_{c_1}+r_{c_2})}\;; \qquad \lambda = 1.70 \qquad (175)$$

with S from Eq. (168). The "united atom" is now an He atom which again lies in the middle between the two protons. The Hamiltonian operator (in a.u.) is now partitioned according to Eq. (17) as follows:

$$H(a|b) = \begin{cases} -\dfrac{1}{2}\Delta_1 - \dfrac{1}{2}\Delta_2 - \dfrac{1}{r_{a1}} - \dfrac{1}{r_{b2}} \\[1ex] -\dfrac{1}{2}\Delta_1 - \dfrac{1}{2}\Delta_2 - \dfrac{1}{r_{a2}} - \dfrac{1}{r_{b1}} \end{cases}$$

$$V(a|b) = \begin{cases} -\dfrac{1}{r_{a2}} - \dfrac{1}{r_{b1}} + \dfrac{1}{r_{12}} \\[1ex] -\dfrac{1}{r_{a1}} - \dfrac{1}{r_{b2}} + \dfrac{1}{r_{12}} \end{cases}$$

$$H(ab) = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{2}{r_{c1}} - \frac{2}{r_{c2}} + \frac{1}{r_2}$$

$$V(ab) = \left(\frac{2}{r_{c1}} - \frac{1}{r_{a1}} - \frac{1}{r_{b1}}\right) + \left(\frac{2}{r_{c2}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}}\right) \qquad (176)$$

and the eigenvalues from Eq. (19) give

$$\mathcal{E}_0(a|b) = -1{,}0\ \text{a.u.}\,, \quad \mathcal{E}_0(ab) = -2{,}9037\cdots\text{a.u.}\,. \qquad (177)$$

The calculation of the integral that arises likewise can be carried through exactly until we reach the three-center integral

$$[a^{-1}|\overset{1}{b}\overset{\lambda}{c}]$$

and

$$[\overset{1}{a}\,\overset{\lambda}{c}\mid\overset{\lambda}{c}\,\overset{1}{b}\,] = \frac{1}{\pi^2}\,\lambda^3\iint\frac{1}{r_{12}}\,e^{-(r_{a_1}+\lambda r_{c_1}+\lambda r_{c_2}+r_{b_2})}d\tau_1 d\tau_2\,. \qquad (178)$$

The above integral was handled according to the Mulliken approximation[21]:

$$[\overset{1}{a}\,\overset{\lambda}{c}|\overset{\lambda}{c}\,\overset{1}{b}] \approx \tfrac{1}{4}\,[\overset{1}{a}\,\overset{\lambda}{c}][\overset{\lambda}{c}\,\overset{1}{b}]\{[\overset{1}{a}\,\overset{1}{a}|\overset{\lambda}{c}\,\overset{\lambda}{c}] + [\overset{1}{a}\,\overset{1}{a}|\overset{1}{b}\,\overset{1}{b}] + [\overset{\lambda}{c}\,\overset{\lambda}{c}|\overset{\lambda}{c}\,\overset{\lambda}{c}] + [\overset{\lambda}{c}\,\overset{\lambda}{c}|\overset{1}{b}\,\overset{1}{b}]\}\,. \qquad (179)$$

Although as yet there is no exhaustive discussion of the integral approximations used for many quantum chemistry calculations, this much can be said at present: These in forms (172) and (179) are better if the

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[21] R. S. Mulliken, J. Chim. Physi. **46**, 497 (1949).

nucleus distances are made smaller. Hence, one may expect a greater exactness for the H_2 bond energy values calculated in this way because the equilibrium is smaller for H_2 than for H_2^+.

The method of atomic associations for function (175) gives a bond energy of −4.71 eV. The bond distance amounts to 1.42 a.u. The exact values are −4.74 eV and 1.40 a.u.

Finally, the *H_3 system* may be handled according to the generalized treatment (Sec. 4). From Eqs. (105), (108), and (109) we have

$$\begin{array}{ccccc} a & \text{—} & b & \text{—} & c \\ \mathrm{H} & & \mathrm{H} & & \mathrm{H} \end{array}$$

$$V(a-b,c) = -\frac{1}{r_{aj}} - \frac{1}{r_{bj}} - \frac{1}{r_{ci}} - \frac{1}{r_{ck}} + \frac{1}{r_{ij}} + \frac{1}{r_{kj}}$$

$$V(c-b,a) = -\frac{1}{r_{bi}} - \frac{1}{r_{ci}} - \frac{1}{r_{ak}} - \frac{1}{r_{aj}} + \frac{1}{r_{ik}} + \frac{1}{r_{ij}} \qquad (180)$$

$$\tilde{\omega}(ab|c) = \mathcal{A}\tilde{\psi}_{ab}(1,2)\varphi_c(3)[\alpha(1)\beta(2) - \alpha(2)\beta(1)]\alpha(3)$$

$$\tilde{\omega}(bc|a) = \mathcal{A}\tilde{\psi}_{bc}(2,3)\psi_a(3)[\alpha(2)\beta(3) - \alpha(3)\beta(2)]\alpha(1) \qquad (181)$$

where α and β represent the spin functions. [$\mathcal{A}$ is explained in Eq. (27).] $\tilde{\psi}_{ab}$ (and, respectively, $\tilde{\psi}_{bc}$) are approximation solutions for the free H_2 molecule and were regarded as expanded Heitler–London–Wang-functions[22]

$$\tilde{\psi}_{\lambda\mu}(i,j) = e^{-\lambda'(r_{\lambda i}+r_{\mu j})} + e^{-\lambda'(r_{\lambda j}+r_{\mu i})} \qquad (182)$$

in which the parameter λ' is still a function of the nucleus separation. In very good approximation

$$\lambda'(R_{\lambda\mu}) = 1 + 1/4R_{\lambda\mu} \qquad (182a)$$

can be written for $0.5 \leqslant R_{\lambda\mu}$. The φ_μ functions are the solutions for the H atoms (ground state)

$$\varphi_\mu = (1/\pi)^{\frac{1}{2}} e^{-r_\mu}. \qquad (182b)$$

Then the matrix elements from Eq. (143) were calculated with function (181), whereby [due to Eq. (109a)] in

$$E(\lambda-\mu,\nu) = \mathcal{E}(\nu) + \mathcal{E}(\lambda-\mu) \qquad (183)$$

the right side represents the energy of the hydrogen atom and the H_2 molecules (ground state)

$$\mathcal{E}(\nu) = -0.5 \text{ a.u.}$$

$$\mathcal{E}(\lambda-\mu) = -1.0 - \frac{1}{R_{\lambda\mu}} + U(R_{\lambda\mu}), \quad \text{(a.u.)}, \quad (184)$$

which were experimentally determined. The function $U(R)$ represents, according to Eqs. (147) and (149), the potential energy curve of H_2.

The H_3 system was calculated for the case $R_{ab} = R_{bc} = R$, which may exist in reality through the reaction

$$\mathrm{H} + \mathrm{H}_2 \rightleftarrows \mathrm{H}_2 + \mathrm{H}\,. \qquad (185)$$

All three-centered integrals must again be estimated, where we first set $\lambda' = 1$ as a good approximation in the place of Eq. (182a). After adding the nucleus repulsion energy $\sigma/2R$, one obtains the energy values $\tilde{\mathcal{E}}(R)$ for the H_3 complex (atomic units) listed in Table III.

TABLE III. Energy values for H_2, when $\lambda' = 1$.

R	1.0	1.25	1.5	1.75
$\mathcal{E}(R)$	+0.303	+0.086	−0.054	−0.099
R	2.0	2.5	3.0	4.0
$\mathcal{E}(R)$	−0.108	−0.085	−0.057	−0.027

In the next step of the calculation, approximation λ' of Eq. (182a) was used and gave the following results (Table IV), which for $R \leqslant 2.5$ are lower than Table III. Thus the lowest energy of the H_3 system is reached at about $R = 1.85$ a.u. and still lies about 0.05 a.u. ≈ 1.36 eV ≈ 30 kcal/mol higher than these of the free H_2 molecule.

TABLE IV. Energy values for H_2, when (182a) is used.

R	1.0	1.25	1.5	1.75	2.0	2.5
$\mathcal{E}(R)$	+0.18	−0.03	−0.097	−0.118	−0.117	−0.086

These results agree very well with the results of other methods,[23] which likewise give a nucleus distance of about 1.80 to 1.90 a.u. From the 30 kcal/mol energy difference for the H_2 molecule nothing as yet can be concluded further about the activation energy of the H_3 process (185) because in the above calculations the position of the diagonals $R_{ab} = R_{bc} = R$ first were determined on the energy surfaces. Because the tunnel effect and the oscillation states must be taken into account for reaction (185) and the process might in no way follow a purely adiabatic course, an essentially small activation energy can be expected. The measured activation energy lies at about 10 kcal/mol.

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[22] W. Heitler and F. London; Z. Physik **44**, 455 (1927); S. C. Wang, Phys. Rev. **31**, 579 (1928).

[23] H. Eyring and M. Polanyi, Z. Phys. Chem. (B) **12**, 297 (1931); J. O. Hirschfelder, H. Eyring, and B. Topley; J. Chem. Phys. **4**, 170 (1936).

In conclusion, we would like to consider some equations of the perturbation theory concept of the method. For this purpose, consider Eq. (163), which we want to apply to the system of three hydrogen atoms. So from Eq. (163a)

$$\Delta' = -5{,}978 \text{ a.u.}$$

$$\Delta_{aa} = \Delta_{\mathrm{HH}} = -1{,}9037 \text{ a.u.} . \qquad (186)$$

The function $P(R)$ of Eq. (148) was determined from analytical potential curves. As stated above, the q values were taken into consideration in approximation form.

One always finds at about $R = 1.9$ a.u. an energy minimum of -0.165 ± 0.05 a.u. for the H_3 system, which corresponds to an increase in energy of about 3–9 kcal/mol over the H_2 molecule (a good result in view of the applied approximation in the q functions).

It is worth remarking that disregarding the q functions in Eq. (160), which led to representation (154), still did not give a reasonable minimum in the potential curve of the H_3 complex if the separation of neighboring H atoms were set equal in the linear system and varied. Likewise omitting the association $[ac|b]$ results in an unsatisfying course of the curve, if the arrangement of the three atoms is a–b–c.

The examples show that the equations of the atomic association method in the frame of a variation treatment or in the perturbation theory representation reproduce, in their simplest form, interactions between atoms that are essentially correct.

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Structure of Fermion Density Matrices

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1. INTRODUCTION

Can the wave function be eliminated from quantum mechanics and its role be taken over, in the discussion of physical systems, by reduced density matrices? The author has believed in the affirmative answer to this question for over ten years. In the present paper, he attempts to muster the main current evidence in support of this belief. Prior to the Hylleraas Symposium, the available evidence, probably, would not have convinced the average physicist. However, the discovery, during the Symposium of Theorem 9.3, and subsequently of Theorem 9.4, gives real substance to the hope that it will soon be possible to calculate the energy of the ground state of an N-fermion system using density matrices as the main mathematical tool.

In his summary[1] of the Boulder Conference on Molecular Quantum Mechanics, June 1959, C. A. Coulson remarking on the striking resurgence of interest in the density matrix approach to the N-body problem stated, "It has frequently been pointed out that a conventional many-electron wave function tells us more than we need to know. . . . There is an instinctive feeling that matters such as electron correlation should show up in the two-particle density matrix . . . but we still do not know the conditions that must be satisfied by the density matrix. Until these conditions have been elucidated, it is going to be very difficult to make much progress along these lines."

Conditions on the *wave function* are known. It must (i) satisfy Schrödinger's equation, and (ii) be symmetric or antisymmetric with respect to the interchange of similar bosons or fermions, respectively. Condition (i) is easily translated into a variational condition on the two-particle density matrix. However, when Professor Coulson spoke there was no convenient formulation of the conditions on a reduced density matrix implied by the symmetry or antisymmetry of the wave function of the system. This is the important lacuna to which Coulson drew attention,

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[1] C. A. Coulson, Rev. Mod. Phys. **32**, 175 (1960).