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Analysis of the Chemical Bond

II. Examination of Some Semi-Empirical Methods

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Starting from the MO-LCAO energy expression with an approximate correction for left–right correlation formalisms are derived that agree with those of some current semi-empirical schemes, but where the parameters usually fitted to experimental results are given explicitly in an *ab initio* way. The approximations necessary for deriving the different schemes as well as the range of their validity are discussed. For π-electron systems *ab initio* values of the β-parameters (both thermochemical and spectral) are derived.

Key words: Analysis of binding energy – One-electron theories – Neglect of overlap – Hückel parameters.

1. Introduction

The progress of computational quantum chemistry in the past 15 years has been such that many properties of small and medium-sized molecules can be calculated to an accuracy competitive with that of experimental determination [1]. Nevertheless this progress had little impact on a qualitative understanding of the chemical bond. In fact, two branches of theoretical chemistry exist independent of and scarcely influenced by the *ab initio* techniques and their applications, namely

a) the qualitative interpretation of the chemical bond which is based on concepts that originated in the early days of quantum chemistry and which is widely used in textbooks of chemistry,
b) the field of the highly simplified semi-empirical methods which are often successful in limited areas of application and which, due to their simplicity, can easily be discussed and interpreted in terms of certain quantities inherent in the theory.

In this series of papers we outline a formalism starting from a rigorous *ab initio* energy expression that allows for a pictorial discussion of the chemical bond, somewhat in the spirit of Ruedenberg [2]. Part I of this series [3] was mainly concerned with point a) mentioned above. In the present Part II our aim is to recast the rigorous equations into formalisms of various semi-empirical schemes, which enables us to perform calculations corresponding to these semi-empirical methods, but with *ab initio* parameters.

This helps us to state both the domains of applicability of these semi-empirical methods and give a direct physical interpretation of the parameters that enter the theories.

Methods have recently been published for deriving an effective valence-shell Hamiltonian from first principles [4, 5]. The corresponding expressions for the semi-empirical parameters are exact in principle but are so terribly complicated that they seem to be of little practical use for the objectives described above. Our formulae, on the other hand, involve certain approximations. Therefore they are exact only in exceptional cases but they are easily related to relevant physical concepts.

In Sect. 2 we give a brief outline of our method and all the definitions and equations necessary for the following derivations. The expression for the binding energy is well suited to serve as a starting point for further approximations that will lead to simplified equations with structures similar to some well-known semi-empirical schemes (Sect. 3). In Sect. 4 we deal with the problem of the justification of one-electron theories, and in Sect. 5 we examine in detail those merits and weaknesses of the different approximate formalisms that our approach is able to reveal.

2. Outline of the Basic Formalism

In Part I of this series ([3], hereafter referred to as I) we started with a comparison of the bonding situations in H_2^+ and H_2 in order to examine the essential differences between a one-electron and a two-electron bond as regards fragmentation and interpretation of the binding energy. The general procedure of energy fragmentation adopted in I, as well as the basic concepts, are closely related to the work of Ruedenberg [2]. In the case of H_2^+ a fragmentation of the binding energy into *quasiclassical*, *promotion*, and *interference* parts has proven very useful for a better understanding of the physical mechanism of bonding [2, 6], and we found that this kind of fragmentation can also be justified for closed-shell molecules with unpolar or weakly polar bonds, provided one takes care of the essential non-classical two-electron effects like *two-electron interference, left–right correlation*, and *sharing penetration.*

Our procedure is as follows:

The energy of a closed-shell molecule in the one-determinant approximation is (atomic units are used throughout this work)

$$E = 2\sum_{i} h_{ii} + \sum_{i,j} [2(ii|jj) - (ij|ji)] + \sum_{\mu<\nu} \frac{Z_\mu Z_\nu}{R_{\mu\nu}} \tag{1}$$

where i, j run over the doubly occupied MO's, μ and ν denote the nuclei, the Mulliken notation for the two-electron integrals is used, and the one-electron operator is defined by

$$\hat{h}(k) = -\tfrac{1}{2}\Delta_k - \sum_{\pi} \frac{Z_\mu}{r_{\mu k}}$$

(k denotes the kth electron).

The MO's are given as linear combinations of atomic orbitals $\{\chi\}$

$$\varphi_i = \sum_{\mu,s} c^i_{\mu,s}\chi_{\mu s} \tag{2}$$

where s counts the AO's at center μ.

The interference parts of the two-electron integrals $(\mu_s\nu_t|\kappa_u\lambda_v)$ are defined as

$$[\mu_s\nu_t|\kappa_u\lambda_v] = (\mu_s\nu_t|\kappa_u\lambda_v) - \tfrac{1}{4}S_{\mu s,\nu t}\, S_{\kappa u,\lambda v}[(\mu_s\mu_s|\kappa_u\kappa_u) + (\mu_s\mu_s|\lambda_v\lambda_v) + (\nu_t\nu_t|\kappa_u\kappa_u) + (\nu_t\nu_t|\lambda_v\lambda_v)] \tag{3}$$

and are contracted to one- and two-center terms:

$$E'_\mu = \sum_{s,t,u,v} R_{\mu s,\mu t}R_{\mu u,\mu v}\{2[\mu_s\mu_t|\mu_u\mu_v] - [\mu_s\mu_v|\mu_u\mu_t]\} \tag{4}$$

$$g_{\mu s,\nu t} = \sum_{\kappa,u}\sum_{\lambda,v} R_{\kappa u,\lambda v}\{2[\mu_s\nu_t|\kappa_u\lambda_v] - [\mu_s\lambda_v|\kappa_u\nu_t] \qquad \text{for } \mu, \nu, \kappa, \lambda \text{ not all equal} \tag{5}$$

where

$$R_{\mu s,\nu t} = \sum_i c^i_{\mu s}c^i_{\nu t}.$$

The energy expression is simplified by introduction of charge and bond orders

$$q_{\mu s} = 2\sum_{\nu,t} R_{\mu s,\nu t}S_{\nu t,\mu s} \tag{6}$$

$$p^2_{\mu s,\nu t} = 2\left[\left(\sum_{\kappa,u} R_{\mu s,\kappa u}S_{\kappa u,\nu t}\right)\left(\sum_{\kappa,u} R_{\nu t,\kappa u}S_{\kappa u,\mu s}\right) + R_{\mu s,\nu t}\sum_{\kappa,u}\sum_{\lambda,v} S_{\mu s,\kappa u}R_{\kappa u,\lambda v}S_{\lambda v,\nu t}\right]. \tag{7}$$

The next step is the separation of the different physical effects by defining a few parameters.

The one-center parameter

$$\alpha_{\mu s} = -\tfrac{1}{2}\langle\chi_{\mu s}|\Delta|\chi_{\mu s}\rangle - Z_\mu(\mu : \mu_s\mu_s) + \tfrac{1}{2}g_{\mu s,\mu s} \tag{8}$$

is essentially the energy of the AO $\chi_{\mu s}$ in the field of nucleus μ, with a relatively small two-electron interference correction. The "penetration integral" is given by

$$(\mu : \mu_s\mu_s) = \int |\chi_{\mu s}(1)|^2 r_{\mu 1}^{-1}\, d\tau_1.$$

The "resonance parameter"

$$\tilde{\gamma}_{\mu s,\nu t} = -\tfrac{1}{2}\langle\chi_{\mu s}|\Delta|\chi_{\nu t}\rangle - \sum_\kappa Z_\kappa(\kappa : \mu_s\nu_t) + \tfrac{1}{2}S_{\mu s,\nu t}\left\{\sum_{\kappa(\neq\mu)} Z_\kappa(\kappa : \mu_s\mu_s) + \sum_{\kappa(\neq\nu)} Z_\kappa(\kappa : \nu_t\nu_t)\right\} + \tfrac{1}{2}g_{\mu s,\nu t} \tag{9}$$

is mainly a two-center term but contains, in addition, the interference parts of the three-center penetration integrals.

Finally, we can remove the quasiclassical contributions in $\tilde{\gamma}$ by the definition of a "reduced resonance parameter" (first used by Mulliken [7])

$$\tilde{\beta}_{\mu s,\nu t} = \tilde{\gamma}_{\mu s,\nu t} - \tfrac{1}{2} S_{\mu s,\nu t}(\alpha_{\mu s} + \alpha_{\nu t}) \tag{10}$$

that contains nothing else but all of the one- and two-electron interference terms (for a detailed justification of this interpretation, see I).

With the use of Eqs. (2)–(10) one can cast the energy expression (1) into the form

$$\begin{aligned} E = {} & \sum_{\mu}\left[\sum_{s} q_{\mu s}\alpha_{\mu s} + E'_{\mu}\right] + 2 \sum\sum_{(\mu,s) \neq (\nu,t)} \sum_{i} c^{i}_{\mu s}\tilde{\beta}_{\mu s,\nu t}c^{i}_{\nu t} \\ & + \tfrac{1}{2}\sum_{\mu,s}\sum_{\nu,t}\left[q_{\mu s}q_{\nu t} - \tfrac{1}{2}p^{2}_{\mu s,\nu t}\right](\mu_s\mu_s|\nu_t\nu_t) \\ & + \sum_{\mu<\nu}\left[\frac{Z_\mu Z_\nu}{R_{\mu\nu}} - Z_\mu\sum_{t} q_{\nu t}(\mu:\nu_t\nu_t) - Z_\nu\sum_{s} q_{\mu s}(\nu:\mu_s\mu_s)\right]. \end{aligned} \tag{11}$$

(11) is still the MO-LCAO energy we started from. Now we replace the term

$$-\tfrac{1}{2}p^{2}_{\mu s,\nu t}(\mu_s\mu_s|\nu_t\nu_t)$$

by

$$-\tfrac{1}{4}p^{2}_{\mu s,\nu t}\left[(\mu_s\mu_s|\mu_s\mu_s) + (\nu_t\nu_t|\nu_t\nu_t)\right],$$

and it is shown in I that in this way we approximately take into account the left–right correlation while neglecting the sharing penetration terms in (11). The "sharing penetration effect" means increase of the intra-atomic and corresponding decrease of the inter-atomic pair density in the process of bond formation. At small and intermediate distances sharing penetration is of considerable importance, and therefore we have to introduce a compensating correction in addition to the correlation correction described above. It turned out that in the H_2 molecule one gets a very accurate potential curve if one replaces the MO interference term by the respective VB term, and so we replace the $\tilde{\beta}$ and $\tilde{\gamma}$ parameters by parameters β and $\gamma(|\beta| \leqslant |\tilde{\beta}|)$ in such a way that the corresponding energy increase compensates the same percentage of the correlation correction as the shift from MO to VB interference does in the case of H_2.

If we split the final energy expression into one- and two-center terms

$$E = \sum_{\mu}(E^{(1)}_{\mu} + E^{(2)}_{\mu}) + \sum_{\mu<\nu}(E^{(1)}_{\mu\nu} + E_{\mu\nu}^{(2)})$$

we get the "one-electron" terms (remember that they contain two-electron interference contributions)

$$\left.\begin{aligned} E^{(1)}_{\mu} &= \sum_{s} q_{\mu s}\alpha_{\mu s} + 2\sum_{i}\sideset{}{'}\sum_{s,t} c^{i}_{\mu s}\beta_{\mu s,\mu t}c^{i}_{\mu t} \\ E^{(1)}_{\mu\nu} &= 4\sum_{i}\sum_{s,t} c^{i}_{\mu s}\beta_{\mu s,\nu t}c^{i}_{\nu t} \end{aligned}\right\} \tag{12a}$$

or, alternatively,

$$\left.\begin{aligned} E_\mu^{(1)} &= 2 \sum_i \sum_s (c_{\mu s}^i)^2 \alpha_{\mu s} + \sum_i \sum_{s,t}{}' c_{\mu s}^i \gamma_{\mu s,\mu t} c_{\mu t}^i \\ E_{\mu\nu}^{(1)} &= 4 \sum_i \sum_{s,t} c_{\mu s}^i \gamma_{\mu s,\nu t} c_{\nu t}^i \end{aligned}\right\} \tag{12b}$$

and the "two-electron" terms

$$\begin{aligned} E_\mu^{(2)} = \tfrac{1}{2} \sum_s &\left[(q_{\mu s})^2 - \tfrac{1}{2} \sum_{\nu(\neq\mu)} \sum_t p_{\mu s,\nu t}^2 - \tfrac{1}{2} p_{\mu s,\mu s}^2 \right] (\mu_s\mu_s|\mu_s\mu_s) \\ &+ \tfrac{1}{2} \sum_{s,t}{}' \left[q_{\mu s} q_{\mu t} - \tfrac{1}{2} p_{\mu s,\mu t}^2 \right] (\mu_s\mu_s|\mu_t\mu_t) + E'_\mu \end{aligned} \tag{13}$$

$$E_{\mu\nu}^{(2)} = \sum_{s,t} q_{\mu s} q_{\nu t} (\mu_s\mu_s|\nu_t\nu_t) + \frac{Z_\mu Z_\nu}{R_{\mu\nu}} - Z_\mu \sum_t q_{\nu t} (\mu : \nu_t\nu_t) - Z_\nu \sum_s q_{\mu s} (\nu : \mu_s\mu_s).$$

The energy of the isolated atom μ can be written as

$$E_\mu^0 = \sum_{\mu,s} n_{\mu s} \alpha_{\mu s}^0 + E_\mu^{0(2)} \tag{14}$$

where $n_{\mu s}$ is the occupation number of AO $\chi_{\mu s}$, and $\alpha_{\mu s}^0$ is given by the first and second terms of Eq. (8). The molecular binding energy is then the sum of promotion, interference and quasiclassical terms, defined by (15):

$$\left.\begin{aligned} \Delta E &= \left[\sum_\mu (E_\mu^{(1)} - \sum_s n_{\mu s} \alpha_{\mu s}^0) + \sum_\mu (E_\mu^{(2)} - E_\mu^{0(2)}) \right] + \sum_{\mu<\nu} E_{\mu\nu}^{(1)} + \sum_{\mu<\nu} E_{\mu\nu}^{(2)} \\ \Delta E &= \qquad\qquad\qquad E_P \qquad\qquad\qquad + \quad E_I \quad + \quad E_{QC} \end{aligned}\right\} \tag{15}$$

The potential curves obtained with (15) give equilibrium distances that are a few percent larger than the SCF values, but the binding energies and the functional behaviour of $\Delta E(R)$ are clearly superior to SCF energies (see I). Even the homonuclear diatomics Li_2, C_2, N_2, and F_2 are described reasonably well, in contrast to the results of SCF calculations. So we are confident that our scheme comprises all the physical effects that are essential for chemical binding, and that it is a good starting point for an examination of certain approximations leading to simplified formalisms.

3. Derivation of Approximate methods

One of the most drastic approximations in simplified quantum mechanical calculations consists in neglecting the *two-electron contributions* altogether. The Hückel (see e.g. [8]) as well as the extended Hückel theories (EHT) [9, 10] are such one-electron methods, and they form the basis for most of the qualitative reasoning of chemistry textbooks. A particularly attractive feature of these methods is the fact that the total energy is supposed to be given as sum over one-electron (orbital) energies. A famous example for the qualitative arguments that exploit this fact is given by the Walsh rules [11]. Indeed, the usefulness of one-electron methods is considerable, and the theoretical concepts of experimental chemists are closely connected to them. The question why these methods work at all is usually not dealt with in the textbooks. It is clear that two-electron effects play an important role in a molecule but one hopes that they somehow cancel each other or that they can be simulated by the empirical fitting of parameters. We will see below that there really occurs a lot of cancellation between atomic and molecular two-electron terms. This implies that one-electron methods are much more likely to work for binding energies than for total energies.

There are also several semi-empirical methods, where one takes account of the most important two-electron terms in the energy expression but reduces the number of two-electron integrals to be calculated by one or the other NDO (neglect of differential overlap) approximation. The ancestor among the all-electron methods, and still the most popular of these, is the CNDO scheme [12] which itself has a predecessor in the PPP π-electron theory [13].

In the following we start with Eqs. (15) and (11) in order to derive approximate formalisms with structures similar to the extended Hückel, Hückel, and CNDO methods.

3.1. A One-Electron Theory "with Overlap"

Consider the two-electron contributions to the binding energy in (15). We have shown in I that in the vicinity of the equilibrium distance the quasiclassical energy E_{QC} is rather small compared with E_I and E_P, if one restricts oneself to molecules with unpolar or weakly polar bonds and excludes such "unusual" molecules like C_2, N_2, CO.

The term

$$E_P^{(2)} = \sum_{\mu} (E_{\mu}^{(2)} - E_{\mu}^{0(2)}) \tag{16}$$

describes the two-electron contributions to the promotion energy and can safely be neglected provided that ground and promotion states of the atoms differ only slightly (e.g. in H_2 only by orbital contraction). A necessary condition for this to be the case is again an unpolar or weakly polar character of the bonds.

So one can expect that for molecules with (at most) weakly polar bonds the two-electron terms in (15) are negligible:

$$\Delta E \approx \Delta E^{(1)} = 2 \sum_{i} \sum_{\mu,s} (c_{\mu,s}^{i})^2 \alpha_{\mu s} + 2 \sum_{i} \sum_{(\mu,s) \neq (\nu,t)} \sum c_{\mu s}^{i} \gamma_{\mu s,\nu t} c_{\nu t}^{i} - \sum_{\mu,s} n_{\mu s} \alpha_{\mu s}^{0}. \tag{17}$$

The variational minimum of ΔE in (17) is obtained with vectors $\boldsymbol{c}^i$ that are solutions of the equation

$$(\tilde{H} - \tilde{e}_i S) c^i = 0. \tag{18}$$

where the matrix $\tilde{\boldsymbol{H}}$ has α and γ as diagonal and non-diagonal elements, respectively. It is apparent, however, that the one-electron problem (18) cannot in general give reasonable MO vectors $\boldsymbol{c}^i$, because even if the two-electron contributions to the promotion energy $E_P^{(2)}$) are negligible at the energy minimum, their variation with the coefficients is not (E_{QC} on the other hand is rather insensitive to small variations in the $\boldsymbol{c}^i$). Therefore, in a heteronuclear bond like C-H in hydrocarbons one gets a charge "collapse" towards the higher charged nucleus.

$E_\mu^{0(2)}$, the atomic contribution to $E_P^{(2)}$ in Eq. (16), does not depend on the $c^i_{\mu s}$, so we have to calculate $\partial E_\mu^{(2)}/\partial c^i_{\mu s}$ in order to get an idea for an improvement of $\tilde{\boldsymbol{H}}$. The formula of this partial derivative is rather lengthy, but if one retains only the dominant terms (the other terms vanish in the limit of small overlap elements $S_{\mu s,\nu t}$) one gets, under the assumption $\partial E_{QC}/\partial c^i_{\mu s} \approx 0$ for the derivative of ΔE (Eq. (15):

$$\frac{\partial \Delta E}{\partial c^i_{\mu s}} \approx 4(\alpha_{\mu s} + \tilde{C}_{\mu s})c^i_{\mu s} + 4 \sum_{\substack{\nu,t\\(\neq \mu s)}} (\gamma_{\mu s,\nu t} + S_{\mu s,\nu t}\tilde{C}_{\mu s})c^i_{\nu t} \tag{19}$$

where

$$\tilde{C}_{\mu s} = \tfrac{1}{2}q_{\mu s}(\mu_s\mu_s|\mu_s\mu_s) + \sum_{\substack{t\\(\neq s)}} q_{\mu t}(\mu_s\mu_s|\mu_t\mu_t). \tag{20}$$

It is seen that in solving an equation of the form (18) one should take $\alpha_{\mu s} + \tilde{C}_{\mu s}$ as a diagonal element, and $\gamma_{\mu s,\nu t} + 1/2 S_{\mu s,\nu t}\,(\tilde{C}_{\mu s} + \tilde{C}_{\nu t})$ as non-diagonal elements of $\tilde{\boldsymbol{H}}$. Apparently, the terms $\tilde{C}_{\mu s}$ describe the Coulomb interaction of the electron in AO $\chi_{\mu s}$ with the other electrons at center μ, and the diagonal element $\alpha_{\mu s} + \tilde{C}_{\mu s}$ represents a screened orbital energy.

These diagonal elements can approximately be regarded as eigenvalues of an atomic Hartree-Fock operator corresponding to a certain valence state. In extended Hückel theory (EHT) one takes the atomic ionization potentials as diagonal elements, and this procedure is indeed justified by our derivation. As we want to attain a close resemblance to EHT we introduce in the following the atomic orbital energies $\epsilon^0_{\mu s}$ that one obtains in a Hartree-Fock calculation.

We define the atomic screening terms $C_{\mu s}$ as sums of some Coulomb and exchange integrals by

$$\epsilon^0_{\mu s} = \alpha^0_{\mu s} + C_{\mu s}$$

and modified one-electron energies, containing the two-electron interference terms, by

$$\epsilon_{\mu s} = \alpha_{\mu s} + C_{\mu s}. \tag{21}$$

From the charge order definition (6) it follows that

$$\sum_i \sum_{\mu,s} \sum_{\nu,t} c^i_{\mu s} S_{\mu s,\nu t} c^i_{\nu t}(C_{\mu s} + C_{\nu t}) = \sum_{\mu,s} q_{\mu s} C_{\mu s}. \tag{22}$$

If in addition to the screened diagonal parameters $\epsilon_{\mu s}$ we define a screened non-diagonal parameter by

$$\gamma'_{\mu s,\nu t} = \gamma_{\mu s,\nu t} + \tfrac{1}{2} S_{\mu s,\nu t}\,(C_{\mu s} + C_{\nu t}) \tag{23}$$

we get from Eqs. (17), (21), (22), (23):

$$\Delta E \approx 2 \sum_i \sum_{\mu,s} (c^i_{\mu s})^2 \epsilon_{\mu s} + 2 \sum_i \sum \sum_{(\mu,s) \neq (\nu,t)} c^i_{\mu s} \gamma'_{\mu s,\nu t} c^i_{\nu t} - \sum_{\mu,s} n_{\mu s} \epsilon^0_{\mu s} + \sum_{\mu,s} (n_{\mu s} - q_{\mu s}) C_{\mu s}. \tag{24}$$

But we have seen that the "screened one-electron expression" (24) can be an acceptable approximation only in the case of weakly polar bonds, where

$$n_{\mu s} \approx q_{\mu s}. \tag{25}$$

Thus, if the approximations leading to (24) are valid at all, then the last term in (24) can be neglected as well (see, however, Sect. 4), and the vectors $\boldsymbol{c}^i$ that make ΔE minimal are the solutions of

$$(\boldsymbol{H}^E - e_i \boldsymbol{S}) \boldsymbol{c}^i = 0 \tag{26}$$

where $\boldsymbol{H}^E$ has ϵ and γ' as diagonal and non-diagonal elements, respectively. For the binding energy we get

$$\Delta E = 2 \sum_i e_i - \sum_{\mu,s} n_{\mu s} \epsilon^0_{\mu s}. \tag{27}$$

So we have expressed the binding energy (not the total energy!) as sum of one-electron energies in a formalism that takes the non-orthogonality of the AO's explicitly into account (26).

3.2. A One-Electron Theory "without Overlap"

In a Hückel type formalism the overlap matrix $\boldsymbol{S}$ does not show up explicitly in the eigenvalue problem:

$$(\boldsymbol{H}^H - \lambda_i \boldsymbol{I}) \boldsymbol{f}^i = \boldsymbol{0} \tag{28}$$

($\boldsymbol{I}$ denotes the unit matrix). This does not mean, however, that the interatomic overlap can simply be neglected, but only that the empirically fitted parameters in the $\boldsymbol{H}^H$ matrix have values different from those in $\boldsymbol{H}^E$, and the coefficients $f^i_{\mu s}$ differ from the $c^i_{\mu s}$. One can interpret this fact by the assumption that the overlap is in some way implicitly contained in the elements of $\boldsymbol{H}^H$.

We start from the screened one-electron expression (24) and neglect the last term to get

$$\Delta E \approx 2 \sum_i \sum_{\mu,s} (c^i_{\mu s})^2 \epsilon_{\mu s} + 2 \sum_i \sum \sum_{(\mu,s) \neq (\nu,t)} c^i_{\mu s} \gamma'_{\mu s,\nu t} c^i_{\nu t} - \sum_{\mu,s} n_{\mu s} \epsilon^0_{\mu s}. \tag{29}$$

Now we express the reduced resonance parameter β as a function of the screened parameters ϵ and γ' by using the definitions (10), (21), (23):

$$\beta_{\mu s,\nu t} = \gamma'_{\mu s,\nu t} - \tfrac{1}{2} S_{\mu s,\nu t} (\epsilon_{\mu s} + \epsilon_{\nu t}). \tag{30}$$

From the equivalency of Eqs. (10) and (30) as well as Eqs. (12a) and (12b) it follows immediately that instead of (29) we can write

$$\Delta E \approx \sum_{\mu,s} q_{\mu s}\epsilon_{\mu s} + 2\sum_{i}\sum_{(\mu,s)\neq(\nu,t)} c^{i}_{\mu s}\beta_{\mu s,\nu t}c^{i}_{\nu t} - \sum_{\mu,s} n_{\mu s}\epsilon^{0}_{\mu s}. \qquad (31)$$

In this formulation the effect of intra-atomic screening is only contained in the diagonal terms (compare (31) and (12a)), and this is completely consistent with our interpretation of β as a reduced resonance parameter that contains neither one-center nor quasiclassical two-center contributions.

In order to arrive at (28) one has to introduce the following two approximations [14]:

1) The MO's c^i are also eigenvectors of S, i.e.

$$Sc^{i} = s_i c^{i}. \qquad (32)$$

The orthogonality relation of the c^i then reads

$$(c^i)^{+}Sc^j = s_j(c^i)^{+}(c)^j = \delta_{ij}.$$

The new vectors

$$f^{i} = s_i^{1/2}c^{i} \qquad (33)$$

fulfil the relation

$$(f^i)^{+}f^j = \delta_{ij}.$$

For the charge orders we have

$$q_{\mu s} = 2\sum_{i} f^{i}_{\mu s}f^{i}_{\mu s}$$

and instead of (31) we get

$$\Delta E = 2\sum_{i}\sum_{\mu,s}(f^{i}_{\mu s})^{2}\epsilon_{\mu s} + 2\sum_{i}\sum_{(\mu,s)\neq(\nu,t)} f^{i}_{\mu s}\beta_{\mu s,\nu t}f^{i}_{\nu t}/s_i - \sum_{\mu,s} n_{\mu s}\epsilon^{0}_{\mu s}. \qquad (34a)$$

2) The overlap integrals are very small,

$$|S_{\mu s,\nu t}| \ll 1 \qquad (\mu s \neq \nu t) \qquad (35)$$

which means that second-order overlap effects are neglected.

It follows that $s_i \approx 1$ for all i, and Eq. (34a) is reduced to the simple form desired.

$$\Delta E = 2\sum_{i}\sum_{\mu,s}(f^{i}_{\mu s})^{2}\epsilon_{\mu s} + 2\sum_{i}\sum_{(\mu,s)\neq(\nu,t)} f^{i}_{\mu s}\beta_{\mu s,\nu t}f^{i}_{\nu t} - \sum_{\mu,s} n_{\mu s}\epsilon^{0}_{\mu s}. \qquad (34b)$$

For the minimum of ΔE we have to solve the secular equation (28) where H^{H} has ϵ and β as diagonal and non-diagonal elements, respectively. The binding energy is obtained from

$$\Delta E = 2\sum_{i}\lambda_i - \sum_{\mu,s} n_{\mu s}\epsilon^{0}_{\mu s}. \qquad (36)$$

An alternative procedure that leads from (26) to (28) without any approximation is the transformation of H^E to an orthogonalized AO (OAO) basis. But the interpretation of H^H as parameter matrix in an OAO basis has a number of rather unpleasant consequences (see Sect. 5).

3.3. A CNDO*-like Approximation*

The CNDO scheme [12] has originally been designed as an approximate form of the SCF procedure. Therefore we have to start from the SCF energy (11) rather than from Eq. (15) that contains the correlation correction. Remember that in the derivation of (11) we have not employed any kind of NDO approximation but have retained the two-electron interference contributions by the definitions of the α and β parameters.

The two-electron one-center terms E'_μ occurring in (11) constitute the essential difference between the CNDO (neglect of E'_μ) and the INDO methods [15] where these terms are taken into account. So we easily could derive an INDO- instead of a CNDO-like scheme by retaining E'_μ, but this would just complicate our formalism without having any impact on the investigation of the overlap approximations because E'_μ is rather insensitive to the variation of internuclear distance. Thus, we prefer to consider a CNDO-like scheme which implies neglect of the E'_μ terms and a treatment of the "one-electron" part of (11) in the same manner as in the foregoing section:

$$E \approx 2 \sum_i \left[\sum_{\mu,s} (f^i_{\mu s})^2 \alpha_{\mu s} + \sum_{(\mu,s)\neq(\nu,t)} \sum f^i_{\mu s} \tilde{\beta}_{\mu s,\nu t} f^i_{\nu t} \right]$$

$$+ \tfrac{1}{2} \sum_{\mu,s} \sum_{\nu,t} [q_{\mu s} q_{\nu t} - \tfrac{1}{2} p^2_{\mu s,\nu t}] (\mu_s \mu_s | \nu_t \nu_t)$$

$$+ \sum_{\mu<\nu} \left[\frac{Z_\mu Z_\nu}{R_{\mu\nu}} - Z_\mu \sum_t q_{\nu t} (\mu : \nu_t \nu_t) - Z_\nu \sum_s q_{\mu s} (\nu : \mu_s \mu_s) \right]. \tag{37}$$

The bond order (7) can be rewritten using (33) as

$$p^2_{\mu s,\nu t} = \frac{1}{2} \left\{ \left(2 \sum_i f^i_{\mu s} f^i_{\mu s} \right)^2 + 4 \sum_{i,j} \frac{s_j}{s_i} (f^i_{\mu s} f^i_{\nu t})(f^j_{\mu s} f^j_{\nu t}) \right\}. \tag{38}$$

Again we apply approximation (35), i.e. neglect of second-order overlap effects, and get

$$p^2_{\mu s,\nu t} = \left(2 \sum_i f^i_{\mu s} f^i_{\nu t} \right)^2. \tag{39}$$

The minimum of E (note that we are dealing with the total energy in this section) is obtained by solving the eigenvalue problem

$$(F - \epsilon_i I) f^i = 0. \tag{40}$$

The matrix F has elements

$$F_{\mu s,\mu s} = \alpha_{\mu s} + \tfrac{1}{2} q_{\mu s}(\mu_s\mu_s|\mu_s\mu_s) + \sum_{\substack{\nu,t \\ (\neq \mu s)}} q_{\nu t}(\mu_s\mu_s|\nu_t\nu_t) - \sum_{\substack{\nu \\ (\neq \mu)}} Z_\nu(\nu : \mu_s\mu_s) \tag{41a}$$

$$F_{\mu s,\nu t} = \tilde{\beta}_{\mu s,\nu t} - \tfrac{1}{2} p_{\mu s,\nu t}(\mu_s\mu_s|\nu_t\nu_t). \tag{41b}$$

The diagonal element contains, in addition to α, not only the intra-atomic Coulomb screening (see (20)) but also the quasiclassical interatomic electron–electron and electron–nucleus interactions. Of course, the F matrix still shows the main deficiencies of the MO approximation, namely the "self-energy" in the second term of (41a) and the improper asymptotic behavior (second term of (41b)) discussed in I.

For the total energy we have the expression

$$E = 2\sum_i \epsilon_i - \frac{1}{2}\sum_{\mu,s}\sum_{\nu,t}\left[q_{\mu s}q_{\nu t} - \frac{1}{2}p^2_{\mu s,\nu t}\right](\mu_s\mu_s|\nu_t\nu_t) + \sum_{\mu<\nu}\frac{Z_\mu Z_\nu}{R_{\mu\nu}}. \tag{42}$$

Let us conclude this section with a remark on the two-electron interference terms that are contained in the α, β, γ parameters. These terms are dependent on the electron density and should therefore be varied in the variational procedure that leads to Eqs. (26), (28), and (40). Accordingly, not only the SCF-like Eq. (40) but also (26) and (28) should be solved iteratively. But the interference part amounts to not more than a few percent of the total electron–electron interaction, and its variation should be of minor importance. This has indeed been confirmed in a number of iterative calculations, and therefore we keep the $g_{\mu s,\nu t}$ terms (5) fixed at their SCF values.

4. The Two-Electron Contributions to ΔE

The results of this and the following sections are obtained with minimal AO bases (described in detail in I) that are based on the (10*s*) (H in H_2) and (3*s*) (H in other molecules), (9*s*) (Li), and (7*s*, 3*p*) (C, N, O, F) bases of Huzinaga [16]. In H_2 the 1*s* AO is properly scaled, in other molecules the scaling factor for H is chosen as 1.3. The experimental values have been taken from [17].

A one-electron expression for the binding energy like (26) can give reasonable equilibrium distances R_e and binding energies ΔE only if the quasiclassical energy as well as the two-electron part of E_P (16) are relatively small compared to the interference and one-electron promotion energies. The quasiclassical energy E_{QC} (15) corresponds to classical electrostatic Coulomb interactions between point charges (nuclei) and "electron clouds" and should in the case of unpolar single bonds show a potential curve-like behavior with a shallow minimum not too far from the equilibrium distance and a steep ascent at small distances where the nuclear repulsion dominates E_{QC} (see I). Fig. 1 shows the functional behavior of $E_{QC}(R)$ in H_2, and this has indeed been found to be typical for other unpolar single bonds. The quasiclassical energies of Li_2 and F_2 at their experimental equilibrium distances are −0.015 and 0.003 a.u., respectively.

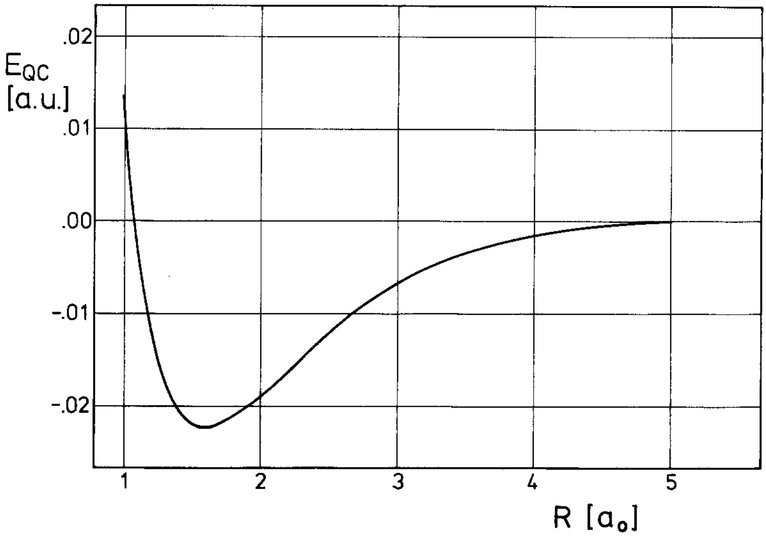

Fig. 1. The quasiclassical energy E_{QC} of H_2, calculated with a scaled minimal basis, as function of the internuclear distance

Unfortunately, a special problem arises with hydrocarbons. According to chemical experience the C-C and C-H bonds in saturated hydrocarbons should be nearly unpolar, and this expectation is essentially confirmed by all of the various existing charge order definitions provided that the AO basis used for the calculation is well balanced or, if minimal, is specially adapted to the molecules in question. But it is well known that in the case of a minimal AO basis as ours, that is taken from atomic calculations, the Mulliken charge orders (6) show an unreasonable charge transfer from H to C. In CH_4, for example, we get $q_H = 0.79$ and $E_{QC} = -0.188$ a.u., which cannot be regarded as small compared to the total binding energy of –0.625 a.u. We shall return to this point below.

In double or triple bonds the quasiclassical energy can be relatively large due to the strong penetration of the "electron clouds". By far the most extreme molecule in this respect is N_2, where we find $E_{QC} = 0.533$ a.u. at $R=R_e$.

At first glance, the difficulties connected with the two-electron part of the promotion energy, $E_P^{(2)}$, look even more depressing than those of E_{QC}. The values of E_P and $E_P^{(2)}$ in Table 1 indicate that H_2, Li_2, and F_2 again are unproblematic. But in saturated hydrocarbons we find that the reasonably small E_P values are the sums of a negative one-electron and a positive two-electron part that are an order of magnitude larger than E_P itself. Obviously, the large charge transfer from H to C, due to our minimal basis and the charge order definition (6), is responsible for this result that would be disastrous for our one-electron theory (26) if this were solely based on the neglect of E_{QC} and $E_P^{(2)}$.

If one does an energy optimization of the 2*s* and 2*p* AO's at carbon one gets $E_P^{(2)} = 2.07$ a.u. in CH_4, so the problem is not solved by a modification of the basis.

Table 1. Total promotion energies E_P and their two-electron parts $E_P^{(2)}$ (in a.u.) for different molecules at experimental geometries

	E_P	$E_P^{(2)}$
H_2[a]	0.037	
Li_2	0.012	0.025
C_2	0.298	0.191
N_2	1.198	0.603
F_2	0.078	0.038
CH_4	−0.087	2.837
C_2H_6	−0.354	4.149

[a] Scaling factor 1.193.

In fact, we are saved by the third approximation introduced in the derivation of (26). Approximation (25) means that we not only neglect E_{QC} and $E_P^{(2)}$ but also a term

$$W = \sum_{\mu, s} (n_{\mu s} - q_{\mu s}) C_{\mu s}. \tag{43}$$

Now it is easily seen that in the case of polar bonds (regardless of the "natural" or "artificial" character of the polarity) W constitutes the main part of $E_P^{(2)}$. In unpolar bonds we have $n = q$ and $W = 0$ but in polar bonds W sums the Coulomb interactions of the transferred charges with the other electrons at the respective atom. Furthermore, W and $E_P^{(2)}$ are of opposite sign. This means that the charge transfer part of $E_P^{(2)}$ is compensated by (43), as can be seen in the following examples (at experimental geometries):

CO	$E_P^{(2)} = 1.37$ a.u.	$W = -0.87$ a.u.
CH_4	$E_P^{(2)} = 2.84$ a.u.	$W = -2.48$ a.u.

There are other contributions to $E_P^{(2)}$, of course, but these are partly compensated by E_{QC} and, what is more important, are not strongly dependent on the internuclear distance. Consequently, we can expect that the EHT-like formalism (26) should yield equilibrium distances not more deviating from experiment than those of Eq. (15), the starting point of our derivation. The binding energies, on the other hand, are likely to show relatively large errors in general.

Equilibrium distances and binding energies calculated with (26) are given in Table 2. The C-H distance in CH_4 and the C-C distance in C_2H_6 are considerably nearer to experiment than those obtained with (15). The accuracy in these cases clearly is fortuitous but one should note that also in H_2, Li_2, and F_2 the R_e values are surprisingly good in view of the drastic approximations introduced in (26), and these results confirm our physical reasoning given above.

So we have found that in the molecules just mentioned the sum of the neglected two-electron terms is little dependent on the internuclear distance, but this does not mean that the sum itself is small. Therefore the binding energies in Table 2 show relatively large deviations from experiment (with the exceptions of H_2 and Li_2) but in the saturated hydrocarbons are still within the +100% range. This result looks rather unfavourable in comparison with the errors in ΔE obtained by (15) (<10% for CH_4, C_2H_6) but it should be remembered that it is an easy matter to shift the potential curves by empirically fitting the parameters that we calculate in an *ab initio* way.

Table 2. Binding energies ΔE (in a.u.), equilibrium distances R_e (in a.u.) and angles obtained with the extended Hückel-type scheme (26) and the "exact" formula (15)

	exp.		Eq. (15)		Eq. (26)	
	ΔE	R_e/Å	ΔE	R_e/Å	ΔE	R_e/Å
H_2	−0.174	1.40	−0.170	1.44	−0.149	1.35
Li_2	−0.042	5.05	−0.026	5.76	−0.054	5.19
C_2	−0.234	2.34	−0.193	2.72	−0.51	3.2
N_2	−0.364	2.08	−0.132	2.31	−0.423	2.59[a]
F_2	−0.062	2.72	−0.082	3.15	−0.488	2.77
CH_4	−0.625	2.05 (CH)	−0.675	2.20	−0.996	2.03
C_2H_6	−1.063	2.93 (CC)	−1.113	3.19	−1.875	3.05
C_2H_4	−0.846	2.55 (CC)	−0.870	2.75	−1.52	≈2.00[a]
CH_2	−0.288	102.5°	−0.241	112°	−0.459	115°[a]
H_2O	−0.350	104.5°	−0.284	115°	−0.909	100°

[a] Solution of (26) gives an unreasonable order of orbital energies (see text).

In molecules with multiple bonds one has rather large $E_P^{(2)}$ values that do not contain charge transfer contributions W. Here a certain cancellation can occur only between E_{QC} and $E_P^{(2)}$, as is shown in Fig. 2 for the N_2 molecule. The much too large R_e value of N_2 (Table 2) can be explained by the fact that the sum of E_{QC} and $E_P^{(2)}$ has its maximum at $R > 3a_0$.

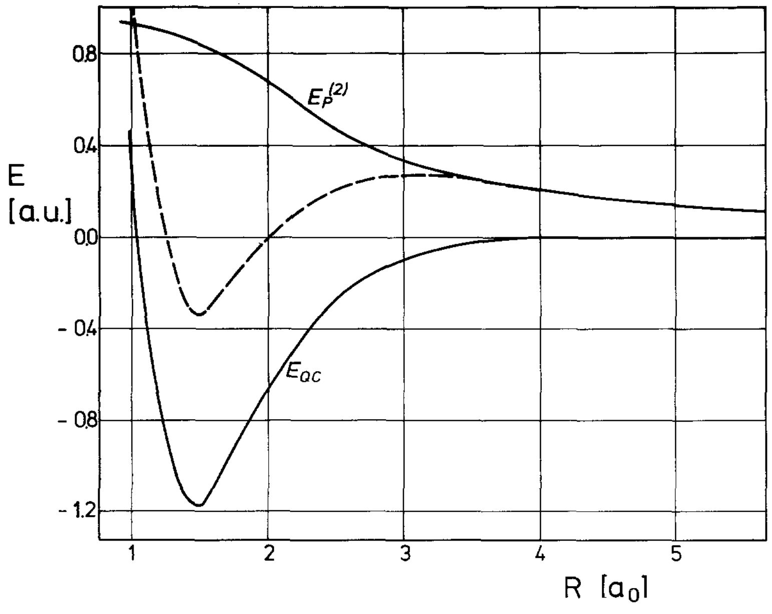

Fig. 2. Two electron contributions to the binding energy of N_2: the quasiclassical energy E_{QC} and the two-electron part of the promotion energy $E_P^{(2)}$. The broken line gives the sum of E_{QC} and $E_P^{(2)}$

In unsaturated molecules there arises a special problem because the diagonalization of H^E gives an order of the one-electron energies e_i where the antibonding π_g orbitals are below the highest occupied σ_g orbital. Indeed, it has already been noted by Hoffmann [9b] that in EHT calculations on unsaturated molecules the highest occupied σ orbitals show a considerable upward shift. So this feature seems to be inherent to EHT (and not to a special parametrization) and must be attributed to the neglect of electron repulsion effects. In an iterative self-consistent extension of EHT that incorporates essential parts of the electron repulsion [10] one gets the correct order of orbital energies. The values in Table 2 have been obtained by summing those of the e_i in Eq. (27) that "should be" occupied.

Two bond angle calculations are included in Table 2. We know from the foregoing discussion that the strongly polar (but single) bonds in H_2O should not cause any trouble as regards the equilibrium angle, and the results are indeed quite acceptable for such a simplified scheme. In CH_2 the $1b_1$ orbital lies below the $3a_1$ orbital, whereas the latter should be the highest occupied orbital. So the order of these orbitals has been reversed in the calculation of ΔE in Table 2.

In summary, we have found that an EHT-type method with *ab initio* calculation of the parameters gives rather accurate equilibrium geometries for saturated molecules. This fact can only partially be regarded as fortuitous but has been shown to result from a physically comprehensible cancellation of the neglected two-electron terms. The remaining error is rather insensitive to distance variations but relatively large in heteronuclear molecules (and F_2) which is reflected in the ΔE values calculated with (27). By a semi-empirical parametrization one can cope with this difficulty rather easily, in contrast to a scheme with an inherently wrong distance dependence of ΔE (discussed in the following section). Finally, the proper order of orbital energies in unsaturated molecules can be obtained by a certain incorporation of electron repulsion into the formalism, and therefore our findings support the soundness of a scheme like the SCEHT [10].

5. The Approximate Schemes "without Overlap"

Let us assume for the moment that Eq. (32) is fulfilled, i.e. that (34a) is still equivalent to (26). In order to get the eigenvectors f^i by a simple matrix diagonalization one would have to employ a special set of parameters $\beta^i = \beta/s_i$ for each of the f^i. Now it is obvious that for bonding MO's c^i we have $s_i > 1$, for antibonding MO's $s_i < 1$, and for non-bonding MO's (core orbitals and lone pairs) $s_i \approx 1$. Approximation (35) therefore means that in molecules where only bonding and non-bonding MO's are occupied the β values are too large in absolute value, and the same is true for the λ_i corresponding to valence MO's (note that non-bonding orbitals are not influenced by the β parameters) as well as the binding energy. In these cases we can do a little better than using (34b) by introducing an averaged overlap eigenvalue

$$\bar{s} = \sum_{i \in \text{val}} s_i / n$$

where i runs over the n valence MO's. The β parameters in (34b) are then replaced by

$$\bar{\beta}_{\mu s, \nu t} = \beta_{\mu s, \nu t}/\bar{s}. \tag{44}$$

In the exceptional molecule H_2 where (32) is indeed fulfilled in a scaled minimal basis the solution of (28) now gives exactly the same ΔE and R_e as the "scheme with overlap" (26) (see Table 2).

In the CNDO-like scheme (40) one also has to divide the $\tilde{\beta}$ parameters by $\bar{s}$. In H_2 the converged solution of (40) is then completely identical to the SCF result due to the definition of the two-electron interference parameters (5).

There are some molecules (e.g. N_2, F_2, H_3^-) where antibonding orbitals are occupied. Still one has $\bar{s} > 1$ but a general reduction of β like (44) cannot be justified because for the antibonding orbitals one should enlarge β instead of reducing it. In these cases we have to use Eqs. (34b) and (40) as they stand, and we can hope that the neglect of the s_i is partly compensated by the use of the same orbital exponents both for the bonding and the antibonding MO (for a discussion of this point see [6]). All the other results given in this section have been obtained after dividing β and $\tilde{\beta}$, respectively, by $\bar{s}$. It is only by this reduction of β that binding energies calculated with the Hückel-type scheme (34b) are "close to" (i.e. within the +100% range) the results of (26). This fact is mainly due to the large overlaps in σ bonds ($s_i \approx 1.6$–1.7) whereas in π bonds one has $s_i \approx 1.3$. In H_2 (experimental geometry) we find $\bar{s} = s_1 = 1.68$, other examples for $\bar{s}$ are: 1.59 in Li_2, 1.72 in CH_4 and C_2H_6, 1.66 in H_2O.

Now we have to examine the basic assumption (32) (i.e. the MO's are eigenvectors of S) that is fulfilled only if S commutes with H^H and F, respectively:

$$[H^H, S] = 0 \qquad [F, S] = 0. \tag{45}$$

In order to get an impression of how closely (45) is satisfied we need a measure for the deviation from (45). Because the commutators are real matrices we simply take a matrix norm as measure, namely the spectral radius defined by

$$\sigma(A) = |\text{max. eigenvalue of } A|. \tag{46}$$

It turns out that the commutators in (45) have spectral radii differing by not more than a few percent, so in the following we deal only with $\sigma([H^H, S])$. Clearly, the spectral radius must be a monotonically decreasing function of the internuclear distance R because for $R \to \infty$ one has $S \to I$. Only in the case of H_2 Eqs. (45) are fulfilled ($\sigma = 0$) for any R. The commutator norms of Li_2, F_2 and CH_4 are given in Table 3 for R values around the experimental equilibrium distances R_e. In Li_2 σ as well as its variation with R are relatively small, so we get an energy minimum that is not too bad: $\Delta E = -0.046$ a.u./$R_e = 4.25a_0$ with Eq. (28) and $\Delta E = -0.033$ a.u./$R_e = 4.30a_0$ with (40). But in F_2 and CH_4 that are typical molecules as regards the variation of σ with the internuclear distance the Hückel-type formalism (28) gives energy minima at very small distances ($R_{FF} < 1$, $R_{CH} < 1a_0$) if it gives minima at all, which has not been checked. The CNDO-type formalism (40, 42) contains the nuclear repulsion which guarantees an energy minimum for $R > 0$. But this minimum is located at much too small distances and much too large binding energies: $R_{FF} < 1a_0$, $\Delta E < -3.5$ a.u. in F_2, and $R_{CH} < 1a_0$,

Table 3. Commutator norm $\sigma([H^H, S])$ of Li_2, F_2 and CH_4 (in a.u.) for different internuclear distances (in a_0)

Li_2		F_2		CH_4	
R_{Li-Li}	σ	R_{F-F}	σ	R_{C-H}	σ
4.0	0.28	2.5	0.90	1.9	1.95 (1.57)[a]
5.0	0.17	2.7	0.62	2.0	1.70 (1.40)
6.0	0.10	2.9	0.43	2.1	1.48 (1.26)

[a] The numbers in parentheses are obtained if only valence AO's are considered.

$\Delta E < -2.5$ a.u. in CH_4. In Table 3 there are given also those σ values for CH_4 that are obtained by considering just the valence AO's. The variation of σ with R is reduced by about one-third if one restricts oneself to valence orbitals, but this reduction obviously is not enough to save assumption (32).

It is apparent from these results that the treatment of the one-electron part in Sect. 3.2 introduces much more serious errors into the computational scheme than does the neglect of E_{QC} and $E_P^{(2)}$, at least in the vicinity of R_e. In agreement with our results, the first CNDO version (CNDO/1), where the two-center penetration integrals $Z_\nu(\nu : \mu_s\mu_s) = v_{\mu\nu}$ were calculated by means of the correct integral formula, gave too short equilibrium distances and too large binding energies [18]. Only if one incorporates new errors into $v_{\mu\nu}$ that partly compensate for the approximation (45), e.g. by $v_{\mu\nu} = Z_\nu\gamma_{\mu\nu}$ in CNDO/2 or by the more refined formula of [19], one can get, after reparametrization, reasonable results for both R_e and ΔE.

The problems connected with the "neglect" of overlap have been recognized long ago, and there have been numerous attempts to justify this approximation. For the one-electron part the neglect of overlap means that Eqs. (32) (the MO's are also eigenvectors of $\boldsymbol{S}$) and (35) ($S_{\mu s, \nu t} \ll 1$) are assumed to be valid. We have found that in the usual (canonical) AO basis the assumption (32) does not hold in the general case. But it is apparent that (32) as well as (35) are exact in a symmetrically orthogonalized [20] AO basis because in this basis we have $\boldsymbol{S} = \boldsymbol{I}$. Therefore in order to arrive at Eq. (28) we simply should transform (26) with $\boldsymbol{S}^{-1/2}$. So one could argue that the parameters of the semi-empirical theories "without overlap" should be interpreted as corresponding to an OAO basis, with the additional advantage that the very drastic ZDO (zero differential overlap) approximation

$$(\mu_s\nu_t | \kappa_u\lambda_v) = \delta_{\mu s, \nu t}\delta_{\kappa u, \lambda v}(\mu_s\mu_s | \kappa_u\kappa_u)$$

that is employed in the CNDO scheme is equivalent to the Mulliken approximation in an OAO basis. But there are severe objections to this point of view (for detailed discussions see e.g. [21-24]):

The Hückel, CNDO, and related schemes originally have been "meant" to correspond to ordinary AO's, thereby being in agreement with the orbital pictures that serve chemists in their understanding of reactions and bonding situations. If the semi-empirical parameters are interpreted as OAO parameters then either one has to accept much more complicated orbital models of bonding or one has to establish the connection between OAO parameters and canonical AO's. This back transformation usually is omitted because one argues that symmetrically orthogonalized AO's are still localized to a high degree. Obviously, this argument has originated from the π-electron theories where indeed the overlap integrals are rather small (~0.3) and (32) as well as (35) are acceptable approximations (first shown by Ruedenberg [14]). But for σ bonds, where one has $S \approx 0.7$, the whole argument breaks down.

Concerning the two-electron terms, it has been shown [21-24], that neither in an OAO nor in an AO basis the ZDO approximation can be reasonably justified. It is only in π-electron theories that the ZDO approximation does not lead to unacceptable errors, because the overlap between neighboring pπ orbitals is relatively small and the Mulliken approximation for two-electron integrals involving just pπ orbitals is in error by only a few percent [21, 25].

We conclude that semi-empirical schemes "without overlap" suffer from several errors in any basis whatsoever, and therefore it is not surprising that for different molecular properties one has to use different sets of fitted parameters.

If we want to compare empirically fitted Hückel parameters with our calculated ones we have to restrict ourselves to π bonds. Furthermore, concerning the two-electron interference terms g (5) we have to distinguish between the following two cases. In the parameter definitions (8), (9) we have multiplied these terms by 0.5 which keeps the subsequent energy expressions simple and, in particular, enables us to write the total binding energy in (36) as sum over the eigenvalue (plus a constant) as is done in Hückel theory. The β parameters calculated in this way have therefore to be compared with empirical Hückel parameters fitted for differences of total energies (e.g. delocalization energies, bond dissociation energies).

If, on the other hand, we had intended to calculate ionization potentials, electron affinities, and excitation energies then the starting point of our derivation should not have been (15) (SCF energy plus left-right correlation) but the SCF energy expression as it stands because the molecular properties mentioned above are related to SCF eigenvalues via Koopmans' theorem. In this case the empirical Hückel β parameters correspond rather to the non-diagonal elements of the CNDO-type matrix F (41b) than to those of H^H. Furthermore, in analogy to the SCF procedure the two-electron interference terms should be doubled, this means we have to drop the factor 0.5 in (8), (9).

The different meaning of the Hückel β in the two cases is reflected by the fact that the respective empirical values for β differ by a factor of 3-5. In the literature usually β_0 values are given corresponding to a C-C bond length of 1.397 Å (as in benzene), and for other compounds one has to apply certain correction factors [26]. The empirically fitted values for β_0 in unsaturated hydrocarbons range from -0.7 to -0.9 eV in case A (total energies etc.) and from -2.5 to -4.0 eV in case B (ionization potentials etc.) [8].

In calculating the corresponding parameters in our scheme we have to modify Eq. (44). Since we are dealing with pure π-electron theory parameters $\bar{s}$ must be the average of those overlap eigenvalues that are associated with π orbitals. So in case A we take the β occurring in H^H, divide it by $\bar{s}(\pi)$ and apply a correction for the bond length, if necessary. From the molecules C_2H_2, C_2H_4, $C_3H_5^+$, C_4H_6, and C_6H_6 we get $\beta_0 = -0.81$ eV (mean square deviation 0.03 eV). This result is in perfect agreement with the empirical fits and lends support to our arguments in the course of the derivation.

In case B we have to take $\tilde{\beta}$ from (41b) but with doubled g terms, divide by $\bar{s}(\pi)$ and correct for bond length to get $\beta_0 = -2.18$ eV (m.s.d. 0.11 eV). The second term in (41b), $-\frac{1}{2}p_{\mu s,\nu t}(\mu_s\mu_s|\nu_t\nu_t)$, is somewhat problematic. In benzene this term amounts to -2.9 eV but we know from I that this special term describes the interatomic sharing penetration that is grossly overestimated in a one-determinant wave function. In H_2 at $R = R_e = 1.4a_0$ about 40% of this term is an artifact due to the MO approximation with an ever-increasing percentage at larger internuclear distances. So our estimate for the sharing penetration term in benzene is about -1.5 eV which gives a non-diagonal element of about -3.7 eV in reasonable agreement with the empirical fit.

We have shown above that the CNDO-type formalism (40) gives unreasonable potential curves like the early versions of the CNDO method. But these versions have proven especially useful for the calculation of charge distributions and dipole moments, therefore we want to finally examine some charge orders as obtained by (40). In Table 4 these charge orders are compared with SCF charges and results of (26) (i.e. the extended Hückel-type scheme). One should keep in mind that (40) is an approximation to the SCF equations, whereas (26) is a nearly pure one-electron approximation to SCF plus left–right correlation. In the unpolar molecules C_2 and F_2 the results of scheme (26) are slightly superior to (40), and in the polar cases both schemes show considerable deviations from the SCF results, a fact that, after all, is really not surprising. But there is one important point about the CNDO-type charge orders: the total charge transfer in polar bonds is much smaller than given by an SCF calculation. This finding offers a possible explanation for the success of the CNDO method. The large transferred charges in minimal basis SCF calculations are mainly due to the poor basis. The "neglect of overlap" in the CNDO methods seems just to compensate for this basis defect which facilitates an easy parametrization for dipole moments.

6. Conclusions

In current semi-empirical methods there are virtually two ways in which one deals with the cumbersome two-electron terms. Either they are dismissed altogether, ending up with the simple one-electron schemes like the EHT [9], or they are simplified by some NDO approximation. In the latter case one usually employs a further approximation, namely the neglect of the overlap matrix in the secular equation (e.g. in the CNDO method [12]).

We have shown that the former procedure can be reasonably justified for molecules with not too polar bonds if one wants to calculate not the total energy but the binding energy. The usefulness of EHT in the case of nearly unpolar bonds, especially in the

Table 4. Charge orders from SCF calculations, the extended Hückel-type (26), and the CNDO-type schemes (40), at experimental geometries

		SCF	Eq. (26)	Eq. (40)
C in C_2	2*s*	1.35	1.37	1.20
	2*pσ*	0.64	0.65	0.80
N in N_2	2*s*	1.63	[a]	1.79
	2*pσ*	1.37		1.21
C in CO	2*s*	1.60	2.03	1.27
	2*pσ*	1.03	0.58	0.79
	2*pπ*	0.53	0.17	0.85
Gross atomic population		5.68	4.96	5.76
O in CO	2*s*	1.74	1.75	1.99
	2*pσ*	1.63	1.65	1.95
	2*pπ*	1.47	1.83	1.15
Gross atomic population		8.32	9.04	8.24
F in F_2	2*s*	1.96	1.97	1.94
	2*pσ*	1.04	1.03	1.06
CH_4	C2*s*	1.21	0.95	0.68
	C2*p*	1.21	1.58	0.95
	H	0.79	0.58	1.12
C_2H_6	C2*s*	1.17	0.85	
	C2*pσ*	1.05	1.66	[a]
	C2*pπ*[b]	1.20	0.73	
	H	0.79	0.71	1.10

[a] An improper order of orbital energies is obtained.

[b] 2*pσ* is oriented along the C-C bond, 2*pπ* perpendicular to it.

case of hydrocarbons, is based on the cancellation of certain terms in the energy expression. This cancellation can be understood from the physical meaning of the respective terms and can thus not be regarded as fortuitous.

The CNDO scheme, on the other hand, seems to be unproblematic only if $S_{\mu\nu} \ll 1$. This condition constrains the justification of CNDO to π-electron systems but here the much simpler Hückel theory appears to work equally well, as can be inferred from our *ab initio* calculation of π-electron Hückel parameters. For σ bonds with their rather large overlap integrals the overlap approximations break down, and therefore it is no surprise that our CNDO-like formalism with *ab initio* parameters does not yield energy minima in the vicinity of the experimental equilibrium distances. Of course, by introducing empirical parameters one can do much better in this respect than we can with our *ab initio* scheme, but the physical meaning of the empirical parameters in CNDO still remains unclear.

The EHT (and the Hückel method) implicitly contains the left-right correlation in contrast to the CNDO method. So, in principle, only the former method is capable of yielding reliable potential curves for a large range of internuclear distances, at least for unpolar bonds.

Among the numerous semi-empirical methods described in the literature that approximate the two-electron integrals in some way probably the least drastic approximations are employed in the MADO method (Mulliken Approximation for Differential Overlap [27], see also [23]). Here the overlap integrals are fully retained and the two-electron terms are simplified by the Mulliken approximation. This method has been very successful in the calculation of excitation energies, but we know from I that the Mulliken approximation (i.e. neglect of two-electron interference effects) is not a good approximation in the general case and has a very large effect on the total energy.

In view of the fact that nowadays standard SCF programs are available for anyone and computer time does not play such a crucial role as it did some years ago we suppose that the future of semi-empirical formalisms lies in methods like [28] (i.e. only the correlation energy is treated semi-empirically) rather than in ever-new refinements of the old semi-empirical schemes with their gross approximations. Nevertheless, the latter are directly related to simple models of bonding and thus are likely to keep their considerable didactic value. Although some caution is indicated in using these schemes, because one might get the proper result for the wrong reason (see e.g. [29], page 15–16), they can in many cases help to improve the understanding of bonding situations and reactions.

It is this aspect of our simplified schemes in I and in this work that we are going to exploit in Part III of this series. There we will consider some special problems, for example, the comparison of the bonding situations in H_3^+ and H_3^-, and the failure of one-electron methods in the latter case.

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