

# Analysis of the Chemical Bond

## I. The Binding Energy of the MO-LCAO Scheme with an Approximate Correction for Left-Right Correlation, and Its Physical Fragmentation

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The energy expression of the MO-LCAO scheme is corrected approximately for the left-right correlation such that it leads to the correct dissociation limit. Together with the correlation correction a correction is applied to the interference term, whereas the sharing penetration effects are neglected. The derivation of this corrected approximate energy formula is suggested from an analysis of binding in  $H_2^+$  and  $H_2$ . The binding energy consists mainly of three contributions: interference, quasiclassical interaction, promotion. Two-electron interference contributions are absorbed into the one-electron terms. The basis dependence of the fragmentation of the binding energy is discussed and an appropriate hybrid basis is constructed. Rotational invariance is found to a high degree of accuracy. In terms of the proposed scheme the binding in several diatomic and polyatomic molecules is analysed. The individual contributions to the binding energy turn out to be physically meaningful.

**Key words:** Chemical bond - Analysis of binding energy - Interference - Promotion state - Left-right correlation

### 1. Introduction

One of the most challenging problems for theoretical chemists has been the elucidation of the physical nature of the chemical bond. The concepts of the "chemical bond", like that of "partial charge of an atom in a molecule", "electronegativity" etc., have their origin in the descriptive chemical theory that has been developed before or during the early years of quantum mechanics. These concepts have proven rather useful for a better understanding of chemical facts but it turned out to be rather difficult to give them a precise meaning in the context of rigorous quantum mechanics.

In order to get an insight into the physical mechanism of the chemical bond one has to break the binding energy into fragments [1-3]. Such a fragmentation can in principle be done in an arbitrary number of ways but it will serve its purpose only if the fragments exhibit a regular behaviour corresponding to a physical model and are thus amenable to physical interpretation. Although the application of the very general and most elaborate of the existing schemes for such an analysis, namely that initiated by Ruedenberg [2], to a number of molecules ([4] and references therein) yielded some interesting results, it is made apparent that one easily loses the direct connection to a simple, pictorial model of molecule formation and that a closer look on the simplest possible molecule,  $H_2^+$ , was desirable.

Careful examination of the bonding situation in  $H_2^+$  by Ruedenberg and coworkers ([5], see also [6]) revealed that fragmentation of the binding energy into *quasiclassical*, *promotion*, and *interference* parts furnished a useful scheme for the understanding of bond formation in this molecule. Due to the presence of electron–electron interaction the situation in a two-electron bond is much more complicated [2]. Nevertheless we regard it as worth-while to examine the question: to what extent can the simple fragmentation of  $H_2^+$  be maintained in the general case, and which modifications are necessary?

In Sect. 2 we introduce the basic considerations and concepts that will guide us in the following derivation. These concepts are developed from a comparison of the bonding situation in  $H_2^+$  and  $H_2$ . The derivation in Sect. 3 starts from the expectation value of a LCAO-MO wave function for a closed-shell molecule and after an approximate correction for the left–right correlation ends up with a partitioning of the binding energy into quasiclassical, promotion, and interference parts. Sect. 4 deals with invariance problems, especially the basis dependence of the general derivation. Finally, in Sect. 5 we present some results, mainly for the homonuclear diatomics and a number of hydrocarbons. The results show how the different bonding situations are reflected in our fragmentation, the physical content of which is discussed.

## 2. Basic Considerations: $H_2^+$ and $H_2$

In this section we briefly review the bonding situation in  $H_2^+$  within the MO-LCAO approximation in order to develop and define the conceptual tools for the general derivation in Sect. 3. From a comparison of the MO, VB, and two-determinant wave functions for the two-electron bond in  $H_2$  we will get an idea for a simple correction of the “unphysical” asymptotic behaviour of the MO energy expression for  $R \rightarrow \infty$  by approximately taking into account the left–right correlation of the bonding electron pair<sup>1</sup>. Later on we will generalize this correction for any closed-shell molecule (Sect. 3). Thus, we start from the basic assumption that the essential features of a covalent two-electron bond in any molecule are the same as in  $H_2$ . Obviously, this does not hold for delocalized or strongly polar bonds, so our general derivation will be reasonably justified only for localizable, unpolar or weakly polar bonds.

### 2.1. Bonding in $H_2^+$

In the simplest possible molecule,  $H_2^+$  [5, 6] the bonding situation can be elucidated by a fragmentation of the binding energy into quasiclassical, interference, and promotion energies. This fragmentation can be visualized as corresponding to subsequent steps in the “process of bond formation”, when a hydrogen atom and a proton are brought together to form  $H_2^+$ . In the physical reality there are no such steps, of course, but they can, nevertheless, serve as pictorial concepts that help to better understand the actually rather complex situation. In the case of  $H_2^+$  it turns out that a simple minimal basis MO-LCAO ansatz is able to describe the essential features of the bonding situation to a good degree of accuracy.

<sup>1</sup> A proper dissociation behaviour could as well be achieved by using an UHF wave function instead of the RHF ansatz, but this would not improve the potential curve in the vicinity of the equilibrium distance. The approximate inclusion of left–right correlation, on the other hand, lowers the energy at all internuclear distances and is likely to give more reliable binding energies than RHF or UHF wave functions.

## 2.1.1. Quasiclassical Energy

Consider a hydrogen atom and a proton at large internuclear distance  $R$ . By  $a$  and  $b$

$$a = N e^{-\eta r_a}$$

$$b = N e^{-\eta r_b}$$

we denote two hydrogen-like ( $\eta = 1$ ) atomic orbitals, centred at nucleus  $A$  and  $B$ , respectively. The probability of finding the electron at nucleus  $A$  (electron density  $\rho = a^2$ ) or at nucleus  $B$  ( $\rho = b^2$ ) being equal, we get the total quasiclassical density as

$$\rho_{QC} = \frac{1}{2}(a^2 + b^2) \quad (1)$$

The quasiclassical picture is based on adding atomic densities rather than wave functions; it hence ignores all interference effects.

The corresponding energy is

$$E = E(H) + E_{QC} \quad (2)$$

where  $E(H)$  is the energy of a hydrogen atom and

$$E_{QC} = \frac{1}{R} - (b : aa) \quad (3)$$

is the quasiclassical (electrostatic) energy.

The “penetration integral” ( $b : aa$ ) is given by

$$(b : aa) = \int \frac{|a(r_a)|^2}{r_b} d\tau$$

For large distances  $R$  one has

$$(b : aa) \approx \frac{1}{R}, \quad E_{QC} \approx 0$$

For distances where nucleus  $B$  penetrates into the “electron cloud” around  $A$ , ( $b : aa$ )  $< 1/R$ , so  $E_{QC}$  becomes repulsive. This repulsion is significant only for distances smaller than the equilibrium distance in  $H_2^+$ .

## 2.1.2. Interference Energy

Instead of adding atomic densities (quasiclassical situation) we have to add atomic wave functions, i.e.

$$\psi = \frac{1}{[2(1+S)]^{1/2}} (a + b), \quad S = \int ab d\tau \quad (4)$$

which gives rise to interference effects:

$$\rho = |\psi|^2 = \frac{1}{2(1+S)} (a^2 + 2ab + b^2) = \rho_{QC} + \rho_I$$

where  $\rho_{QC}$  is given by (1) and the interference density by

$$\rho_I = \frac{1}{1+S} [ab - \frac{1}{2}S(a^2 + b^2)] = \frac{1}{1+S} [ab - S\rho_{QC}] \quad (5)$$

Eq. (5) shows that interference shifts the electron density partly from the vicinity of the nuclei into the bonding region. Furthermore, Eq. (5) allows for a useful interpretation of the Mulliken approximation [7] in terms of quasiclassical and interference densities that will be important in the general derivation (Sect. 3). An orbital product  $ab$  “contains” a quasiclassical part,  $\frac{1}{2}S(a^2 + b^2)$ , which is the contribution of the respective Mulliken approximation to it. The difference,  $ab - \frac{1}{2}S(a^2 + b^2)$ , can then be interpreted as interference part of  $ab$ , i.e. as “purely quantum mechanical effect”.

With the definition of the one-electron operator (atomic units are used throughout this work)

$$\hat{h} = -\frac{1}{2}\Delta - \frac{1}{r_a} - \frac{1}{r_b}$$

the energy of  $\text{H}_2^+$  with wave function (4) is in an obvious notation given by

$$\begin{aligned} E &= \frac{1}{2(1+S)} (h_{aa} + h_{bb} + 2h_{ab}) + \frac{1}{R} \\ &= h_{aa} + \frac{1}{1+S} [\gamma - \frac{1}{2}S(h_{aa} + h_{bb})] + \frac{1}{R} \\ &= \alpha + \frac{\beta}{1+S} - (b : aa) + \frac{1}{R} \\ &= E(\text{H}) + E_I + E_{QC} \end{aligned} \quad (6)$$

The one-centre parameter  $\alpha$  (in this case simply the energy of a hydrogen atom), the “resonance integral”  $\gamma$  and the “reduced resonance integral”  $\beta$  are given by

$$\begin{aligned} \alpha &= \left\langle a \left| -\frac{1}{2}\Delta - \frac{1}{r_a} \right| a \right\rangle \\ \gamma &= h_{ab} \quad \beta = h_{ab} - \frac{1}{2}S(h_{aa} + h_{bb}) \end{aligned} \quad (7)$$

The name “reduced resonance integral” (first used by Mulliken [7]) for  $\beta$  is apparent from Eq. (7):  $\beta$  is the difference between  $h_{ab}$  and the Mulliken approximation to  $h_{ab}$ . The interpretation given above applies, i.e.  $\beta$  contains just the interference effects. Therefore

$$E_I = \frac{\beta}{1+S}$$

is called “interference energy”. The interference is the dominant effect of bond formation in  $\text{H}_2^+$  and  $E_I$  gives the bulk of the binding energy.  $E_I$  is negative at all distances  $R > 0$ , and has its minimum near the equilibrium distance  $R_e$  of  $\text{H}_2^+$ .

### 2.1.3. Promotion Energy

A wave function that can be taken as a reasonable approximation for the exact one ought to obey the virial theorem. This is not the case with wave function (4) if  $a$  and  $b$  are hydrogen 1s orbitals (exponent  $\eta = 1$ ). A variation of  $\eta(R)$  yields an energy minimum for  $\eta = 1.25$  at  $R = R_e$ . With this contractive promotion of the 1s orbitals (4) fulfills the virial theorem, and the following changes of the energy fragments in (6) are observed.

$E_{QC}$  remains essentially unchanged. There is a pronounced decrease of the reduced resonance integral  $\beta$  and thus of  $E_I$  which is partly compensated by a slight increase of the parameter  $\alpha$ . This increase of  $\alpha$  is the net effect of a strong increase of the kinetic energy part and a strong decrease of the potential energy part of  $\alpha$ .  $\alpha$  is called the energy of a hydrogen atom in a “promotion state”.

The binding energy of  $\text{H}_2^+$  can now be written as

$$\Delta E = E_p + E_I + E_{QC}$$

where

$$E_p = \alpha - E(\text{H})$$

is the promotion energy.

The order of the three steps in bond formation can equally well be taken in a different order, e.g.: 1) Promotion of an H atom to a state that is best suited for the final bonding situation (effecting a slight increase of the energy); 2) Switching on of the quasiclassical interaction of this hydrogen atom with a proton located at the equilibrium distance (also a slight increase of the energy); 3) Finally introduction of the interference effect, thereby overcompensating the first two energy increasing effects by an amount that is equal to the binding energy of  $\text{H}_2^+$ .

## 2.2. Bonding in $\text{H}_2$

As is well known, the MO wave function for a two-electron bond is an acceptable approximation only in the vicinity of the equilibrium distance but shows an unphysical asymptotic behaviour at large and intermediate distances. Thus, the MO energy expression cannot be regarded as an acceptable basis for our energy analysis but we have to take into account the left-right correlation in an approximate way. On the other hand, we have to start with the one-electron picture of the MO approximation in order to keep our energy expression as simple as possible. Furthermore, most of the former approaches to an energy analysis have been based on the MO approximation, and therefore we want to stay in the MO framework as far as possible.

To get an idea for a simple correction of the MO energy let us compare the MO, VB, and two-determinant (CI) energy expressions for  $\text{H}_2$  in a minimal basis. The wave functions for the MO and VB ansatz are

$$\Psi_{\text{MO}} = \frac{1}{2(1+S)} [a(1) + b(1)][a(2) + b(2)]$$

$$\Psi_{\text{VB}} = \frac{1}{[2(1+S^2)]^{1/2}} [a(1)b(2) + b(1)a(2)]$$

and the corresponding energy expressions (using the Mulliken notation for the two-electron integrals)

$$E_{\text{MO}} = 2\alpha + \frac{2\beta}{1+S} - 2(b : aa) + \frac{1}{R} + \frac{1}{2} [(aa | aa) + (aa | bb)] \quad (8)$$

$$E_{\text{VB}} = 2\alpha + \frac{2S\beta}{1+S^2} - 2(b : aa) + \frac{1}{R} + (aa | bb) + \frac{S^2}{2(1+S^2)} [(aa | aa) - (aa | bb)] \quad (9)$$

In Eqs. (8) and (9) the Mulliken approximation has been applied to the two-electron integrals for a better comparison, i.e. we neglect the two-electron interference energy. In the case of  $\text{H}_2$  this is a very good approximation (see Sect. 6).

$E_{\text{MO}}$  and  $E_{\text{VB}}$  differ in two terms: the interference energy

$$E_{\text{MO}}^I = \frac{2\beta}{1+S} \quad (10)$$

$$E_{\text{VB}}^I = \frac{2S\beta}{1+S^2} \quad (11)$$

and the two-electron energy

$$E_{\text{MO}}^{(2)} = \frac{1}{2}[(aa|aa) + (aa|bb)] = \frac{1}{2}[(aa|aa) - (aa|bb)] + (aa|bb) \quad (12)$$

$$E_{\text{VB}}^{(2)} = \frac{S^2}{2(1+S^2)} [(aa|aa) - (aa|bb)] + (aa|bb) \quad (13)$$

The best wave function within the given basis is a two-determinant ansatz which gives the energy (again the Mulliken approximation for two-electron integrals is applied)

$$E_{\text{CI}} = 2\alpha - \frac{2S\beta}{1-S^2} - 2(b : aa) + \frac{1}{R} + \frac{1}{2}[(aa|aa) + (aa|bb)] \\ + \frac{1}{2(1-S^2)} [16\beta^2 + [(aa|aa) - (aa|bb)]^2]^{1/2} \quad (14)$$

It is seen that the interference and two-electron terms are unseparably connected by the last term in (14). But for large ( $|4\beta| \ll (aa|aa) - (aa|bb)$ ) and small ( $|4\beta| \gg (aa|aa) - (aa|bb)$ ) distances one can approximate the square root by the first two terms of the respective expansion. The error introduced into  $E_{\text{CI}}$  by this truncation is  $< 0.001$  a.u. for  $R \leq 2a_0$  and  $R \geq 4a_0$ . If one adds the first term of the expansion to the corresponding (interference or two-electron) part of  $E_{\text{CI}}$  and the second (coupling) term to the other part one gets a formal separation of interference and two-electron terms the result of which is shown in Fig. 1 together with the respective MO and VB energies.

The energy expansion we are looking for should contain interference and two-electron terms that furnish a good interpolation between the respective CI values. Fig. 1 shows the failure of  $E_{\text{MO}}^{(2)}$  in this respect, but also  $E_{\text{MO}}^I$  exhibits an unacceptable behaviour for intermediate distances. The interpolation behaviour of the VB terms, on the other hand, looks rather promising but the two-electron term (13) is too complicated for our purpose. Now the first term in (13) should be very small at all distances, and indeed (see Fig. 1)  $E_{\text{VB}}^{(2)} \approx (aa|bb)$  is a rather accurate approximation.

Thus, our sought-for simple energy expression is

$$E = 2\alpha + \frac{2S\beta}{1+S^2} - 2(b : aa) + \frac{1}{R} + (aa|bb) \\ = 2\alpha + E_I + E_{\text{QC}} \quad (15)$$

and again we have a partition of the energy into one-centre, interference and quasiclassical terms.

If we regard  $E_{\text{MO}}$  as a starting point we have to introduce two replacements into (8) in order to end up with (15):

$$\text{a) Replace } \frac{1}{2}[(aa|aa) + (aa|bb)] \text{ by } (aa|bb) \quad (16)$$

$$\text{b) Replace } \frac{2\beta}{1+S} \text{ by } \frac{2S\beta}{1+S^2} \quad (17)$$

Both replacements have been suggested by approximately taking into account the left-right correlation of the bonding pair. That means, compared to the one-electron picture of the MO approximation, the left-right correlation causes a reduction of the one-centre

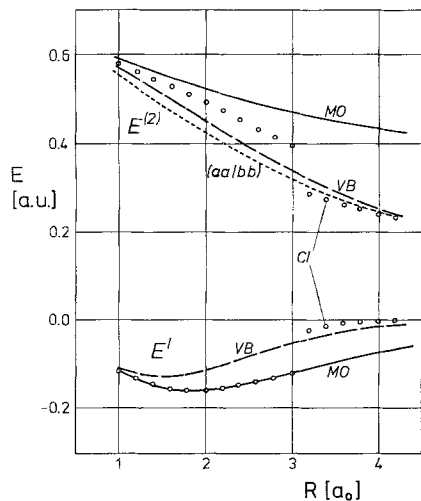


Fig. 1. Two-electron energies  $E^{(2)}$  and interference energies  $E^I$  in MO and VB approximation, compared to extrapolated CI values and  $(aa|bb)$

pair density in favour of the two-centre pair density and at the same time a decrease of the interference energy. The effect of these two changes on the energy is of opposite sign. The energy expression (15) is based partly on the MO and partly on the VB ansatz. Such a combination of the two approximations goes back to Mulliken [8] who followed this procedure in his construction of a “magic formula” for atomization energies of molecules.

Fig. 2 shows the potential curve of  $H_2$  calculated with (15) in a properly scaled minimal basis, compared to the MO energy and the “exact” potential curve. The improvement due to the change from (8) to (15) is very satisfactory but of course we cannot expect our simple formula to work equally well for other molecules.

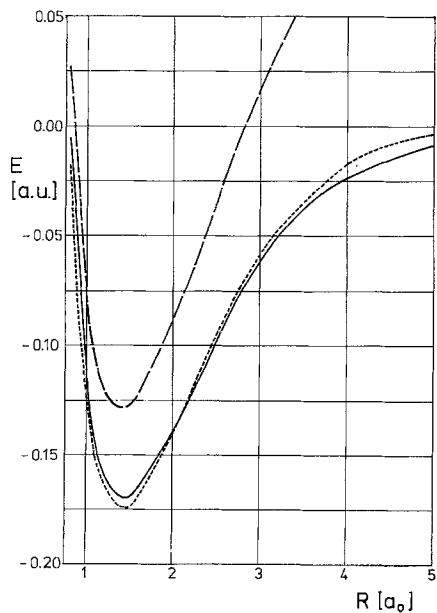


Fig. 2. Potential curves of  $H_2$ : scaled minimal basis calculation with Eq. (15) (—), SCF results (---), and “exact” curve [19] (.....)

### 2.3. Promotion State and Valence State

In order to clarify the physical meaning of (16) and (17) we make use of the concepts of “promotion state” and “valence state” that are defined in the literature in a number of slightly different ways. We stick to the definitions of Ruedenberg [2] that are based on his analysis of the one-electron and pair densities of the molecule. Both densities can formally be partitioned into one-centre and two-centre parts, and we call “promotion state” that hypothetical state of a free atom that has a one-electron density equal to the one-centre one-electron density of this atom within the molecule. Thus, promotion of an atom means deformation of the atomic density (e.g. by contraction or hybridization) until it matches the molecular situation, and the molecular one-electron density can be regarded as the sum of the densities of atoms in their promotion states plus the molecular interference density.

On the contrary, the molecular pair density can in no way be obtained by summing up the pair densities of promoted atoms and an interference part. This fact can most easily be seen by considering the  $H_2$  molecule. In a free hydrogen atom, promoted or not, there is no intra-atomic pair density whatsoever, but in  $H_2$  there is a considerable probability of finding both electrons at one centre, i.e. there is an intraatomic pair density. In the VB language one speaks of the increasing weight of “ionic structures” when the distance between two hydrogen atoms is decreased. This increase of intraatomic and the corresponding decrease of interatomic pair densities are referred to as “sharing penetration” by Ruedenberg [2]. In the process of bond formation the energy-increasing two-electron effect of sharing penetration parallels the energy-decreasing one-electron effect of interference, and we have seen in the preceding section how intimately these two effects are connected with each other.

Now we are in a position to define the “valence state” as a molecular entity in contrast to the promotion state that can be regarded as a hypothetical atomic entity. The one-electron densities of the two states are the same but the valence state differs from the promotion state by the increase of the pair density due to sharing penetration.

Let us now again turn our attention to Eqs. (12), (13) and Fig. 1. From the above discussion it is apparent that the two-electron parts of  $E_{MO}$  and  $E_{VB}$  differ in the respective term that can be attributed to the sharing penetration effect, i.e. decrease of interatomic in favour of intraatomic pair density:

$$E_{MO}^{SP} = \frac{1}{2} [(aa|aa) - (aa|bb)]$$

$$E_{VB}^{SP} = \frac{S^2}{2(1+S^2)} [(aa|aa) - (aa|bb)]$$

$E_{MO}^{SP}$  is too large at all distances and we can correct it by taking into account the left-right correlation via a two-determinant wave function. At the equilibrium distance  $R_e = 1.4a_0$  this CI leads to a reduction of  $E_{MO}^{SP}$  by 40%.  $E_{VP}^{SP}$  on the other hand is considerably too small, compared to  $E_{CI}^{SP}$ , as can be seen by rewriting the two-determinant wave function into the Weinbaum function [9], where “ionic terms” are added to the VB wave function. Finally, our simple energy expression (15) contains no sharing penetration terms at all, thus the replacement (16) overshoots the correction for left-right correlation by neglecting *all* of the sharing penetration energy. This rather drastic approximation has the very convenient effect that in (15) we have, besides quasiclassical and interference terms, only promotion state energies  $\alpha$ , and that we do not have to bother



Table 1. Sharing penetration and interference energies (in a.u.) of  $\text{H}_2$  at  $R_e = 1.4a_0$  with and without scaling of the minimal basis AO's

	$\eta = 1$		$\eta = 1.193$	
	$E^{SP}$	$E^I$	$E^{SP}$	$E^I$
MO	0.0608	-0.1512	0.0937	-0.2374
CI	0.0326	-0.1390	0.0589	-0.2227
VB	0.0220	-0.1273	0.0295	-0.1849

about valence states. In the second correction (17) the error introduced by neglecting  $E_{\text{SP}}^{\text{CI}}$  is partly compensated by a reduction of the interference term. Here we adopt the VB formula because  $E_{\text{VB}}^{\text{SP}}$  is relatively small compared to  $E_{\text{CI}}^{\text{SP}}$ , and because  $E_{\text{VB}}^I$  shows the appropriate behaviour for small and intermediate internuclear distances.

Table 1 shows the sharing penetration and interference energies of  $\text{H}_2$  at  $R_e = 1.4a_0$  in the different approximations with and without scaling. In order to get the CI values the expansion coefficients in the two-determinant wave function have to be known.  $E_{\text{CI}}$  can then be written as

$$\begin{aligned} E_{\text{CI}} &= 2\alpha + E_{\text{QC}} + 2 \frac{c_1^2 - c_2^2 - S}{1 - S^2} \beta + \left( \frac{1}{2} + \frac{c_1 c_2}{1 - S^2} \right) (J_{aa} - J_{ab}) \\ &= 2\alpha + E_{\text{QC}} + E_{\text{CI}}^I + E_{\text{CI}}^{\text{SP}} \end{aligned}$$

and a separation of interference and sharing penetration terms is possible. The proper values of  $c_1$  and  $c_2$  at  $R_e$  are 0.995 and  $-0.101$ , respectively.

The sum of the correlation correction (16) and interference correction (17) overshoots the CI energy by  $\Delta = -E_{\text{CI}}^{\text{SP}} + (E_{\text{VB}}^I - E_{\text{CI}}^I)$ , and one has  $\Delta = -0.021$  a.u. independent of scaling.

### 3. Derivation of the General Energy Formula

With the definition of the one-electron operator  $\hat{h}$

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

( $k$  denotes the  $k$ th electron,  $\mu$  counts the nuclei) the energy of a closed-shell molecule in the MO approximation can be written as

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

where  $i, j$  run over the doubly occupied MO's.

The MO's  $\varphi_i$  are expanded in a given AO basis  $\{\chi\}$ :

$$\varphi_i = \sum_{\mu,s} c_{\mu s}^i \chi_{\mu s}$$

( $s$  counts the AO's at the centre  $\mu$ ), and we get

$$E = 2 \sum_i \sum_{\mu,s} \sum_{\nu,t} c_{\mu s}^i h_{\mu s, \nu t} c_{\nu t}^i + \sum_{\mu < \nu} \frac{Z_\mu Z_\nu}{R_{\mu\nu}} \quad (18)$$

$$+ \sum_{i,j} \sum_{\mu,s} \sum_{\nu,t} \sum_{\kappa,u} \sum_{\lambda,v} c_{\mu s}^i c_{\nu t}^j c_{\kappa u}^j c_{\lambda v}^i [2(\mu_s \nu_t | \kappa_u \lambda_v) - (\mu_s \lambda_v | \kappa_u \nu_t)]$$

Now we split the two-electron integrals  $(\mu_s \nu_t | \kappa_u \lambda_v)$  into their quasiclassical parts (given by the Mulliken approximation) and their interference parts, defined by

$$[\mu_s \nu_t | \kappa_u \lambda_v] = (\mu_s \nu_t | \kappa_u \lambda_v) - \frac{1}{4} S_{\mu_s, \nu_t} S_{\kappa_u, \lambda_v} [(\mu_s \mu_s | \kappa_u \kappa_u) + (\mu_s \mu_s | \lambda_v \lambda_v) + (\nu_t \nu_t | \kappa_u \kappa_u) + (\nu_t \nu_t | \lambda_v \lambda_v)] \quad (19)$$

The two-electron interference terms are contracted to one- and two-centre terms according to the definitions

$$E'_\mu = \sum_{s,t,u,v} R_{\mu_s, \mu_t} R_{\mu u, \mu v} \{2[\mu_s \mu_t | \mu_u \mu_v] - [\mu_s \mu_v | \mu_u \mu_t]\} \quad (20)$$

$$g_{\mu_s, \nu_t} = \sum_{\kappa, u} \sum_{\lambda, v} R_{\kappa u, \lambda v} \{2[\mu_s \nu_t | \kappa_u \lambda_v] - [\mu_s \lambda_v | \kappa_u \nu_t]\} \quad \text{for } \mu, \nu, \kappa, \lambda \text{ not all equal} \quad (21)$$

where

$$R_{\mu_s, \nu_t} = \sum_i c_{\mu s}^i c_{\nu t}^i$$

The choice of (21) for this contraction is simple and reasonable but, of course, arbitrary.

In order to simplify the energy expression (18) we have to introduce charge and bond orders in the following way:

$$\text{Covariant coefficients: } d_{\mu s}^i = \sum_{\nu, t} S_{\mu_s, \nu_t} c_{\nu t}^i$$

$$\text{Charge } q_{\mu s} = 2 \sum_i c_{\mu s}^i d_{\mu s}^i \quad (22)$$

$$\text{Bond orders } \left. \begin{aligned} p_{\mu_s, \nu_t}^{(1)} &= 2 \sum_i c_{\mu s}^i d_{\nu t}^i \\ p_{\mu_s, \nu_t}^{(2)} &= 2 \sum_i c_{\mu s}^i c_{\nu t}^i \\ p_{\mu_s, \nu_t}^{(3)} &= 2 \sum_i d_{\mu s}^i d_{\nu t}^i \end{aligned} \right\} \quad (23)$$

$$p_{\mu_s, \nu_t}^2 = \frac{1}{2} (p_{\mu_s, \nu_t}^{(1)} p_{\nu_t, \mu_s}^{(1)} + p_{\mu_s, \nu_t}^{(2)} p_{\mu_s, \nu_t}^{(3)}) \quad (24)$$

Eq. (22) is simply Mulliken's charge definition [10] but (24) has not been used so far. In Sect. 4 some properties of this bond order definition will be examined.

With the help of the definitions (19)–(24) Eq. (18) can now be written as

$$E = 2 \sum_i \sum_{\mu, s} \sum_{\nu, t} c_{\mu s}^i h_{\mu s, \nu t} c_{\nu t}^i + \sum_{\mu, s} \sum_{\nu, t} [\frac{1}{2} q_{\mu s} q_{\nu t} - \frac{1}{4} p_{\mu_s, \nu_t}^2] (\mu_s \mu_s | \nu_t \nu_t) + \sum_{\mu < \nu} \frac{Z_\mu Z_\nu}{R_{\mu\nu}} + \sum_\mu E'_\mu + \sum_i \sum_{\mu, s} \sum_{\nu, t} c_{\mu s}^i g_{\mu_s, \nu_t} c_{\nu t}^i \quad (25)$$

The matrix elements of  $\hat{h}$  contain one-centre, interference, and quasiclassical parts that we want to separate by defining the following parameters:

1. A one-centre parameter

$$\bar{\alpha}_{\mu s} = -\frac{1}{2}\langle \chi_{\mu s} | \Delta | \chi_{\mu s} \rangle - Z_{\mu}(\mu : \mu_s \mu_s) \quad (26)$$

that is simply the energy of the AO  $\chi_{\mu s}$  in the field of nucleus  $\mu$ .

2.  $h_{\mu s, \nu t}$  ( $\mu \neq \nu$ ) contains three-centre penetration integrals. By the definition of a resonance parameter

$$\begin{aligned} \bar{\gamma}_{\mu s, \nu t} = & -\frac{1}{2}\langle \chi_{\mu s} | \Delta | \chi_{\nu t} \rangle - \sum_{\kappa} Z_{\kappa}(\kappa : \mu_s \nu_t) \\ & + \frac{1}{2}S_{\mu s, \nu t} \left\{ \sum_{\kappa(\neq \mu)} Z_{\kappa}(\kappa : \mu_s \mu_s) + \sum_{\kappa(\neq \nu)} Z_{\kappa}(\kappa : \nu_t \nu_t) \right\} \end{aligned} \quad (27)$$

only the interference parts of these three-centre integrals are retained whereas their quasiclassical parts (last term in (27)) enter into the quasiclassical energy to be defined below. Thus  $\bar{\gamma}$  is a two-centre parameter plus three-centre interference terms.

3. The appropriate definition for a reduced resonance parameter is therefore (as in the case of  $H_2$ )

$$\bar{\beta}_{\mu s, \nu t} = \bar{\gamma}_{\mu s, \nu t} - \frac{1}{2}S_{\mu s, \nu t}(\bar{\alpha}_{\mu s} + \bar{\alpha}_{\nu t}) \quad (28)$$

$\bar{\beta}_{\mu s, \nu t}$  contains all of the two- and three-centre one-electron interference terms contained in  $h_{\mu s, \nu t}$ .

Finally we have to deal with the two-electron interference terms, and at this point the arbitrariness of (21) becomes apparent. But it is not unreasonable to consider  $g_{\mu s, \mu s}$  as an additional one-centre ( $\mu_s$ ) parameter arising from the existence of interference density in the molecule, and  $g_{\mu s, \nu t}$  ( $\mu \neq \nu$ ) as an interference parameter mainly arising from the interaction with all of the Coulomb charges.

Thus, with the definitions

$$\left. \begin{aligned} \alpha_{\mu s} &= \bar{\alpha}_{\mu s} + \frac{1}{2}g_{\mu s, \mu s} \\ \gamma_{\mu s, \nu t} &= \bar{\gamma}_{\mu s, \nu t} + \frac{1}{2}g_{\mu s, \nu t} \\ \tilde{\beta}_{\mu s, \nu t} &= \gamma_{\mu s, \nu t} - \frac{1}{2}S_{\mu s, \nu t}(\alpha_{\mu s} + \alpha_{\nu t}) \end{aligned} \right\} \quad (29)$$

we can consider the  $\tilde{\beta}$  parameters as containing all one- and two-electron interference terms.

Inserting (26)–(29) into (25) gives the energy expression

$$\begin{aligned} E = & \sum_{\mu} \left[ \sum_s q_{\mu s} \alpha_{\mu s} + E'_{\mu} \right] + 2 \sum_{(\mu, s) \neq (\nu, t)} \sum_i c_{\mu s}^i \tilde{\beta}_{\mu s, \nu t} c_{\nu t}^i + \frac{1}{2} \sum_{\mu, s} \sum_{\nu, t} [q_{\mu s} q_{\nu t} - \frac{1}{2}P_{\mu s, \nu t}^2] \times \\ & \left[ (\mu_s \mu_s | \nu_t \nu_t) + \sum_{\mu < \nu} \left[ \frac{Z_{\mu} Z_{\nu}}{R_{\mu \nu}} - Z_{\mu} \sum_t q_{\nu t} (\mu : \nu_t \nu_t) - Z_{\nu} \sum_s q_{\mu s} (\nu : \mu_s \mu_s) \right] \right] \end{aligned} \quad (30)$$

The second and third term in the last sum in (30) contain the quasiclassical terms removed from  $h_{\mu s, \nu t}$  in Eq. (27).

So far we have been busy with a rearrangement of the MO-LCAO energy (18), and Eq. (30) shows the same unphysical behaviour for large distances as does (18). For example in the case of  $H_2$   $q_\mu = q_\nu = 1$  and  $p_{\mu\nu}^2 = 1$  for all  $R$ , so the third sum in (30) yields  $E_{MO}^{(2)}$  of Eq. (12).

Now, we have to generalize the correlation and interference corrections (16) and (17). A straightforward extension of the correlation correction (16) is:

$$\text{a) Replace } -\frac{1}{2}p_{\mu_s\nu_t}^2(\mu_s\mu_s|\nu_t\nu_t) \text{ by } -\frac{1}{4}p_{\mu_s\nu_t}^2[(\mu_s\mu_s|\mu_s\mu_s) + (\nu_t\nu_t|\nu_t\nu_t)] \quad (31)$$

If  $p_{\mu_s\nu_t}^2 > 0$  (as is usually the case, see Sect. 4) (31) apparently leads to an energy decrease.

For the general interference correction we cannot retain the formula (17) because it works well only in the case of  $H_2$  and some other similar bonds. So our procedure is as follows:

$$\text{b) Replace } \tilde{\beta}_{\mu_s\nu_t} \text{ by } \beta_{\mu_s\nu_t} (|\beta| \leq |\tilde{\beta}|) \text{ in such a way that the corresponding energy increase compensates the same percentage of the correlation correction as Eq. (17) does in the case of } H_2. \quad (32)$$

Our final energy expression, split into one- and two-centre and one- and two-electron parts, then reads

$$E = \sum_{\mu} E_{\mu} + \sum_{\mu < \nu} E_{\mu\nu}$$

where  $E_{\mu} = E_{\mu}^{(1)} + E_{\mu}^{(2)}$ ,  $E_{\mu\nu} = E_{\mu\nu}^{(1)} + E_{\mu\nu}^{(2)}$

$$\left. \begin{aligned} E_{\mu}^{(1)} &= \sum_s q_{\mu s} \alpha_{\mu s} + 2 \sum_i' \sum_{s,t} c_{\mu s}^i \beta_{\mu s, \mu t} c_{\mu t}^i \\ E_{\mu}^{(2)} &= \frac{1}{2} \sum_s \left[ (q_{\mu s})^2 - \frac{1}{2} \sum_{\nu (\neq \mu)} \sum_t p_{\mu s, \nu t}^2 - \frac{1}{2} p_{\mu s, \mu s}^2 \right] (\mu_s \mu_s | \mu_s \mu_s) \\ &\quad + \frac{1}{2} \sum_{s,t}' [q_{\mu s} q_{\mu t} - \frac{1}{2} p_{\mu s, \mu t}^2] (\mu_s \mu_s | \mu_t \mu_t) + E_{\mu}' \\ E_{\mu\nu}^{(1)} &= 4 \sum_i' \sum_{s,t} c_{\mu s}^i \beta_{\mu s, \nu t} c_{\nu t}^i \\ E_{\mu\nu}^{(2)} &= \sum_{s,t} q_{\mu s} q_{\nu t} (\mu_s \mu_s | \nu_t \nu_t) + \frac{Z_{\mu} Z_{\nu}}{R_{\mu\nu}} - Z_{\mu} \sum_t q_{\nu t} (\mu : \nu_t \nu_t) - Z_{\nu} \sum_s q_{\mu s} (\nu : \mu_s \mu_s) \end{aligned} \right\} (33)$$

Remember that  $E_{\mu}^{(1)}$ ,  $E_{\mu\nu}^{(1)}$  do not denote pure one-electron terms but contain the two-electron interference terms as well.

If we write the energy of the isolated atom  $\mu$  as

$$E_{\mu}^0 = \sum_{\mu, s} n_{\mu s} \bar{\alpha}_{\mu s} + E_{\mu}^{0(2)}$$

( $n_{\mu s}$  = occupation number of AO  $\chi_{\mu s}$ ) we get the binding energy of the molecule as sum of promotion, interference and quasiclassical terms, defined by Eqs. (34):

$$\left. \begin{aligned} \Delta E &= \left[ \sum_{\mu} \left( E_{\mu}^{(1)} - \sum_s n_{\mu s} \bar{\alpha}_{\mu s} \right) + \sum_{\mu} \left( E_{\mu}^{(2)} - E_{\mu}^{0(2)} \right) \right] + \sum_{\mu < \nu} E_{\mu\nu}^{(1)} + \sum_{\mu < \nu} E_{\mu\nu}^{(2)} \\ \Delta E &= \qquad \qquad \qquad E_p \qquad \qquad \qquad + E_I \qquad \qquad \qquad + E_{QC} \end{aligned} \right\} (34)$$

If the molecule is not described by the same AO's as the free atoms, e.g. in the case of scaling, different  $\bar{\alpha}_{\mu s}$  have to be used in  $E_{\mu}^{(1)}$  and  $\sum_s n_{\mu s} \bar{\alpha}_{\mu s}$ .

#### 4. Basis and Rotational Invariance

In the preceding section we did not impose any restriction on the AO basis  $\{\chi\}$ , so the formulae, in principle, are valid for minimal or extended bases, canonical or hybrid AO's. But the crucial points in our derivation, i.e. correlation and interference correction (31), (32), and the splitting of the two-electron energy by (19) are very sensitive to the choice of basis. Before we consider this problem in detail we need to know some properties of the bond order definition (24), because the correlation correction (31) as the main correction to the SCF energy is proportional to  $p^2$ .

##### 4.1. Properties of the Bond Order

In the literature there exist a large number of different "bond order" definitions (see e.g. [11] and references therein). The adoption of a particular definition is usually suggested by the choice of wave function and approximations (e.g. neglect of overlap) or by a physical requirement that the definition should fulfil. The former is true with our definition, and indeed a similar (but simpler) form of a bond order has been defined in a paper of Ruedenberg [12] that deals with an energy partitioning within  $\pi$ -electron theory where overlap between next neighbours is taken into account. Apparently, the choice of an MO-LCAO wave function in a non-orthogonal AO basis "naturally" leads to (24).

Let us consider the first term in (24), i.e.  $p_{\mu s, \nu t}^{(1)} p_{\nu t, \mu s}^{(1)}$ . This term looks like a generalization of the Wiberg bond index [13] (that has been defined in an OAO basis) to a non-orthogonal basis. In fact, it is an easy matter to show that the main property of the Wiberg index holds also for  $p^{(1)}$ , namely

$$\sum_{\substack{\nu, t \\ (\neq \mu s)}} p_{\mu s, \nu t}^{(1)} p_{\nu t, \mu s}^{(1)} = 2q_{\mu s} - q_{\mu s}^2 \quad (35)$$

It is apparent from (35) that the total bond order of AO  $\chi_{\mu s}$  cannot become negative and that its maximum value is 1, for  $q_{\mu s} = 1$ . If the charge of  $\chi_{\mu s}$  is smaller or larger than 1, the total bond order decreases and reaches 0 for  $q_{\mu s} = 0$  or 2. Thus, the first term in (24) corresponds to the concept of a "covalent bond"; the larger the polarity of a bond the smaller the bond order. If  $\chi_{\mu s}$  is involved in purely ionic interactions then the total bond order of  $\chi_{\mu s}$  is zero.

Now we take into account the second term in (24). Instead of (35) we have

$$\sum_{\substack{\nu, t \\ (\neq \mu s)}} p_{\mu s, \nu t}^2 = 2q_{\mu s} - \frac{1}{2}q_{\mu s}^2 - \frac{1}{2}p_{\mu s, \mu s}^{(2)} p_{\mu s, \mu s}^{(3)} \quad (36)$$

An inspection of the definitions (23) suggests that the second and third terms in (36) should not be very different except for strongly antibonding interactions or very small distances (large overlaps), and our calculations indeed confirm this assumption.

The total bond order of atom  $\mu$  can be defined as

$$B_{\mu} = \sum_s \sum_{\substack{\nu, t \\ (\neq \mu)}} p_{\mu s, \nu t}^2$$

Inserting (36) gives

$$B_{\mu} = 2 \sum_s q_{\mu s} - \sum_{s,t} p_{\mu s, \mu t}^2 \quad (37)$$

The first as well as the second term in (37) can be written as trace of a product of matrices (density and overlap) that are transformed unitarily under a unitary transformation of the AO's of atom  $\mu$ . Therefore,  $B_{\mu}$  is invariant under a unitary transformation of the AO basis.

#### 4.2. Construction of the Proper AO Basis

The correlation and interference correction are based on ideas that have been inferred from the  $H_2$  molecule within a minimal AO basis. So they correspond to the pictorial model of a molecule consisting of (promoted) atoms and covalent two-centre two-electron bonds between them. That means that the two corrections are consistent in our conceptual frame only if we apply them in a minimal hybrid AO basis. These hybrids should be oriented along the bond directions such that each of the two-centre bonds is formed essentially by two hybrid AO's. The corrections should then be applied only to those orbital pairs  $\chi_{\mu s}, \chi_{\nu t}$  that build up a covalent bond. But the foregoing discussion has shown that such a hybrid AO  $\chi_{\mu s}$  will have only one matrix element  $p_{\mu s, \nu t}^2 \approx 1$ , all the other  $p_{\mu s, \kappa u}^2$  being very small. Thus, in molecules with unpolar or weakly polar bonds it does not really make any difference in the hybrid basis whether we apply the full general correlation correction (31) or take just the bonding pairs  $\mu_s, \nu_t$ . On the other hand, the interference correction can easily be applied selectively to those  $\beta$  parameters that correspond to a covalent (or nearly covalent) bond. As a criterion for "near covalency" we take the threshold  $p_{\mu s, \nu t}^2 \geq 0.7$ , for all other  $\beta$  parameters we set  $\beta = \tilde{\beta}$ .

The hybrid orbitals that serve as basis for the two corrections are constructed in the following way:

1. Localization of the canonical SCF-MO's by the method of Boys [14].
2. From the  $n \times m$  matrix of the localized MO's ( $n$  = number of basis functions,  $m$  = number of occupied MO's) we take the block belonging to atom  $\mu$  and calculate the norms of the  $m$  column vectors of this block. If  $k$  denotes the number of bonds involving atom  $\mu$  plus the number of lone pairs at  $\mu$ , then the  $k$  vectors with the largest norms constitute the new hybrid AO basis at  $\mu$ .
3. These hybrids are directed along the localized bonds reached at by the Boys localization but are not orthonormal. We construct orthonormal AO's by the Löwdin procedure [15] because in this way the symmetry properties of the AO's are retained and the final basis resembles the non-orthogonal one as closely as possible.
4. If the number of basis functions at atom  $\mu(1)$  is larger than the number of hybrids ( $k$ ) we construct  $1-k$  more hybrids by the Schmidt method. These additional hybrids do not influence the following calculations and can therefore be chosen rather arbitrarily.

The steps 2-4 have to be performed for every atom  $\mu$ , and finally one gets a block-diagonal unitary matrix that transforms the original AO basis into the desired hybrid basis. As we have seen, the total bond order of  $\mu$  is not affected by this transformation but the bond orders are "localized" in the bonds.

### 4.3. Rotational Invariance

In many semiempirical methods there exists the problem that by introduction of certain approximations the energy and other molecular properties become dependent on the orientation of the molecule in the co-ordinate system that serves as frame for the approximations. In order to enforce “rotational invariance” one usually averages over local (one-centre)  $p$ -orbital components within the two-electron integrals. This procedure leads to rather large errors [16], especially in the case of a strongly anisotropic environment of an atom in a molecule.

If we would perform our calculations totally in the hybrid basis described above, our total energy as well as the energy fragments would be rotationally invariant. But this would require a transformation of the two-electron integrals, a very time-consuming step that we want to avoid. Therefore, the splitting of the two-electron integrals into quasiclassical and interference parts (19) is done in the original AO basis. This has the consequence that the energy fragmentation (not the total energy!) gets a bit orientation dependent but even in the most anisotropic cases this dependence amounts to a few per cent only.

Consider for example the  $F_2$  molecule (minimal basis), one of the worst cases as regards rotational dependence. The orientation of the  $p$ -orbitals is fixed along the co-ordinate axes, and the nuclei are a) placed on the  $z$ -axis, b) rotated around the  $x$ -axis by  $45^\circ$ . The values of the  $\beta$  parameter that corresponds to the  $\sigma$ -bond in the hybrid basis are a)  $-0.2655$ , b)  $-0.2791$ , thus the variance of  $\beta$  amounts to  $\approx 5\%$ . The corresponding change of  $E_{\mu\nu}^{(1)}$  (33) is compensated by a change mainly of  $E_{\mu}^{(1)}$ .

Since the interference correction (32) always compensates a certain percentage of the correlation correction (31) we have only to consider the rotational dependence of the latter. The correlation correction is calculated in a hybrid basis, so the only source of rotational dependence is the fact that the Boys localization is an iterative process that is terminated when a given convergence threshold has been reached. Different basis representations of the molecular density can therefore lead to slightly different hybrids. In the  $F_2$  example (the worst case we could find) the correlation corrections differ by 2%. For comparison, consider at the other extreme the nearly isotropic molecule  $CH_4$  in the following orientations: a) the protons occupy the corners of a cube with planes parallel to the co-ordinate axes, b) situation a) rotated by  $45^\circ$  around the  $z$ -axis. In this case the correlation corrections differ by only 0.1%.

In summary, the rotational variance of our energy fragmentation amounts to a few per cent of the correlation correction only and is thus negligible compared to the inherent approximations of the method. It is desirable, however, to fix the relative orientation of the AO basis as uniquely as possible in order to make the results easily reproducible. For this purpose we follow an idea by Halgren and Lipscomb [17]: the  $p$ -orbitals at each of the atomic centres are transformed to the local principal axes. These principal axes are obtained as eigenvectors of a matrix  $U^\mu$  with elements

$$U_{s,t}^\mu = \langle \chi_{\mu s} | \hat{h} | \chi_{\mu t} \rangle$$

where  $\hat{h}$  is the molecular one-electron operator and  $\chi_{\mu s}$ ,  $\chi_{\mu t}$  are  $p$ -orbitals at centre  $\mu$ . By this procedure only those  $p$ -orbitals are not uniquely defined that belong to a two- or three-dimensional representation of the local symmetry group. For example, in ethane only one and in methane none of the  $p$ -orbitals is fixed but here the environment of the unfixed orbitals is rather “isotropic”. Thus, the rotational variance of the energy analysis is reduced to  $< 1\%$  of the correlation correction in all of the molecules considered.

#### 4.4. Basis Dependence of the Corrections

Now we know how to handle the initial AO basis during an energy analysis calculation. Before the integral evaluation the  $p$ -orbitals are transformed to local principle axes, and before the correlation correction is applied one has to transform to a hybrid basis according to Sect. 4.2. But we still have to examine the dependence of the correlation and interference corrections on the size, that means flexibility, of the basis. To this end we turn our attention to the  $H_2$  molecule again where the essential features of the basis dependence can be demonstrated most clearly.

In  $H_2$  one has always  $p_{\mu,\nu}^2 = 1$ , so the correlation correction is proportional to the difference between the one- and two-centre Coulomb integrals

$$(\mu\mu | \mu\mu) - (\mu\mu | \nu\nu)$$

of those hybrids  $\chi_\mu, \chi_\nu$  that form the bond. It is apparent that this difference will be the smaller the better  $\chi_\mu, \chi_\nu$  are localized into the direction of the bond. Thus, compared to  $\chi_\mu, \chi_\nu$  being simply hydrogen  $1s$  orbitals, a scaling of the orbitals (contraction) will enlarge the correlation correction whereas addition of polarization functions ( $p_z$ ) will reduce it.

The interference correction (17) amounts to a multiplication of  $\beta$  by a factor

$$F_I = \frac{S + S^2}{1 + S^2}$$

Again, the better the hybrids are directed towards each other, the larger is their overlap, the nearer is  $F_I$  to 1, and the smaller the effect of the interference correction.

For the following discussion let us consider three different basis sets: basis I consists of two hydrogen  $1s$  functions (10 Gaussians contracted to one group [18]), in basis II the contraction is (7, 2, 1), i.e. this basis allows for scaling, and basis III contains an additional polarization function  $p_z$  ( $\eta = 0.65$ ). Table 2 shows the factor  $F_I$  and the  $\beta$  parameter for different distances  $R_{HH}$  in basis I and III.  $F_I$  is considerably larger in the flexible than in the minimal basis, and in addition,  $|\beta|$  is significantly smaller. As a result, in basis III the interference correction (17) is negligible at all internuclear distances. We conclude that the VB formula (11) for the interference energy is the proper choice for a minimal basis, but in a flexible basis there is not much difference between (10) and (11).

Another important feature of the basis dependence is shown in Fig. 3. Here the potential curves of  $H_2$  in basis I, II, III are compared with the "exact" one [19] and the SCF energy in basis III. At small and intermediate distances the (3s) basis II is comparable to a scaled minimal basis (see Fig. 2), and the most flexible basis shows considerably smaller deviations

Table 2. Interference correction factor  $F_I$  and  $\beta$  of  $H_2$  in different basis sets

$R_{H-H} [a_0]$	Basis I		Basis III	
	$F_I$	$ \beta $	$F_I$	$ \beta $
1.0	0.918	0.109	0.989	0.062
1.4	0.842	0.131	0.967	0.069
2.0	0.692	0.127	0.890	0.088
3.0	0.419	0.084	0.692	0.069
5.0	0.105	0.023	0.447	0.001



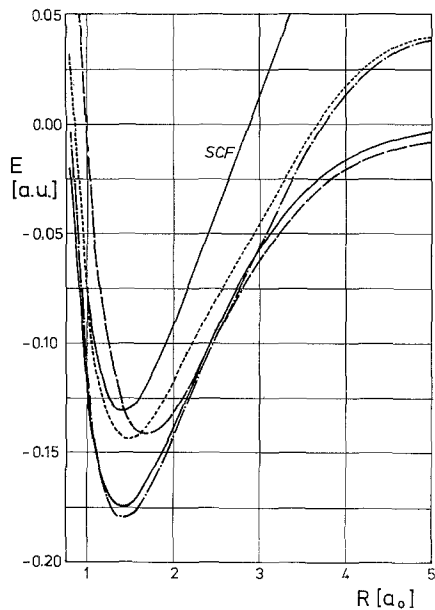


Fig. 3. Potential curves of  $H_2$  with basis I (---), II (-.-.-), and III (-.-.-.-), compared with the SCF energy in basis III and the "exact" [19] curve (——). For details see text

from  $E_{SCF}$ , as we have expected. But at large distances only basis I shows the proper asymptotic behaviour, whereas II and III for  $R \rightarrow \infty$  converge to an energy limit of  $\Delta E = 0.028$  a.u. The reason for this behaviour is the equivalency of our procedure of subtracting  $\frac{1}{2}(\mu\mu|\mu\mu)$  from the SCF energy and the "half electron" method applied to two separated hydrogen atoms [20]. Therefore, for  $R \rightarrow \infty$  our hybrid AO's do not converge to hydrogen  $1s$  orbitals but to the more diffuse orbitals one gets by the half electron method. The energy of H within this method is indeed too high by 0.014 a.u. [21] in agreement with our limit.

We conclude that in our formalism the use of flexible basis sets is justified only at small and intermediate distances because only a minimal basis can ensure the proper asymptotic behaviour for  $R \rightarrow \infty$ . Nevertheless, it should be noted that even with a flexible basis the error of the energy limit for  $R \rightarrow \infty$  is an order of magnitude smaller in our formalism than in the SCF approximation.

## 5. Results

Most of our energy analysis calculations have been done within a minimal Gaussian type AO basis (if not stated otherwise) chosen in the following way.

H in  $H_2$ : ( $10s$ ) basis from [18] contracted to one function (with appropriate scaling factor)

H in other molecules: ( $3s$ ) from [18], contracted to one function with scaling factor 1.3

Li, C-F: ( $9s$ ) (Li) and ( $7s, 3p$ ) basis (C-F) from [22]. The first five  $s$  functions (7 in Li) were contracted to give the  $1s$  orbital, the remaining two forming the non-orthogonal  $2s$  orbital. Orthogonality was obtained by adding two more energy optimized  $s$  functions, the resulting  $2s$  orbitals are given in the appendix. The three  $p$  functions were fully contracted.

In some calculations (especially in hydrocarbons) a “flexible basis” has been employed: by this we simply mean a contraction of the three  $p$  functions into two  $p$  groups (2, 1).

The experimental values for equilibrium distances  $R_e$  and binding energies  $\Delta E$  were taken from [23] and [24].

### 5.1. Two-Electron Interference Contributions

Suppose that an MO-LCAO wave function of a given molecule is already at hand. Then the energy analysis formulated above still requires the calculation of all of the  $\approx N^4/8$  ( $N$  = dimension of the AO basis) two-electron integrals for the evaluation of the two-electron interference contributions (19). It is of considerable interest whether we can neglect the four- and three-centre parts of these contributions, i.e. whether the Mulliken approximation can be applied to the four and three-centre integrals.

In a paper by Brown and Burton [25] on the NDDO approximation it has been shown that neglect of four- and three-centre two-electron integrals (if “balanced” by a neglect of the one-electron three-centre terms) can give reasonable results as regards the relative ordering of one-electron energies. As we are interested in total energies our situation is much more crucial in spite of the fact that we are considering only the interference part of the two-electron integrals.

The binding energies of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  in different approximations are given in Table 3. “A” denotes the total binding energy, “B” neglect of four-centre two-electron contributions, and “C” neglect of four- and three-centre contributions. “D” is a “balanced” version: in addition to C the three-centre one-electron interference contributions are neglected as well, i.e. the Mulliken approximation is applied to the three-centre penetration integrals. Table 3 shows that in a medium size molecule like  $\text{C}_2\text{H}_6$  even the four-centre two-electron interference contributions constitute a considerable fraction of the binding energy. The balanced version D is in error by about 20% in  $\text{CH}_4$  and 25% in  $\text{C}_2\text{H}_6$ , thus for the purpose of our analysis we have to take into account all of the two-electron interference contributions, and this is done in the results presented below.

### 5.2. Physical Significance of the Energy Fragments

In the derivation of Sect. 3 we have generalized the definitions of promotion, interference and quasiclassical energy that originated from the  $\text{H}_2^+$ ,  $\text{H}_2$  comparison. But it is not immediately apparent that our generalized definitions (see Eqs. (33, 34)) are still physically meaningful, i.e. are still consistent with the concepts on which the energy analysis is based.

Let us first consider the quasiclassical energy  $E_{QC}$  between two atoms  $\mu$  and  $\nu$ .  $E_{\mu\nu}^{(2)}$  is the sum of the repulsive electron–electron and nucleus–nucleus and the attractive electron–

Table 3. Binding energy (in a.u., experimental geometry) in different approximations (see text)

	A	B	C	D	exp
$-\Delta E$ $\text{CH}_4$	0.657	0.660	0.156	0.796	0.625
$\text{C}_2\text{H}_6$	1.104	0.930	<0	1.374	1.063

nucleus interactions, and at large internuclear distances  $R$  one has  $E_{\mu\nu}^{(2)} = 0$  because each interaction term is proportional to  $1/R$ . When  $R$  is decreased the electron clouds of  $\mu$  and  $\nu$  eventually begin to overlap, the electron–electron interaction increases slower than  $1/R$ , and  $E_{\mu\nu}^{(2)}$  becomes negative. At still smaller  $R$  the nuclei begin to penetrate into the electron cloud of the other atom, and now the nucleus–nucleus repulsion dominates the other quasiclassical interactions. Thus, we expect  $E_{\mu\nu}^{(2)}$  to exhibit a potential curve-like functional behaviour and this has indeed been confirmed in all types of bonds calculated so far. (The only small deviation is due to the fact that the correlation correction is performed within a hybrid AO basis affecting a maximization of the first term in (31). Because the basis dependence of the correlation correction is largest (though still relatively small) at intermediate distances, one can get for  $R < \infty$  a small positive  $E_{QC}$  before it drops down to its minimum for smaller  $R$ .)

Still there remains a problem with the definition of  $E_{QC}$  because it depends on the Mulliken charges  $q$ . As is well known, these charges are strongly basis dependent and for heteropolar bonds sometimes give quite unreasonable descriptions, e.g. for hydrocarbons with a minimal basis. For  $\text{CH}_4$  we get a charge on hydrogen of only 0.79, and accordingly rather large quasiclassical interactions:

$$E_{\text{CH}}^{(2)} = -1.8 \text{ eV} \quad E_{\text{HH}}^{(2)} = 0.33 \text{ eV} \quad \sum_{\mu < \nu} E_{\mu\nu}^{(2)} = -5.1 \text{ eV}$$

If we use a flexible basis on C we get  $q_{\text{H}} = 0.87$  and

$$E_{\text{CH}}^{(2)} = -0.26 \text{ eV} \quad E_{\text{HH}}^{(2)} = 0.12 \text{ eV} \quad \sum_{\mu < \nu} E_{\mu\nu}^{(2)} = -0.35 \text{ eV}$$

Another effect of the large negative excess charge on C in minimal basis hydrocarbons is an unphysical negative promotion energy  $E_P$  of C. Thus, for a reasonable energy fragmentation of hydrocarbons we have to employ a flexible basis on C.

We now have to show that the  $E_P$  term in (34) actually can be regarded as a sum of promotion energies. This is not clear from the outset because of our peculiar bond order definition. In Table 4 we compare our  $E_P$  values with promotion energies from [4] (minimal basis MO-LCAO calculations) as well as the respective “valence energies”. In our formalism the valence energy  $E_V$  differs from  $E_P$  in the term  $E_{\mu}^{(2)}$  (Eqs. (33, 34)). Instead of  $E_{\mu}^{(2)}$  the valence energy contains the one-centre two-electron terms from Eq. (30). For

Table 4.  $E_P$  and  $E_V$  compared to promotion and valence energies (in eV, at experimental geometries). The hydrocarbons and  $\text{H}_2\text{O}$  have been calculated with a flexible AO basis

Atom/Molecule	$E_P$	Promotion Energy [4, 26]	$E_V$	Valence Energy [4]
H in $\text{H}_2$	0.5 <sup>a</sup>	0.5 <sup>b</sup>	5.6 <sup>a</sup>	3.5 <sup>b</sup>
Li in $\text{Li}_2$	0.2	-0.1	1.7	1.7
C in $\text{C}_2$	4.1	6.1	18.7	18.9
C in $\text{CH}_4$	3.3	6.5	21.5	—
$\text{C}_2\text{H}_4$	3.1	6.8	20.5	—
$\text{C}_2\text{H}_2$	6.3	7.2	23.8	26.0 <sup>c</sup>
N in $\text{N}_2$	16.4	8.1	30.3	22.2
O in $\text{H}_2\text{O}$	10.9	8.0	22.0	18.8
F in $\text{F}_2$	1.4	1.7	7.6	8.7

<sup>a</sup> Scaling factor 1.193.

<sup>b</sup> Calculated with a Weinbaum function [9].

<sup>c</sup> C in HCN.

hydrocarbons comparison is made with promotion energies from [26] that have been obtained in the following way: the energy of the isolated atom is calculated with AO's restricted to  $s, p, sp, sp^2, sp^3$  form, the charges  $q_{\mu,s}$  are chosen as integers, and the energies of the different spectroscopic terms belonging to the given configuration are averaged over.

The numbers in Table 4 compare reasonably well, with the exception of  $N_2$ . The exceptional bonding situation in this molecule is reflected in our analysis and will be discussed in detail in Sect. 5.4. The other deviations in Table 4 are easily explained. In Sect. 2 it was shown that a MO wave function of  $H_2$  gives too much one-centre pair density whereas the Weinbaum function is rather accurate in this respect: this explains the difference in the valence energies of  $H_2$ . The promotion energies of hydrocarbons from Ref. [26] have been calculated with integer AO charges, therefore an exact reproduction of these values would be fortuitous. Finally,  $H_2O$  is a very polar molecule (therefore calculated with a flexible basis) and in an energy analysis of it one should introduce special charge transfer terms, as is done in [4]. So our  $E_P$  and  $E_V$  values contain some charge transfer effects but their difference, i.e. the energy due to sharing penetration, compares favourably with [4]. This last statement is also true for  $N_2$ . In summary, we are confident that the generalization of the promotion and valence concepts in Sect. 3 is physically meaningful and that  $E_P$  corresponds to the pictorial promotion concept, at least in molecules with unpolar or weakly polar bonds.

The third term in (34),  $E_I$ , contains all the purely quantum mechanical interference effects that are responsible for bonding or antibonding. If  $E_{QC}$  and  $E_P$  are relatively small, as is e.g. the case for hydrocarbons (see Sect. 5.4),  $E_I$  is roughly equal to the binding energy. But in our model of bond formation obviously  $E_I$  and  $E_P$  should be strongly basis dependent (whereas  $E_{QC}$  should change relatively little with basis size). In a basis more flexible than minimal the electron density can better adjust to the molecular situation causing larger deviations from the free atom densities. The corresponding increase of  $E_P$  is, of course, overcompensated by a decrease of  $E_I$  giving rise to a small net decrease of the SCF energy. On the other hand, if the AO basis is further enlarged,  $E_P$  as well as  $E_I$  should converge to some limit if there is any physical meaning associated with these quantities. Table 5 shows the basis dependence of the binding energy fragments of  $H_2$  and  $F_2$ . Apparently, the results are consistent with our model considerations giving support to the soundness of the underlying assumptions.

Finally we want to mention that Eq. (34) can serve as starting point for an examination of assumptions and approximations of some current semiempirical methods.  $E_{QC}$  is relatively small at intermediate internuclear distances, and if the two-electron part of  $E_P$  can be neglected as well we have justification for a "one-electron" expression of the

Table 5. Binding energy fragments and total binding energy (in a.u.) of  $H_2$  and  $F_2$  in different AO basis sets (experimental geometry)

	$H_2$			$F_2$			
	a	b	c	a	b	c	
$E_{QC}$	-0.021	-0.020	0.048	0.003	-0.037	-0.050	<sup>a</sup> Minimal basis; scaling factor in $H_2$ 1.193.
$E_P$	0.036	0.166	0.151	0.077	0.524	0.619	<sup>b</sup> $H_2$ : basis II of Sect. 4.4; $F_2$ : flexible basis.
$E_I$	-0.185	-0.323	-0.341	-0.140	-0.548	-0.616	<sup>c</sup> $H_2$ basis III of Sect. 4.4; $F_2$ : complete decoupling of the two $2s$ and three $2p$ Gaussians.
$\Delta E$	-0.169	-0.179	-0.142	-0.060	-0.061	-0.047	

binding energy that can be compared with the further simplified semiempirical methods. These problems will be dealt with in a forthcoming paper [27].

### 5.3. Equilibrium Distances and Binding Energies

In our derivation we have corrected the SCF energy for the left-right correlation in an approximate way, so one should expect our binding energies to compare considerably better with experiment than the SCF results. On the other hand, equilibrium distances as given by SCF calculations usually are surprisingly accurate even in minimal basis. It is clear from the discussion in Sect. 2 that at intermediate bond lengths both the sharing penetration and the interference SCF energies are considerably too large in absolute value. But in the neighbourhood of the equilibrium distance  $R_e$  both errors partly cancel each other, and what is more important for the determination of  $R_e$  there is a nearly complete cancellation of the variations of both errors with distance. We cannot expect that after application of the two approximate corrections (31, 32) there will be an equally good cancellation of the remaining errors, so our equilibrium distances will in general show larger deviations from the experimental results than do the SCF distances.

In Table 6 equilibrium distances  $R_e$  and binding energies  $\Delta E$  calculated with Eq. (34), with and without interference correction (32), are compared with the experimental and SCF values. In addition to homonuclear diatomics and hydrocarbons two polar molecules are included for comparison. As one would expect, our formalism works best with bonds similar to  $H_2$ , i.e. the C-C and C-H bonds in hydrocarbons. The equilibrium distances obtained for these molecules are only a few per cent larger than the SCF values, whereas the binding energies are in remarkably good agreement with experiment. In the homonuclear diatomics one has bonding situations differing very much from  $H_2$ . Indeed, despite their unpolar nature these molecules are rather hard test cases for approximate quantum

Table 6. Equilibrium distances (in  $a_0$ ) and binding energies (in a.u.) with (A) and without (B) interference correction (32). The calculated equilibrium distances are given in percentage deviation from the experimental values, all the calculated equilibrium distances are too large ( $\Delta R_e > 0$ ). All calculations have been done with a minimal AO basis

Bond	exp		A		B		SCF	
	$R_e$	$\Delta E$	$\Delta R_e(\%)$	$\Delta E$	$\Delta R_e(\%)$	$\Delta E$	$\Delta R_e(\%)$	$\Delta E$
$H_2$	1.40	-0.175	3	-0.170	9	-0.225	0	-0.128
$Li_2$	5.05	-0.042	14	-0.026	25	-0.045	5	-0.009
$C_2$	2.34	-0.234	16	-0.193	11	-0.376	14	0.020
$N_2$	2.08	-0.364	11	-0.182	20	-0.372	8	0.004
$F_2$	2.72	-0.062	16	-0.082	13	-0.184	1	0.053
$CH_4/RCH$	2.05	-0.625	7	-0.675	15	-0.834	2	-0.516
$C_2H_6/RCC^a$	2.93	-1.063	9	-1.113	14	-1.274	3	-0.860
$C_2H_4^b/RCC$	2.55	-0.846	8	-0.870	13	-1.016	3	-0.637
$C_2H_2/RCC^c$	2.27	-0.618	7	-0.656	12	-0.784	2	-0.425
$CH^cR$	2.00	-0.618	8	-0.655	13	-0.787	4	-0.429
$CO/RCO$	2.17	-0.413	11	-0.290	17	-0.426	8	-0.137
$CO_2/RCO$	2.19	-0.608	12	-0.432	16	-0.670	5	-0.153

<sup>a</sup> Geometry as in [28], all angles and distances fixed except  $R_{CC}$ .

<sup>b</sup>  $R_{CH} = 2.034a_0$  &  $\angle HCH = 117^\circ$ .

<sup>c</sup> The other distance fixed at the experimental value.

mechanical methods, including the SCF approximation. Also, semiempirical methods that fit the same number of parameters per atom in general describe the hydrocarbons much better than the homonuclear diatomics, especially as regards the binding energy (see e.g. [29]). In view of this we conclude that our binding energies of the homonuclear diatomics, differing by “only” 20–50% from the experimental values, are surprisingly good. The equilibrium distances show rather large deviations from experiment that can be explained by the effect of the interference correction. This correction was introduced in order to partly compensate for the too large correlation correction, and Table 6 shows that without interference correction (B) both  $R_e$  and  $\Delta E$  are much too large in absolute value. Now the compensating interference correction (32) treats every bond like  $H_2$ , therefore the reduction of  $R_e$  in  $H_2$  by a few per cent is also accomplished in hydrocarbons. The equilibrium distances of the homonuclear diatomics do not show such uniform behaviour and this reflects their peculiar bonding situations. The molecules CO and  $CO_2$  should not be too polar for a reasonable description by our formalism, and the results for these molecules are indeed rather similar to  $N_2$ .

Note that all calculations of Table 6 have been performed in a minimal basis. If a flexible basis is used,  $\Delta E$  in most cases changes by less than 10%, and  $\Delta R_e$  slightly decreases or remains the same. The largest effects of a flexible basis are shown by  $N_2$  and  $F_2$  where one gets substantial improvement (version A): 4% /  $-0.286$  a.u. for  $N_2$  and 7% /  $-0.072$  a.u. for  $F_2$ .

#### 5.4. Analysis of Binding Energies

After having shown that the energy partition (34) is physically meaningful and corresponds to our qualitative picture of bond formation, at least for not too polar bonds, we finally want to examine how different bonding situations show up in the behaviour of the binding energy fragments. Let us briefly recall the essential differences between the energy partition in the  $H_2^+$  molecule and the general case. In  $H_2^+$  (Sect. 2.1) the definition of the energy fragments (quasiclassical, promotion, and interference energy) based on pictorial model considerations was a rather straightforward matter. In general there are a number of additional terms due to electron–electron interaction that we have dealt with in the following way:

- a) Coulomb and exchange two-electron interactions; these we have split into quasiclassical and interference contributions.
- b) Electron correlation, approximately taken into account by the correction of the wrong asymptotic behaviour of the MO-LCAO energy.
- c) Sharing penetration, totally neglected by the same correction (b) but afterwards again corrected for by a reduction of the interference energy. Only by this “trick” did it become possible to interpret the one-centre terms  $E_P$  as promotion energies.

Thus, the quasiclassical and promotion energies of Eq. (34) are “natural” extensions of the corresponding terms in  $H_2^+$ . The interference energy, on the other hand, contains in addition to the one-electron interference terms the other essential non-classical contributions. These are the two-electron interference terms and that part of the sharing penetration that remains after correcting the MO-LCAO energy for left–right correlation. The importance of sharing penetration has already been shown in Table 6 (version B versus A) whereas we still have to examine whether the two-electron part of  $E_I$  can perhaps be neglected. Certainly, the  $g_{\mu,s,\nu,t}$  terms (Eq. (21)) cannot be neglected as regards the total binding energy (Sect. 5.1) but only a small part of these contribute to  $E_I$ . Nevertheless, as is shown

Table 7. One-electron ( $E_I^{(1)}$ ) and two-electron ( $E_I^{(2)}$ ) contributions to  $E_I$  (in a.u.)

	$E_I^{(1)}$	$E_I^{(2)}$	$E_I$
H <sub>2</sub>	-0.187	0.002	-0.185
N <sub>2</sub>	-0.765	-0.051	-0.816
F <sub>2</sub>	-0.098	-0.042	-0.140
CH <sub>4</sub>	-0.679	-0.199	-0.878

in Table 7, the two-electron contributions in general constitute a considerable fraction of  $E_I$  and can safely be neglected only in the H<sub>2</sub> molecule. Hardly surprising, we conclude that in an attempt to describe the chemical bonding one cannot dispense with non-classical two-electron effects without a serious loss of accuracy both in the calculated results and in the physical model of bonding.

At this point we want to mention that there are two-electron effects not explicitly taken care of in our scheme, i.e. mainly angular and in-out correlation. Whereas at large inter-nuclear distances these effects are negligible they are of the same order of magnitude as the left-right correlation at small distances, but unfortunately there is no possibility of including them in a simple way. One could argue that the total neglect of sharing penetration partly accounts for these additional correlation effects, but this, presumably, would be too bold.

We are now prepared to attack the final problem of this work, i.e. the elucidation of different bonding situations by binding energy analysis. In Table 8 we present the results for the first row homonuclear diatomics, some hydrocarbons, and the polar molecules CO and H<sub>2</sub>O.

The quasiclassical energy  $E_{QC}$  is very small for molecules with unpolar single bonds. The relatively large value of C<sub>2</sub>H<sub>6</sub> is partly due to the improper Mulliken charges (Sect. 5.2) even in a flexible basis ( $q_H = 0.86$ ) but  $E_{QC}$  per bond still has the same magnitude as in H<sub>2</sub>. According to our discussion in Sect. 5.2  $E_{QC}$  of double and triple bonds should be

Table 8. Binding energy fragments and total binding energy (in a.u.) at the experimental geometries. Hydrocarbons and H<sub>2</sub>O are calculated with a flexible AO basis, the other molecules with minimal basis. Scaling factor in H<sub>2</sub> is 1.193

	$E_{QC}$	$E_P$	$E_I$	$\Delta E$	$\Delta E$ (exp)
H <sub>2</sub>	-0.021	0.036	-0.185	-0.169	-0.175
Li <sub>2</sub>	-0.015	0.021	-0.020	-0.023	-0.042
C <sub>2</sub>	-0.242	0.298	-0.258	-0.202	-0.234
N <sub>2</sub>	-0.533	1.198	-0.816	-0.151	-0.364
F <sub>2</sub>	0.003	0.077	-0.140	-0.060	-0.062
CH <sub>4</sub>	-0.013	0.204	-0.878	-0.687	-0.625
C <sub>2</sub> H <sub>6</sub>	-0.156	0.216	-1.220	-1.160	-1.063
C <sub>2</sub> H <sub>4</sub>	-0.119	0.321	-1.143	-0.941	-0.846
C <sub>2</sub> H <sub>2</sub>	-0.132	0.521	-1.107	-0.727	-0.618
CH <sub>2</sub>	-0.030	0.320	-0.552	-0.262	-0.288
CO	-0.592	1.051	-0.701	-0.242	-0.413
H <sub>2</sub> O	-0.178	0.148	-0.253	-0.283	-0.350

larger because of the larger overlap between the atomic densities, and this is confirmed by the results in Table 8. The most extreme value of  $E_{QC}$  among the unpolar molecules is shown by  $N_2$ . Obviously, this cannot be attributed to the triple bond, as is shown by a comparison with  $C_2H_2$ , but to the unusually strong polarization of the atomic densities into the bonding region. In acetylene the two protons serve as opposing forces that prevent the bond from such a strong polarization.

The promotion energy  $E_P$  exhibits a pattern somewhat similar to  $E_{QC}$ : how can this behaviour be explained? There are four effects contributing to  $E_P$ . The scaling contribution is relatively small: although the scaling factor in  $H_2$  is extreme and  $E_P$  in this molecule is solely due to scaling one gets only 0.036 a.u. More important are atomic "excitations" in the preparation for bonding, especially the  $1s^2 2s^2 2p^2 \rightarrow 1s^2 2s 2p^3$  process of C in hydrocarbons. Our expectation that this contribution (that one could denote as "promotion in the classical sense") should constitute the main part of  $E_P$  in  $CH_4$  and  $C_2H_6$  (the two  $E_P$  values should differ by a factor of  $\approx 2$ ) is not born out by our results. This is due to the third contribution to  $E_P$ , charge transfer, that is zero in homonuclear diatomics and should be very small in saturated hydrocarbons but actually is not in our calculations. So it is  $E_P$  where the deficiencies of our charge order definition come in, not  $E_{QC}$  where the different charge transfer contributions largely cancel each other. Finally, in molecules with double and triple bonds  $E_P$  is dominated by the fourth contribution, a large polarization of the atomic densities into the bonding region. Now it is clear that such a polarization causes a strong penetration of the atomic charges and thus a decrease of  $E_{QC}$ . This means that there is a certain coupling between  $E_P$  and  $E_{QC}$  in these molecules, and that a large part of  $E_{QC}$  can be classified as "promotion-induced" quasiclassical energy. Again  $N_2$  shows the most extreme value of  $E_P$  reflecting its strong polarization. In comparison, the promotion energy of  $C_2H_2$  is only half as large. Below we shall say a few more words about the "pathological" case of  $N_2$ .

The interference energy  $E_I$  contains, as we know from Sects. 2 and 3, all the quantum mechanical effects that are responsible for chemical bonding. This does not mean, however, that  $E_I$  in general is the dominating term in our fragmentation of the binding energy. Only in molecules with " $H_2$ -like" bonds have we  $E_I \approx \Delta E$ , e.g. in saturated hydrocarbons. In  $Li_2$  we find very small  $E_{QC}$  and  $E_P$  values and the overlap between the  $2s$  orbitals that form the bond is almost as large as that between the  $1s$  AO's in  $H_2$ , so we have in some sense an  $H_2$ -like character of the  $Li_2$  bond. The peculiar features of this bond are due to the diffuseness of the  $2s$  orbitals, Therefore the lowering of the kinetic energy in the bond direction [6] (or the "contragradiance" [3]) that is responsible for bond formation has to be rather small, and indeed the three fragments of  $\Delta E$  are all of the same order of magnitude.

Table 8 shows clearly that the bonding situation in  $Li_2$  is rather "untypical" for unpolar single bonds. In fact,  $H_2$  is a much better prototype for this type of bond, despite of the fact that the Li atom has a core whereas H has not.

In  $F_2$  and the unsaturated hydrocarbons, where  $E_{QC}$  is still negligible in contrast to  $E_P$ , our results correspond to the usual concept of bonding in unpolar molecules, namely: the essential reason for bonding as well as the largest part of the binding energy are due to interference, though  $\Delta E$  can further be lowered by some promotion. The minimal  $\Delta E$  is the optimal compromise between promotion and interference, i.e. by further promotion  $E_P$  would increase faster than  $E_I$  would decrease. It is then just this point of optimal compromise where the wave function satisfies the virial theorem.



In most molecules we can adopt this view of bonding but there exist the exceptional cases of  $C_2$  and  $N_2$  where not only  $|E_P| > |E_I|$  but also  $E_{QC} < \Delta E$ . Here one could argue that the quasiclassical interaction alone is sufficient to ensure bonding, so why should promotion occur at all?

But let us recall that a very important part of  $E_P$  is the polarization of atomic densities into the bonding region and that this polarization should more or less lower  $E_{QC}$ . So we can suspect that in any molecule promotion lowers *both*  $E_I$  and  $E_{QC}$  but apparently the lowering of  $E_{QC}$  is, in general, too small to substantially influence the extent of promotion. Only in  $N_2$  and  $C_2$  is the polarization into the bond so strong, associated with a pronounced decrease of  $E_{QC}$ , that a further promotion “pays” for the binding energy. Thus,  $E_I$  as well as  $E_{QC}$  contain a negative part that we would get without polarization promotion and a second part, also negative, that can be regarded as induced by polarization (i.e. hybridization) promotion.

Finally, in order to demonstrate the influence of bond polarity on the energy fragmentation we have included in Table 8 two polar molecules. The weakly polar CO shows energy fragments very similar to  $N_2$ , whereas the energy terms of  $H_2O$  are quite different from those of  $CH_2$ . This difference is due to charge transfer terms that we have not separated in our formalism.

## 6. Conclusions

We have developed a scheme for analysing the chemical bond by a fragmentation of the binding energy into interference, promotion, and quasiclassical contributions. Our scheme is closely related to that of Ruedenberg [2] but it is much simpler because a) it is based on the MO-LCAO approximation corrected for left-right correlation, b) it is focused on a simple model of bonding, c) certain terms are grouped together on physical reasoning.

It is not easy to reconcile the MO picture with a correct dissociation behaviour but we have to use the MO framework if we want to have some relation to existing theories of bonding. The usefulness of *ab initio* MO calculations as regards equilibrium geometries can be attributed to the fact that the positive two-electron energy as well as the negative interference energy are overestimated by nearly the same amount at small internuclear distances. Our approximate correction for left-right correlation leads to a certain combination of MO and VB formulae, and this idea goes back to Mulliken [8].

Since our formalism is not restricted to minimal basis calculations we can in principle reach the SCF limit but there seems to be no simple way to approximately include correlation effects other than left-right correlation.

The concepts of bonding that originated from an examination of the binding energies of  $H_2^+$  and  $H_2$  turn out to be transferable to other molecules, except that the Mulliken approximation does not hold in general, i.e. two-electron interference effects have to be included into the interference energy. Also, the combination of correlation and interference corrections work well for bonds “similar” to  $H_2$  if they are applied in a proper hybrid AO basis. In the general case there are perhaps improvements possible by taking into account sharing penetration effects that are neglected in the present formalism. Furthermore, for an extension of the formalism to polar bonds one certainly has to separate off charge transfer terms as a fourth contribution. Heteronuclear bonds also reveal the strong dependence of the Mulliken charge order definition on the size of the basis. Unfortunately, it seems to

be rather difficult to incorporate a more basis independent charge order into our scheme, because after the splitting of the two-electron integrals into quasiclassical and interference parts (see Eq. (19)) the Mulliken charge order occurs "naturally" in our formulae. Finally, a special problem is posed by molecules with conjugated double bonds where the general interference correction is not applicable.

The rotational variance of the binding energy is kept very small by the use of a hybrid AO basis and by the transformation of  $p$ -orbitals to local principal axes. The dependence of the energy fragments on the size of the basis is negligible for the quasiclassical and very large for the promotion and interference terms. It has been shown that this dependence is completely consistent with our physical model of bonding.

Potential curves calculated with our energy formula are not competitive with accurate calculations but show a qualitatively correct behaviour. The equilibrium bond lengths are somewhat poorer than SCF results (consistently too large) whereas binding energies are considerably better.

The analysis of binding energies shows that some kinds of bonds may indeed be regarded as "H<sub>2</sub>-like". These are the single bonds in hydrocarbons and, to a certain degree, the Li<sub>2</sub> bond. In the latter case one has an unusually small interference part. In unsaturated hydrocarbons the special features of the double and triple bonds show up in the quasiclassical and promotion part of the binding energy. The homonuclear diatomics C<sub>2</sub>, N<sub>2</sub> and F<sub>2</sub>, that are rather tough molecules even for semiempirical methods, show very special features. Although their peculiarities can be reasonably explained on physical arguments it is apparent that these molecules do not easily fit on the "bed of Procrustes" of a simple three-term model of bonding.

Let us finally note that the structure of the equation for the binding energy (34) is such that it is easily related to certain semiempirical schemes. So it allows for an examination of some of their assumptions and approximations, and this will be the concern of a forthcoming paper [27].

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## Appendix

In the following tables the orthogonalized 2s orbitals are listed ( $\eta$  = exponent,  $c$  = contraction coefficient).

Li	$c$	$\eta$	C	$c$	$\eta$
	-0.1555998	1.7		-0.105	21.0
	-0.14548	0.46		-0.2351868	3.9
	0.556791	0.07648		0.464259	0.56663
	0.544211	0.02869		0.652431	0.17717

N	<hr/>		O	<hr/>	
	<i>c</i>	$\eta$		<i>c</i>	$\eta$
	-0.112	27.0		-0.11764	36.0
	-0.2331024	5.4		-0.2339926	7.3
	0.503845	0.78115		0.507147	1.07056
	0.61795	0.23733		0.617813	0.32145
	<hr/>			<hr/>	
F	<hr/>			<hr/>	
	<i>c</i>	$\eta$		<i>c</i>	$\eta$
	-0.120	46.0			
	-0.2367783	9.3			
	0.509115	1.40145			
	0.618129	0.41673			
	<hr/>			<hr/>	

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