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Connections between Current π-Electron Theories**

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Connections are given between the theoretical π-electron theory in an ordinary atomic orbital basis and semiempirical theories in an orthogonalized basis, neglecting terms of third order. An expression is derived for a one-electron operator with the properties, usually assigned to the effective Hamiltonian of the Hückel method. The non-local part of this operator is shown to give only small contributions also for heteromolecules and lone pairs. Not only short-range forces but also long-range forces, originating from the exchange operator, contribute essentially to the effective bonding. Numerical applications have been made *e.g.* to aniline and *p*-benzoquinone.

Es wird der Zusammenhang zwischen einer reinen π-Elektronentheorie mit Atomeigenfunktionen als Basis einerseits und semiempirischen Theorien mit orthogonaler Basis andererseits aufgezeigt, wobei Glieder dritter Ordnung in Überlappungsintegralen vernachlässigt werden. Dabei läßt sich ein Einelektronenoperator mit den Eigenschaften, die für gewöhnlich für den effektiven Hamiltonoperator der Hückel-Theorie postuliert werden, finden. Sein nichtlokaler Anteil liefert nur geringe Beiträge für Heteroatome und einsame Elektronenpaare. Für die Bindung sind neben den Kräften des Austauschoperators mit kurzer Reichweite auch weitreichende von Bedeutung. Numerische Werte für Anilin und *p*-Benzochinon werden gegeben.

Des connections entre la méthode théorique des électrons π sur base d'orbitales atomiques ordinaires, et des théories semiempiriques sur une base orthogonalisée sont données, en négligeant les termes du troisième ordre. On dérive une expression pour un opérateur monoélectronique ayant les propriétés attribuées usuellement à l'opérateur hamiltonien effectif de la méthode de Hückel. On montre que la partie non-locale de cet opérateur ne donne que de contributions petites, même pour les hétéroatomes et les paires libres d'électrons. Non seulement les forces à portée courte, mais aussi celles à portée longue dérivant de l'opérateur d'échange, contribuent essentiellement à la liaison effective. Des applications numériques, p.e. pour l'aniline et le *p*-benzoquinone, ont été effectuées.

I. Introduction and Summary

For theoretical studies of π-electron systems it is possible to choose between several more or less semiempirical procedures. The following three will be considered here: (i) the theoretical self-consistent-field (SCF) linear combination of atomic orbitals (LCAO) method, (ii) the Pariser-Parr-Pople method, (iii) the Hückel method. The connections between these methods has been studied previously many times. Among the more recent articles, dealing with these problems, are the investigations by RUEDENBERG [*17*], DEL RE and PARR [*1*], MCWEENY [*7*] and FISCHER-HJALMARS [*3*]. Although, so far, many points have been discussed and

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clarified, several obscurities still remain, especially for the general case, where heteroatoms and lone pairs are present. The main source of these difficulties seems to be that no operator with the properties, usually assigned to the effective Hamiltonian of the Hückel method, has yet been deduced. Since this problem is essential for the understanding of the success of the Hückel method, it will be treated in the present paper together with some related questions.

The considerations are based on the author's previous analysis of the zero differential overlap (ZDO) approximation by means of an expansion method [*3*]. There it was demonstrated that the Pariser-Parr-Pople method is equivalent to a systematic inclusion of second order terms of the overlap integral S, but neglect of higher order terms. Furthermore, the Hückel method was shown to be essentially equivalent to a first order theory with respect to S. These results are utilized in the present study. After a brief review of the theoretical method in Section 2, the OAO basis in the second order approximation is introduced in Section 3. In this approximation, the Fock operator F takes the form of Eq. (23) with the Coulomb and exchange operators defined in Eqs. (24) and (25). Then, the connection between the Mulliken population analysis and the concepts of charge and bond order are discussed. It is pointed out that the OAO's are *more* localized than the AO's [cf. Eqs. (26), (27)]. Thus, charge and bond order are meaningful concepts in the OAO basis. It is shown that the gross atomic populations $N_{\mu\mu}$ in the AO basis and the atomic charges $P_{\mu\mu}$ in the OAO basis are identical in the second order approximation [Eq. (30)]. A relation between overlap populations $n_{\mu\nu}$ and bond orders $P_{\mu\nu}$ is also given [Eq. (32)]. In Section 4 an expression is derived for an effective one-electron Hamiltonian operator H^{eff} [Eq. (36)], which can be interpreted as the Hückel Hamiltonian. This operator has the property that the sum over its eigenvalues will give the total energy of the system, *i.e.* the sum of the π-electron energy E^{π} and the core repulsion energy E^{repuls}, cf. Eq. (35). A comparison of the operators F and H^{eff} shows that the non-local contributions to H^{eff} will be an order of magnitude smaller than to F [cf. Tab. 1]. Hence, an electron in the potential from H^{eff} and close to a specific atom "sees" a potential well of substantial depth at this very atom but the rest of the molecule as essentially neutral. Finally, the concept of effective bonding energy, introduced by RUEDENBERG [*17*], is discussed and extended to heteronuclear molecules including lone pairs [Eq. (48)]. The importance of short-range forces, stressed by RUEDENBERG, is confirmed. However, it is shown that also long-range interaction, originating from the exchange operator, is of considerable importance [cf. Tab. 2].

2. The Theoretical Method

For simplicity the presentation here will be confined to closed-shell systems with $2n$ π-electrons. The π-electronic part of the Hamiltonian is

$$H = \sum_{s=1}^{2n} H^{\mathrm{core}}(s) + \sum_{s>u} 1/r_{su} \,. \tag{1}$$

The eigenfunction of this operator is supposed to be an antisymmetrized product of molecular orbitals composed of atomic orbitals $\chi_{\mu}^{t}(s)$. The AO χ_{μ}^{t} is a Slater-type atomic $2p\pi$ orbital centered on atom μ. Since we will have different basic orbitals in the different methods the superscript t is introduced to distinguish the theoretical method. Assuming that there is just one AO χ^t_μ on each center μ we can write

$$H^{\text{core},t} = T + \sum_{\varkappa=1}^{\text{all atoms}} (U_\varkappa - n_\varkappa J^t_{\varkappa\varkappa}) . \tag{2}$$

In Eq. (2) T is the kinetic energy, $U_\varkappa$ is the potential from the *neutral* atom and $n_\varkappa$ is the number of π-electrons contributed by atom $\varkappa$ ($n_\varkappa = 0$, 1 or 2). $J^t_{\varkappa\varkappa}$ is the ordinary Coulomb operator, defined in terms of the AO's $\chi^t_\varkappa$.

In the LCAO approximation the space part of the ith molecular orbital is

$$\varphi_i = \sum_{\mu=1}^{m} \chi^t_\mu C^t_{\mu i} = \boldsymbol{\chi}^t \boldsymbol{C}^t_i , \tag{3}$$

where m is the number of atoms, contributing π-electrons. $\boldsymbol{\chi}^t$ is a row matrix and $\boldsymbol{C}^t_i$ a column matrix. Collecting all the n doubly filled orbitals into a row matrix we have

$$\boldsymbol{\varphi} = \boldsymbol{\chi}^t \boldsymbol{C}^t , \tag{4}$$

where $\boldsymbol{C}^t$ is a rectangular $m \times n$ matrix. Introducing the orbital representation of the density matrix

$$\boldsymbol{P}^t = 2\, \boldsymbol{C}^t (\boldsymbol{C}^t)^\dagger \tag{5}$$

we can write the Fock operator of the one-electron problem

$$F^t = H^{\text{core},\, t} + G^t = T + \sum_{\varkappa} (U_\varkappa - n_\varkappa J^t_{\varkappa\varkappa}) + \sum_{\varkappa}\sum_{\lambda} P^t_{\varkappa\lambda} (J^t_{\varkappa\lambda} - \tfrac{1}{2} K^t_{\varkappa\lambda}) , \tag{6}$$

where $K^t_{\varkappa\lambda}$ is the exchange operator with the usual definition.

The electronic density, obtained after solution of the self-consistent-field problem, can be analysed according to the scheme developed by MULLIKEN [*10*]. The *net* atomic populations $n_{\mu\mu}$ are given by the diagonal elements of the density matrix in Eq. (5):

$$n_{\mu\mu} = P^t_{\mu\mu} . \tag{7}$$

According to Mulliken's definition the *gross* atomic populations $N_{\mu\mu}$ are

$$N_{\mu\mu} = \sum_{\nu} P^t_{\mu\nu} S_{\nu\mu} , \tag{8}$$

where

$$S_{\nu\mu} = \int \chi^{t*}_\nu \chi^t_\mu \, d\tau . \tag{9}$$

As pointed out by GLADNEY [*4*] the gross atomic populations are the diagonal elements of a matrix $\boldsymbol{N}$

$$\boldsymbol{N} = \tfrac{1}{2} (\boldsymbol{P}^t \boldsymbol{S} + \boldsymbol{S} \boldsymbol{P}^t) . \tag{10}$$

The off-diagonal elements of this matrix are bond-order-like quantities [*4*]. However, MULLIKEN [*10*] has pointed out that the overlap populations $n_{\mu\nu}$

$$n_{\mu\nu} = 2\, P^t_{\mu\nu} S_{\nu\mu} , \qquad \mu \neq \nu , \tag{11}$$

may have certain merits for the description of bonding properties in comparison to bond-order like quantities.

3. The Pariser-Parr-Pople Method

a) The Fock operator in an OAO basis

As is well known, the full SCF–LCAO–MO treatment can be simplified in the way suggested by PARISER and PARR [*12*] and POPLE [*16*]. These simplifications can be *formally* described by the assumption of zero differential overlap. It has also been pointed out many times that the correct interpretation of this simplification can be made along two different lines. The one includes a regrouping of terms and the introduction of the Mulliken approximation [*8*] in the complete MO expression for the electronic repulsion. This interpretation was first given by MULLIKEN [*9*]. According to the other line, first pointed out by LÖWDIN [*6*], a change from the ordinary AO basis to an orthogonalized AO basis will lead to the simplifications suggested by the ZDO formalism. Both these interpretations are discussed in detail by PARR [*14*], where further references are given. The approximations inherent in the OAO interpretation have recently been analyzed by the present author by an expansion method [*3*]. As pointed out above, the Pariser-Parr-Pople scheme was shown to be equivalent to a second order treatment in terms of $S_{\mu,\mu+1}$, where the atome μ and $\mu + 1$ are nearest neighbors. This implies that the scheme can only be expected to give reasonable results when

$$S_{\mu,\,\mu+1} < 0.5\,. \tag{12}$$

This condition is fulfilled for most π-electron systems but in general not for σ-electron systems.

According to LÖWDIN [*5*] the orthogonalization transformation can be written

$$\chi = \chi^t\, \boldsymbol{S}^{-\frac{1}{2}}\,, \tag{13}$$

where χ is the OAO set. Then the transformation of any one-electron operator M is given by

$$\boldsymbol{M} = \boldsymbol{S}^{-\frac{1}{2}}\, \boldsymbol{M}^t\, \boldsymbol{S}^{-\frac{1}{2}}\,, \tag{14}$$

where $\boldsymbol{M}$ is the representation in the OAO basis. In the second order approximation we can put [*3*]

$$\boldsymbol{S} = 1 + \varepsilon\, \boldsymbol{a}_1 + \varepsilon^2\, \boldsymbol{c}_2 + O\,(\varepsilon^3)\,. \tag{15}$$

The matrices $\boldsymbol{a}_1$ and $\boldsymbol{c}_2$ are the overlap matrices between nearest and next-nearest neighbors respectively:

$$(\mu \mid \varepsilon\, a_1 \mid \nu) = S_{\mu,\,\mu-1}\, \delta_{\mu-1,\,\nu} + S_{\mu,\,\mu+1}\, \delta_{\mu+1,\,\nu}\,, \tag{16}$$

$$(\mu \mid \varepsilon^2\, c_2 \mid \nu) = S_{\mu,\,\mu-2}\, \delta_{\mu-2,\,\nu} + S_{\mu,\,\mu+2}\, \delta_{\mu+2,\,\nu}\,. \tag{17}$$

Then

$$\boldsymbol{S}^{\frac{1}{2}} = 1 + \tfrac{1}{2}\, \varepsilon\, \boldsymbol{a}_1 + \varepsilon^2\, (\tfrac{1}{2}\, \boldsymbol{c}_2 - \tfrac{1}{8}\, \boldsymbol{a}_1^2) + O\,(\varepsilon^3)\,, \tag{18}$$

$$\boldsymbol{S}^{-\frac{1}{2}} = 1 - \tfrac{1}{2}\, \varepsilon\, \boldsymbol{a}_1 - \varepsilon^2\, (\tfrac{1}{2}\, \boldsymbol{c}_2 - \tfrac{3}{8}\, \boldsymbol{a}_1^2) + O\,(\varepsilon^3)\,. \tag{19}$$

In the OAO basis the MO's are

$$\varphi = \chi\, \boldsymbol{C} = \chi^t\, \boldsymbol{S}^{-\frac{1}{2}}\, \boldsymbol{C} = \chi^t\, \boldsymbol{C}^t\,. \tag{20}$$

Eq. (20) immediately gives the connection between coefficients and electronic densities in the two different bases:

$$\boldsymbol{C} = \boldsymbol{S}^{\frac{1}{2}}\, \boldsymbol{C}^t, \quad \boldsymbol{C}^\dagger = (\boldsymbol{C}^t)^\dagger\, \boldsymbol{S}^{\frac{1}{2}}\,, \tag{21}$$

$$\boldsymbol{P} = 2\, \boldsymbol{C}\boldsymbol{C}^\dagger = \boldsymbol{S}^{\frac{1}{2}}\, \boldsymbol{P}^t\, \boldsymbol{S}^{\frac{1}{2}}\,. \tag{22}$$

The connections in Eqs. (21) and (22) are, of course, correct to the second order only, since the matrix $\boldsymbol{C}$ is obtained from the solutions of a Fock equation, where the Coulomb and exchange operators do not include more than second order terms in $\boldsymbol{S}$. A Fock operator with these properties can be given the following form

$$F = T + \sum_{\varkappa} (U_{\varkappa} - n_{\varkappa} J_{\varkappa\varkappa}) + \sum_{\varkappa} P_{\varkappa\varkappa} J_{\varkappa\varkappa} - K \,, \tag{23}$$

if we define the electron interaction operators as

$$J_{\varkappa\varkappa} = \sum_{\lambda} | \lambda \rangle \gamma_{\varkappa\lambda} \langle \lambda | \,, \tag{24}$$

$$K = \tfrac{1}{2} \sum_{\varkappa} \sum_{\lambda} | \varkappa \rangle P_{\varkappa\lambda} \gamma_{\varkappa\lambda} \langle \lambda | \,. \tag{25}$$

$\gamma_{\varkappa\lambda}$ in Eqs. (24) and (25) are the Coulomb integrals in terms of the OAO's χ.

There is another feature of the Pariser-Parr scheme which also has bearing upon its connection with the theoretical method, *i.e.* the determination of integral values by semiempirical methods. We will not make any further comment on this question here. It should only be pointed out that the underlying assumption for the presentation is that the Slater orbitals χ^t of Eqs. (3) and (13) are the same.

b) Population analysis

The population analysis in the Pariser-Parr-Pople scheme is usually given in terms of atomic charges $P_{\mu\mu}$ and bond orders $P_{\mu\nu}$, *i.e.* the matrix elements of $\boldsymbol{P}$ in Eq. (22). It has been pointed out by PEACOCK [*15*] that these quantities do not give a direct description of the charge distribution in the molecule. PEACOCK therefore suggests that the Mulliken net atomic and overlap populations of Eqs. (7) and (11) should be used to describe the distribution. These quantities are easily obtained from the $\boldsymbol{P}$ matrix by the inverse of the transformation in Eq. (22).

It has been pointed out many times that the OAO's χ_μ are delocalized, many-center orbitals and accordingly not so well adapted as the AO's χ^t_μ to depict the electron distribution in the molecule. However, it has not been stressed so frequently that this delocalization will only appear in a rather formal way. In fact, as discussed previously [*3*, *7*], in the expression for χ_μ the coefficient of χ^t_μ is *larger* than unity, inferring a *concentration* of the orbital around the center μ. As an example, in the case of benzene Eqs. (13) and (19) give

$$\chi_1 = \chi^t_1 \left(1 + \tfrac{3}{4} S^2_{12}\right) - \tfrac{1}{2} S_{12} \left(\chi^t_2 + \chi^t_6\right) + \left(\tfrac{3}{8} S^2_{12} - \tfrac{1}{2} S_{13}\right) \left(\chi^t_3 + \chi^t_5\right) + O\left(\varepsilon^3\right) . \tag{26}$$

The overlap integrals between χ_1 and χ^t_μ are in this case

$$\langle \chi^t_1 | \chi_1 \rangle = 0.98 \,, \qquad \langle \chi^t_2 | \chi_1 \rangle = 0.13 \,, \qquad \langle \chi^t_3 | \chi_1 \rangle = 0.01 \,. \tag{27}$$

The corresponding AO values are: $S_{11} = 1$, $S_{12} = 0.27$, $S_{13} = 0.04$. The Eqs. (26) and (27) illustrate the important fact that the orthogonalization procedure tends to localize the orbitals rather than to delocalize them. Accordingly, *the orthogonalized atomic orbitals are more localized than the ordinary orbitals.*

This local property of the OAO's indicate that the use of the $\boldsymbol{P}$ matrix to depict the electron distribution should be reconsidered. Obviously, the quantities $P_{\mu\mu}$ cannot be expected to correspond to the net atomic populations $P_{\mu\mu}$, but rather to the gross atomic populations $N_{\mu\mu}$. In fact, from Eqs. (10) and (22) we find

$$\boldsymbol{N} = \tfrac{1}{2}\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{P} \boldsymbol{S}^{\frac{1}{2}} + \boldsymbol{S}^{\frac{1}{2}} \boldsymbol{P} \boldsymbol{S}^{-\frac{1}{2}}\right) . \tag{28}$$

Introducing Eqs. (18) and (19) into (28) we obtain

$$\boldsymbol{N} = \boldsymbol{P} + \tfrac{1}{8}\,\varepsilon^2\,(\boldsymbol{a}_1^2\,\boldsymbol{P} + \boldsymbol{P}\,\boldsymbol{a}_1^2 - 2\,\boldsymbol{a}_1\,\boldsymbol{P}\,\boldsymbol{a}_1) + O\,(\varepsilon^3)\,. \tag{29}$$

Hence,

$$P_{\mu\mu} = N_{\mu\mu} + O\,(\varepsilon^3)\,. \tag{30}$$

The atomic charges $P_{\mu\mu}$ are thus equal to the gross atomic populations within the accuracy of the semiempirical method. The connection between bond orders and overlap populations is more involved. From Eqs. (22), (19) and (11) we find

$$P^t_{\mu\nu} = P_{\mu\nu} - S_{\mu\nu}, + O\,(\varepsilon^2)\,, \tag{31}$$

$$n_{\mu\nu} = 2\,P_{\mu\nu}\,S_{\mu\nu} - 2\,S^2_{\mu\nu} + O\,(\varepsilon^3)\,. \tag{32}$$

The merits and disadvantages of the different possible definitions of overlap populations and bond orders have been discussed in detail by MULLIKEN [*10*]. Useful, though somewhat different information may be obtained from both the quantities considered here, $P_{\mu\nu}$ and $n_{\mu\nu}$. However, McWEENY [*7*] has shown that the quantities $P_{\mu\nu}$ are intimately connected with bond energies. Furthermore, SKANCKE [*19*] has shown that the relation between the bond orders $P_{\mu\nu}$ and bond distances $R_{\mu\nu}$ is the same in the Pariser-Parr-Pople scheme as in the Hückel scheme. Thus the $\boldsymbol{P}$ matrix seems to give at least as useful information within the semiempirical scheme as the population quantities derived from the $\boldsymbol{P}^t$ matrix.

4. The Hückel Method

a) Population analysis

The Hückel method is often used without any explicit reference to an orbital basis. However, it seems to be appropriate to refer the method to orthogonalized atomic orbitals. If this is accepted it is possible to show [*3*] that the Hückel method is mainly equivalent to a first order treatment with respect to the overlap integral S. Hence, the coefficient matrix $\boldsymbol{C}$ and the density matrix $\boldsymbol{P}$ of Eq. (22) will not be quite the same in the Hückel method as in the Pariser-Parr-Pople method. For simplicity, we will neglect this difference and use the same notations for both methods.

b) The effective Hamiltonian

A more intricate question is how to define an effective one-electron Hamiltonian operator, H^{eff}, corresponding to the Fock operator of Eqs. (6) or (23). One answer to the question is the one given by RUEDENBERG [*17*]. He stresses that the topology of the molecule is the main important thing, and the precise nature of H^{eff} a subordinate question. Although this may be true, it can nevertheless be of interest from the interpretational point of view to look closer into the problem. McWEENY [*7*] points out that the connection between the Hückel and SCF one-electron operators may be made in different ways, when the interest is focused on different observables. He suggests that for the discussion of one-electron properties, the Fock operator with some average bond order values may be considered as the effective Hamiltonian. For other observables, where the total energy of the system is of importance, *e.g.* for the calculation of delocalization energies, the connection must be made differently. A well-known feature of the Hückel method is that the total energy is obtained as the sum over the orbital energies. It is also well-known that this is no longer true when the interelectronic repulsion is considered explicitely. Thus, it is suggestive to start the search for an operator with the properties, attributed to H^{eff}, from the expression for the total energy.

In a method with explicit consideration of the electronic repulsion, the total energy of the π-electron system can be written

$$E^{\pi} = \operatorname{Tr} \boldsymbol{P} \left(\boldsymbol{H}^{\text{core}} + \tfrac{1}{2} \boldsymbol{G}\right) . \tag{33}$$

Starting from this Eq. PARR [*13*], and more recently McWEENY [*7*], have suggested that $(\boldsymbol{H}^{\text{core}} + \frac{1}{2} \boldsymbol{G})$ may be interpreted as the effective Hamiltonian in cases, where the additivity of energies is important. However, as pointed out by POPLE [*16*], RUEDENBERG [*17*], and others [*1, 2*] the repulsion between the positively charged core atoms, E^{repuls}, must be added to E^{π}. Only this sum, which we call E^{total}, can be used for a meaningful comparison between systems with different cores, as is done *e.g.* in the calculation of delocalization energies.

As discussed *e.g.* by DEL RE and PARR [*1*] it is convenient to express the repulsive energy in the following way

$$E^{\text{repuls}} = \tfrac{1}{2} \sum_{\mu} \sum_{\nu \neq \mu} n_{\mu} \, n_{\nu} \, \gamma_{\mu\nu} \, . \tag{34}$$

After some rearrangements (cf. the Appendix) the total energy can be written:

$$E^{\text{total}} = E^{\pi} + E^{\text{repuls}} = \operatorname{Tr} \boldsymbol{P} \boldsymbol{H}^{\text{eff}} \, . \tag{35}$$

The expression for the one-electron operator H^{eff} in Eq. (35) is

$$H^{\text{eff}} = T + \sum_{\varkappa} \left(U_{\varkappa} + \tfrac{1}{2} Q \, Q_{\varkappa} \, J_{\varkappa\varkappa}/P\right) - \tfrac{1}{2} n^{2} \gamma/P - \tfrac{1}{2} K \, , \tag{36}$$

where we have introduced the notation Q_{μ} for the net atomic charge

$$Q_{\mu} = n_{\mu} - P_{\mu\mu} \, . \tag{37}$$

The operators in Eq. (36), which have not been defined previously, are local, one-center operators. Using a similar representation as in Eqs. (24) and (25) we have

$$n^{2} \gamma/P = \sum_{\lambda} |\, \lambda\rangle \, n_{\lambda}^{2} \, \gamma_{\lambda\lambda}/(P_{\lambda\lambda}) \, \langle \lambda \,| \, , \tag{38}$$

$$Q \, Q_{\varkappa} \, J_{\varkappa\varkappa}/P = \sum_{\lambda} |\, \lambda\rangle \, Q_{\lambda} \, Q_{\varkappa} \, \gamma_{\varkappa\lambda}/(P_{\lambda\lambda}) \, \langle \lambda \,| \, . \tag{39}$$

A comparison of Eqs. (23) and (36) indicates that in spite of the obvious similarities there is an important difference between the operators F and H^{eff}. To clarify this point it may be instructive to write down the diagonal and the off-diagonal matrix elements. For this purpose we introduce the notations:

$$H^{\text{neutr}} = T + \sum U_{\varkappa} \, , \tag{40}$$

$$W_{\mu}^{n} = \langle \mu \,|\, H^{\text{neutr}} - n_{\mu} \, J_{\mu\mu} \,|\, \mu \rangle \, . \tag{41}$$

Then we have

$$F_{\mu\mu} = W_{\mu}^{n} + \tfrac{1}{2} \, P_{\mu\mu} \, \gamma_{\mu\mu} - \sum_{\varkappa \neq \mu} Q_{\varkappa} \, \gamma_{\varkappa\mu} \, , \tag{42}$$

$$H_{\mu\mu}^{\text{eff}} = W_{\mu}^{n} + \tfrac{1}{4} \, P_{\mu\mu} \, \gamma_{\mu\mu} + \tfrac{1}{2} \, Q_{\mu}/(P_{\mu\mu}) \sum_{\varkappa \neq \mu} Q_{\varkappa} \, \gamma_{\varkappa\mu} \, , \tag{43}$$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{neutr}} - \tfrac{1}{2} \, P_{\mu\nu} \, \gamma_{\mu\nu}, \qquad \mu \neq \nu \, , \tag{44}$$

$$H_{\mu\nu}^{\text{eff}} = H_{\mu\nu}^{\text{neutr}} - \tfrac{1}{4} \, P_{\mu\nu} \, \gamma_{\mu\nu}, \qquad \mu \neq \nu \, . \tag{45}$$

Eqs. (44) and (45) show that the off-diagonal parts of $\boldsymbol{F}$ and $\boldsymbol{H}^{\mathrm{eff}}$ are rather similar, although the absolute values of $H^{\mathrm{eff}}_{\mu\nu}$ are somewhat smaller than those of $F_{\mu\nu}$. As discussed previously [*3*], the matrix elements $H^{\mathrm{neutr}}_{\mu\nu}$ are independent of the surrounding and will vanish for pairs of non-neighbors, when S^3 terms are neglected. However, the second term will not vanish in this approximation. Keeping this term in Eq. (44) for non-neighbors leads to the method, suggested by ORLOFF and FITTS [*11*].

In the diagonal elements, Eqs. (42) and (43), the only term of non-local character is the sum over $\varkappa$. For alternant hydrocarbons this sum will always vanish (all $Q = 0$). On the other hand it can give appreciable contributions to $F_{\mu\mu}$ in the case of strongly polar compounds. In the case of Eq. (43), however, the sum is multiplied by the net charge Q_μ. Accordingly, the non-local contribution to $H^{\mathrm{eff}}_{\mu\mu}$ will be an order of magnitude smaller than in the case of $F_{\mu\mu}$. In consequence of Eq. (36), an electron in the immediate vicinity of an atom will "see" a potential well of considerable depth at this very atom but the rest of the molecule as essentially neutral. To illustrate this point the numerical values for some typical cases are given in Tab. 1. The numbers in parentheses are the non-local parts of the matrix elements. Since these parts are of the same magnitude as those terms, which are neglected anyway in the S^2 approximation, the success of the Hückel method becomes understandable.

Table 1. *Numerical values in* eV *of the diagonal matrix elements of the Fock operator, Eq. (42), and the effective Hamiltonian, Eq. (43), for some typical cases. The non-local contributions are the numbers in parentheses*

Atom μ	$F_{\mu\mu}$		$H^{\mathrm{eff}}_{\mu\mu}$	
		Benzene		
C	-3.519	(0)	- 6.460	(0)
		Aniline		
N	-9.496	(+0.568)	-17.389	(-0.017)
C_1	-3.556	(+0.108)	- 6.533	(-0.001)
C_2	-3.602	(-0.502)	- 6.267	(-0.017)
C_3	-3.131	(+0.524)	- 6.533	(-0.006)
C_4	-3.349	(-0.069)	- 6.341	(-0.001)
		p-Benzoquinone		
O	-6.081	(-2.035)	- 9.916	(-0.178)
C_1	-3.166	(+1.430)	- 7.158	(-0.160)
C_2	-4.194	(-0.591)	- 6.497	(+0.004)

c) Effective bonding energy

As mentioned above, the quantity E^{total} of Eq. (35) is more suitable than E^{π} of Eq. (33) for estimates of *e.g.* the delocalization energy. This is illustrated by the energy values for ethylene and benzene, listed in Tab. 2. Obviously, the difference between the values of E^{π} for the two systems does not give any immediate information. On the other hand, for a comparison of two systems with different numbers of π-electrons it is found that neither E^{π} nor E^{total} are very useful quantities

Table 2. *Numerical values in* eV *of the different energy quantities,* E^{π} *of Eq. (33),* E^{total} *of Eq. (35), and* E^{bonding} *of Eq. (48). The different terms of Eq. (48) are also given separately*

Energy term	3 Ethylene	Benzene	Aniline	*p*-Benzoquinone
E^{π}	−90.171	−163.248	−259.596	−261.773
E^{total}	−66.407	− 68.476	−103.107	−101.016
E^{bonding}	−10.006	− 12.075	− 12.838	− 13.755
$-\sum\limits_{\mu} Q_\mu W_\mu^n$	0	0	+ 1.724	− 2.552
$\sum\limits_{\mu} (\frac{1}{4} P_{\mu\mu}^2 - n_\mu + 1)\gamma_{\mu\mu}$	+17.643	+ 17.643	+ 16.645	+ 29.147
$\sum\limits_{\mu,\nu\neq\mu} \frac{1}{2} Q_\mu Q_\nu \gamma_{\mu\nu}$	0	0	− 0.083	− 0.676
$\sum\limits_{\mu,\nu\neq\mu} P_{\mu\nu} H_{\mu\nu}^{\text{neutr}}$	−15.767	− 18.530	− 19.613	− 23.507
$-\sum\limits_{\mu,\nu\neq\mu} \frac{1}{4} P_{\mu\nu}^2 \gamma_{\mu\nu}$	−11.882	− 11.188	− 11.511	− 16.166

[cf. the values for benzene and aniline of Tab. 2]. For such a comparison it is more informative to consider the quantity, which RUEDENBERG [*17*] calls "effective bonding energy of π-electrons with respect to the carbon valence state", just changing the last three words to "atomic valence states". According to the definition of RUEDENBERG [*17*], this quantity, which we will denote E^{bonding}, is

$$E^{\text{bonding}} = E^{\text{total}} - E^{\text{atoms}} . \tag{46}$$

The most dubious quantity in Eq. (46) is perhaps E^{atoms}, since the definition of the valence state is an unclear point [*18*]. Although aware of this fact, we will for the present purpose simply write

$$E^{\text{atoms}} = \sum [n_\mu W_\mu^n + (n_\mu - 1)\gamma_{\mu\mu}] . \tag{47}$$

After insertion of Eqs. (43), (45) and (47), Eq. (46) reads

$$\begin{aligned} E^{\text{bonding}} = \sum_{\mu} \{ & - Q_\mu W_\mu^n + (\tfrac{1}{4} P_{\mu\mu}^2 - n_\mu + 1)\gamma_{\mu\mu} + \\ & + \tfrac{1}{2} Q_\mu \sum_{\nu\neq\mu} Q_\nu \gamma_{\mu\nu} + \sum_{\nu\neq\mu} P_{\mu\nu} H_{\mu\nu}^{\text{neutr}} - \tfrac{1}{4} \sum_{\nu\neq\mu} P_{\mu\nu}^2 \gamma_{\mu\nu} \} . \end{aligned} \tag{48}$$

Eq. (48) is an extension to arbitrary π-systems of RUEDENBERG's expression for the π-electron binding in hydrocarbons [*17*]. RUEDENBERG has pointed out the importance of the short-range forces due to the operator H^{neutr}. He has also illustrated this fact by numerical values for benzene. Nevertheless, it might be informative to look upon the different terms of Eq. (48) for some heteronuclear molecules as well. Moreover, both the present grouping of the terms and the computational method (semi-empirical) are different from those of RUEDENBERG. Therefore, benzene and ethylene are also included in Tab. 2. The first sum in E^{bonding} arises from the transfer of electrons from one kind of atoms to another, in the case of aniline from the N atom to C atoms and in *p*-benzoquinone from C atoms to O atoms. This is a sizeable term, repulsive in the lone pair case, but otherwise attractive. The next sum represents the increase in electronic repulsion due to pairing of the unpaired valence state electrons. This is always a large term. However, according to SILVERSTONE's definition of the valence state [*18*], the main part of this term should be assigned to the atomic valence state energy. The part left will be of a size similar to the first term of E^{bonding} but of opposite sign. The third term is the contribution from the electrostatic interaction between the final, net charges. This term is attractive, but an order of magnitude smaller than any other term. The forth term is due to the short-range forces. It is always attractive and considerable. The last term originates from the exchange operator K and represents long-range forces. It is also always attractive.

Summing up, we find that *the π-electron bonding is partly due to short-range forces from the neutral framework potential, partly to long-range, exchange forces.* In the examples, given here, the short-range part is somewhat larger than the long-range part, but they are of comparable magnitudes. The net charges will only modify this picture slightly.

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Appendix

The expression for E^{total} of Eqs. (35) and (36) can be derived as follows. Since

$$\begin{aligned} Tr\,\boldsymbol{P}\,\boldsymbol{G} &= \sum_{\mu}\sum_{\nu} P_{\mu\nu} \sum_{\varkappa}\sum_{\lambda} P_{\varkappa\lambda}\,(\gamma_{\varkappa\mu}\,\delta_{\varkappa\lambda}\,\delta_{\mu\nu} - \tfrac{1}{2}\,\gamma_{\mu\nu}\,\delta_{\lambda\mu}\,\delta_{\varkappa\nu}) \\ &= \sum_{\mu} P_{\mu\mu}\,\{\tfrac{1}{2}\,P_{\mu\mu}\,\gamma_{\mu\mu} + \sum_{\varkappa\neq\mu} P_{\varkappa\varkappa}\,\gamma_{\varkappa\mu}\} - \sum_{\mu}\sum_{\nu\neq\mu} \tfrac{1}{2}\,P^2_{\mu\nu}\,\gamma_{\mu\nu}\,, \end{aligned} \tag{A 1}$$

we have by Eqs. (33), (34), (40) and (41):

$$\begin{aligned} E^{\pi} + E^{\text{repuls}} &= E^{\text{total}} \\ &= \sum_{\mu} P_{\mu\mu}\,\{W^n_{\mu} + \tfrac{1}{4}\,P_{\mu\mu}\,\gamma_{\mu\mu} - \tfrac{1}{2}\sum_{\nu\neq\mu}(n_{\nu} - P_{\nu\nu})\,\gamma_{\mu\nu}\} + \\ &+ \sum_{\mu}\sum_{\nu\neq\mu}\{\tfrac{1}{2}\,\gamma_{\mu\nu}\,(n_{\mu}\,n_{\nu} - P_{\mu\mu}\,n_{\nu}) + P_{\mu\nu}\,(H^{\text{neutr}}_{\mu\nu} - \tfrac{1}{4}\,P_{\mu\nu}\,\gamma_{\mu\nu}\}\,. \end{aligned} \tag{A 2}$$

Using Eq. (37), Eq. (A 2) can be written

$$\begin{aligned} E^{\text{total}} &= \sum_{\mu}\{P_{\mu\mu}\,(W^n_{\mu} + \tfrac{1}{4}\,P_{\mu\mu}\,\gamma_{\mu\mu}) + \tfrac{1}{2}\,Q_{\mu}\sum_{\nu\neq\mu} Q_{\nu}\,\gamma_{\mu\nu}\} + \\ &+ \sum_{\mu}\sum_{\nu\neq\mu} P_{\mu\nu}\,(H^{\text{neutr}}_{\mu\nu} - \tfrac{1}{4}\,P_{\mu\nu}\,\gamma_{\mu\nu})\,. \end{aligned} \tag{A 3}$$

Now it is easily seen that introduction of Eqs. (43) and (45) into Eq. (35) will give Eq. (A 3).

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