

Operator Equations in Approximate Molecular Orbital Theories

II. Integral Approximations and Charge Distributions

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The general concept of integral approximations based on the Heisenberg equation of motion $[r, h] = p$ is developed for one- and two-electron operators in polyatomic molecules. The formalism leads to a new definition of atomic charge distributions in molecules. Mulliken's integral approximation and population analysis are included as special cases.

Das allgemeine Konzept von Integralapproximationen, die auf der Heisenbergschen Bewegungsgleichung $[r, h] = p$ basieren, wird für Ein- und Zweielektronenoperatoren in mehratomigen Molekülen entwickelt. Der Formalismus führt zu einer neuen Definition von Atomladungen in Molekülen. Mullikens Integralapproximation und Verteilungsanalyse sind als Spezialfälle enthalten.

1. Introduction

In a previous paper [1], we tested the suitability of commutator relations $[t, x] = u$ with hermitian and antihermitian operators t , x and u as a basis for approximations in semiempirical molecular orbital methods. In particular, we were interested in integral approximations based on the Heisenberg uncertainty principle $[r, p] = -1$ and the Heisenberg equation of motion $[r, h] = p$. The approximate integral relations resulted from truncated expansions of the commutator integrals. We derived formulas for $\bar{\beta}$'s over non-orthogonal atomic orbitals and β 's over orthogonalized atomic orbitals [2]. The accuracy of the relations was tested for $2s$ -, $2p\sigma$ - and $2p\pi$ -orbitals in homonuclear diatomics. A way to generalize the concept to polyatomics was briefly described. In the present paper, we want to develop the general formalism for polyatomic molecules both for one- and two-electron operators. This leads also to a new definition of atomic charge distributions in molecules.

2. One-Electron Integrals

From the commutator equation

$$u = [t, x] \tag{2.1}$$

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we obtain an infinite expansion

$$u_{\mu\nu} = \sum_{\lambda} t_{\mu\lambda} x_{\lambda\nu} - x_{\mu\lambda} t_{\lambda\nu} \quad (2.2)$$

for integrals $u_{\mu\nu} = \langle \mu | u | \nu \rangle$ etc. over hermitian or antihermitian operators u , t , x and atomic orbitals μ , ν . λ is taken over a complete, orthogonal set of orbitals. In case that a truncated expansion consisting of two orthogonalized orbitals [2] corresponding to μ and ν is used, the following approximations result for integrals over one-electron operators [1].

$$\begin{aligned} \bar{x}_{ab} = & \frac{1}{2} S_{ab} (\bar{x}_{aa} + \bar{x}_{bb}) + \frac{\bar{t}_{ab} - \frac{1}{2} S_{ab} (\bar{t}_{aa} + \bar{t}_{bb})}{t_{aa} - t_{bb}} (\bar{x}_{aa} - \bar{x}_{bb}) \\ & + \frac{(1 - S_{ab}^2)}{t_{aa} - t_{bb}} \bar{u}_{ab}, \end{aligned} \quad (2.3)$$

$$x_{ab} = \frac{t_{ab}}{t_{aa} - t_{bb}} (x_{aa} - x_{bb}) + \frac{1}{t_{aa} - t_{bb}} u_{ab}. \quad (2.4)$$

Quantities with bar refer to non-orthogonal AO's \bar{a} , \bar{b} , without bar to symmetrically orthogonalized AO's a , b . These approximations have been investigated for cases where \bar{a} and \bar{b} are orbitals of the same type on different centers A and B, e.g. $2s_a - 2s_b$, $2p\sigma_a - 2p\sigma_b$, $2p\pi_a - 2p\pi_b$. Approximation (2.3) was previously [1] denoted by (B), (2.4) by (B').

In case that we use $t = r$, $x = T$, $u = p$, we obtain for the kinetic energy

$$\bar{T}_{ab} = \frac{1}{2} S_{ab} \left[(\bar{T}_{aa} + \bar{T}_{bb}) + \frac{\Delta R}{R} (\bar{T}_{aa} - \bar{T}_{bb}) \right] + \frac{1 - S_{ab}^2}{R} \frac{dS_{ab}}{dR}, \quad (2.5)$$

$$T_{ab} = \frac{\frac{1}{2} S_{ab}}{(1 - S_{ab}^2)^{\frac{1}{2}}} \frac{\Delta R}{R} (T_{aa} - T_{bb}) + \frac{1}{R} \frac{dS_{ab}}{dR} \quad (2.6)$$

$$\Delta R = R - 2R_0.$$

In case that \bar{a} and \bar{b} are orbitals of the same type, $\Delta R = R - 2R_0$ is twice the shift of the center of charge from the midpoint between atoms A and B toward either A or B. R_0 is the distance between the center of charge and atom A. ΔR is positive if the center of charge is moved toward A and negative otherwise.

For Coulombic potential energy operators V , we obtain $t = r$, $x = V$, $u = 0$, so that

$$\bar{V}_{ab} = \frac{1}{2} S_{ab} \left[(\bar{V}_{aa} + \bar{V}_{bb}) + \frac{\Delta R}{R} (\bar{V}_{aa} - \bar{V}_{bb}) \right], \quad (2.7)$$

$$V_{ab} = \frac{\frac{1}{2} S_{ab}}{(1 - S_{ab}^2)^{\frac{1}{2}}} \frac{\Delta R}{R} (V_{aa} - V_{bb}). \quad (2.8)$$

For a single-electron Hamiltonian

$$h = T + V$$

with

$$V = \sum_i^{\text{nuclei}} V_i,$$

(2.5) and (2.7) resp. (2.6) and (2.8) yield the general formulas for polyatomics

$$\bar{\beta}_{ab} = \frac{1}{2} S_{ab} \left[(\bar{\alpha}_a + \bar{\alpha}_b) + \frac{\Delta R}{R} (\bar{\alpha}_a - \bar{\alpha}_b) \right] + \frac{1 - S_{ab}^2}{R} \frac{dS_{ab}}{dR}, \quad (2.9)$$

$$\beta_{ab} = \frac{\frac{1}{2} S_{ab}}{(1 - S_{ab}^2)^{\frac{1}{2}}} \frac{\Delta R}{R} (\alpha_a - \alpha_b) + \frac{1}{R} \frac{dS_{ab}}{dR}. \quad (2.10)$$

These formulas were derived previously¹ for diatomics, here we have shown in a simple breakdown that they are the same in polyatomics.

3. Two-Electron Integrals

A generalization to two-electron integrals is straightforward and was hinted at in an earlier paper [3]. We generalize Eqs. (2.1) and (2.2) to the suitable many-electron form

$$u = [t, x] \quad (3.1)$$

with

$$u = \sum_i u_i, t = \sum_i t_i, x = \sum_i x_i + \sum_{i < j} x_{ij} \quad (3.2)$$

$$u_{ab, cd} = \sum_{\lambda, \mu} t_{a\lambda, c\mu} x_{\lambda b, \mu d} - x_{a\lambda, c\mu} t_{\lambda b, \mu d}$$

with

$$u_{ab, cd} = \langle ac | u | bd \rangle \text{ etc.}$$

Since the case of two electrons is representative, we shall pursue it for the Heisenberg equation of motion. From

$$\mathbf{p}_1 + \mathbf{p}_2 = \left[\mathbf{r}_1 + \mathbf{r}_2, T_1 + T_2 + V_1 + V_2 + \frac{1}{r_{12}} \right] \quad (3.3)$$

the one-electron part can be separated so that

$$\mathbf{0} = \left[\mathbf{r}_1 + \mathbf{r}_2, \frac{1}{r_{12}} \right]. \quad (3.4)$$

Eq. (3.4) is all we need for the general two-electron problem. If we use the two pairs of orthogonalized orbitals a, b and c, d in the double expansion of

$$\left\langle \bar{a}\bar{c} \left| \left[\mathbf{r}_1 + \mathbf{r}_2, \frac{1}{r_{12}} \right] \right| \bar{b}\bar{c} \right\rangle = \mathbf{0}, \quad (3.5)$$

where $\bar{a}, \bar{b}, \bar{c}, \bar{d}$ are non-orthogonal orbitals on various centers, we obtain the simplest approximation for a multi-center electron repulsion integral

$$(\bar{a}\bar{b} | \bar{c}\bar{c}) = \frac{1}{2} S_{ab} \left\{ [(\bar{a}\bar{a} | \bar{c}\bar{c}) + (\bar{b}\bar{b} | \bar{c}\bar{c}) + \frac{\Delta R_{ab}}{R_{ab}} [(\bar{a}\bar{a} | \bar{c}\bar{c}) - (\bar{b}\bar{b} | \bar{c}\bar{c})]] \right\}. \quad (3.6)$$

The general approximation for a multi-center integral is obtained by the same expansion of

$$\left\langle \bar{a}\bar{c} \left| \left[\mathbf{r}_1 + \mathbf{r}_2, \frac{1}{r_{12}} \right] \right| \bar{b}\bar{d} \right\rangle = \mathbf{0} \quad (3.7)$$

¹ In [1], several quantities were lumped together in the definition of ΔQ ; the relation of ΔQ and ΔR here is $\Delta Q = \frac{1}{2} S_{ab}^2 \Delta R$. The above definition of ΔR is possible for all cases where S is different from zero, otherwise the definition of ΔQ is preferable.

with subsequent elimination of the hybrid integrals by means of (3.6). The result is

$$\begin{aligned}
 (\bar{a}\bar{b}|\bar{c}\bar{d}) &= \frac{1}{4}S_{ab}S_{cd} \left\{ [(\bar{a}\bar{a}|\bar{c}\bar{c}) + (\bar{b}\bar{b}|\bar{c}\bar{c}) + (\bar{a}\bar{a}|\bar{d}\bar{d}) + (\bar{b}\bar{b}|\bar{d}\bar{d})] \right. \\
 &+ \frac{\Delta R_{ab}}{R_{ab}} [(\bar{a}\bar{a}|\bar{c}\bar{c}) - (\bar{b}\bar{b}|\bar{c}\bar{c}) + (\bar{a}\bar{a}|\bar{d}\bar{d}) - (\bar{b}\bar{b}|\bar{d}\bar{d})] \\
 &+ \frac{\Delta R_{cd}}{R_{cd}} [(\bar{a}\bar{a}|\bar{c}\bar{c}) + (\bar{b}\bar{b}|\bar{c}\bar{c}) - (\bar{a}\bar{a}|\bar{d}\bar{d}) - (\bar{b}\bar{b}|\bar{d}\bar{d})] \\
 &\left. + \frac{\Delta R_{ab}\Delta R_{cd}}{R_{ab}R_{cd}} [(\bar{a}\bar{a}|\bar{c}\bar{c}) - (\bar{b}\bar{b}|\bar{c}\bar{c}) - (\bar{a}\bar{a}|\bar{d}\bar{d}) + (\bar{b}\bar{b}|\bar{d}\bar{d})] \right\}. \quad (3.8)
 \end{aligned}$$

It is obvious that (3.8) includes (3.6) as a special case. It also contains many other special cases as $c = a$ and $d = b$ etc. The formula (3.8) reduces any kind of multi-center hybrid and exchange integral to a combination of Coulomb integrals. It represents the simplest generalization of the Mulliken approximation [4]. Cases where charge distributions $\bar{a}\bar{b}$ or $\bar{c}\bar{d}$ are composed of different orbitals on the same center are excluded.

If we base our approximations on (3.4) but use orthogonalized orbitals a, b, c, d in the expansion, our results are

$$(ab|cc) = \frac{\frac{1}{2}S_{ab}}{(1-S_{ab}^2)^{\frac{1}{2}}} \frac{\Delta R_{ab}}{R_{ab}} [(aa|cc) - (bb|cc)] \quad (3.9)$$

$$\begin{aligned}
 (ab|cd) &= \frac{\frac{1}{4}S_{ab}S_{cd}}{(1-S_{ab}^2)^{\frac{1}{2}}(1-S_{cd}^2)^{\frac{1}{2}}} \frac{\Delta R_{ab}\Delta R_{cd}}{R_{ab}R_{cd}} \\
 &\cdot [(aa|cc) - (aa|dd) - (bb|cc) + (bb|dd)]. \quad (3.10)
 \end{aligned}$$

The integrals $(ab|cc)$ and $(ab|cd)$ vanish, if equivalent orbitals, i.e. of same type and equal exponents, on different centers are involved. This special case of equivalence between (3.9) or (3.10) and the Mulliken approximation for the non-orthogonal counterpart of the orbitals was discussed by Löwdin [5]. The approximations (3.9) and (3.10) are not as good as (3.6) and (3.8). For example, they imply that the exchange integrals are generally smaller than the hybrid integrals. A counter example can be found in a paper by Fischer-Hjalmars [6]. The above conclusion about the relative accuracy of electron repulsion integral formulas on non-orthogonal and orthogonalized basis sets parallels our findings for $\bar{\beta}$'s and β 's [1].

4. Charge Distributions

A careful investigation of (3.6) and (3.8) shows the underlying pattern: the charge distribution $\bar{a}\bar{b}$ (or $\bar{c}\bar{d}$) of each electron is expanded in the following way

$$\bar{a}\bar{b} = \frac{1}{2}S_{ab} \left[(\bar{a}\bar{a} + \bar{b}\bar{b}) + \frac{\Delta R_{ab}}{R_{ab}} (\bar{a}\bar{a} - \bar{b}\bar{b}) \right]. \quad (4.1)$$

It is not difficult to show that the underlying operator equation is

$$[r, 1] = 0. \quad (4.2)$$

This opens the way to a new definition of atomic charges in molecules. Mulliken's population analysis [7] distributes overlap distributions $c_a c_b S_{ab}$ equally over atoms A and B. Instead, we obtain from (4.1) by regrouping of the terms and integration

$$S_{ab} = \frac{1}{2} \kappa_a S_{ab} + \frac{1}{2} \kappa_b S_{ab} \quad (4.3)$$

with

$$\kappa_a = 1 + \frac{\Delta R_{ab}}{R_{ab}}$$

$$\kappa_b = 1 - \frac{\Delta R_{ab}}{R_{ab}}.$$

κ_a is the weighting factor for the part of the distribution belonging to atom A, κ_b the corresponding factor for atom B. They are equal only if the center of charge of the distribution $\bar{a}\bar{b}$ is in the middle between atoms A and B. In this case $\Delta R_{ab} = 0$ holds.

5. Discussion and Conclusion

The derivation of approximate formulas in Sect. 2 and 4 was based on a two-orbital expansion. This seems to be a reasonable approach if \bar{a} and \bar{b} are orbitals of the same type. In this case the movement of the center of charge from the midpoint toward one of the atoms is a useful consideration². However, in molecular orbital methods, integrals $S_{ab'}(\bar{a}\bar{b}|\bar{c}\bar{c})$ etc. occur where \bar{a} and \bar{b} are not of the same type. We have investigated this case also and found that the form of the relations remains unchanged, if we generalize our definition of ΔR . Let us start with the non-orthogonal expansion corresponding to (2.2)

$$\bar{u}_{ab} = \sum_{\chi, \chi'} \bar{t}_{a\chi}(S^{-1})_{\chi\chi'} \bar{x}_{\chi'b} - \bar{x}_{a\chi}(S^{-1})_{\chi\chi'} \bar{t}_{\chi'b}. \quad (5.1)$$

In case that a and b are not orbitals of the same type on atoms A and B, we include also the corresponding orbitals of the same type on both atoms in the expansion. Let us denote \bar{a}' corresponding to \bar{b} and \bar{b}' corresponding to \bar{a} . The shielding exponents of the corresponding orbitals are allowed to be different. χ, χ' are taken as $\bar{a}, \bar{b}, \bar{a}', \bar{b}'$. If we rearrange the terms according to their magnitude and keep only the dominant ones, the following definition of ΔR would be the simplest, more general than (2.6).

$$-S_{ab} \Delta R = 2\bar{z}_{ab} - (S_{a'b} \bar{z}_{aa'} + S_{ab'} \bar{z}_{bb'}) - S_{ab} (\bar{z}_{aa} + \bar{z}_{bb}). \quad (5.2)$$

z is an axis through atoms A and B. The second term in (5.2) is the one which did not occur previously. It refers to atomic dipole moments of distribution $\bar{a}\bar{b}$. So ΔR is defined as twice the distance between the midpoint of atoms A and B and that point on the internuclear axis for which the higher averaged dipole moments in the expansion of \bar{z}_{ab} can be neglected. This means that we define R_0

² The case of $2p\sigma_a 2p\sigma_b$ is more sophisticated for different exponents, because the centers of negative and positive part of the distribution will be separated. Here $\Delta Q \sim S \Delta R$ is relevant. It will be non-vanishing and non-singular for $S = 0$, when ΔR itself is not finite.

so that $z_a = z_0 + R_0$ with

$$2\langle \bar{a} | z_0 | \bar{b} \rangle = S_{a'b} \bar{z}_{aa'} + S_{ab'} \bar{z}_{bb'} . \quad (5.3)$$

It is obvious that (5.2) contains (2.6) as a special case if the right side of (5.3) vanishes. This is approximately correct for \bar{a} , \bar{b} of same type because the two terms on the right side of (5.3) try to cancel each other.

We have qualitatively investigated the consequences of (5.2) for the case $\bar{a} = 2s_a$, $\bar{b} = 2p\sigma_b$ and found the formula without singularities³. It is worthwhile to note that in the case of an asymmetrical $2s_a 2p\sigma_b$ charge distribution, the partitioning cannot be equal among atom A and B, even if the exponents are the same. In a superficial conclusion, one might consider this as a shortcoming. However, one has also to consider that in a homonuclear bond, there should exist also a $2p\sigma_a 2s_b$ charge distribution the partitioning of which counterbalances the one of $2s_a 2p\sigma_b$. This allows for an equal gross atomic population on two atoms despite intermediate asymmetrical partitioning.

The formalism developed in this paper is sufficient for use in approximate molecular orbital theories. However, one word of caution may be appropriate. The Heisenberg equation of motion $\dot{p} = [p, h]$ is valid for the exact Hamiltonian and certain model Hamiltonians, but not for an SCF Hamiltonian. The reason is that the exchange operator does in general not commute with the position operator. This means that approximations for β 's which refer to an SCF Hamiltonian cannot be valid in the same way as those derived for effective single-electron Hamiltonians.

The formulas developed so far seem to offer a greater insight into integral approximations. To complement the qualitative aspects of this work, we plan to investigate applications in the future. In particular, effects of these formulas for gross atomic populations in hetero molecules is one of our aims.

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³ For some cases, e.g. $1s_a 2p\sigma_b$ and $2s_a 2p\sigma_b$, the value of $S_{ab} \Delta R/R$ may go to infinity as R approaches zero. This is, however, of no practical importance, because it involves a single-center charge redistribution.