

# On Rüdberg's Integral Approximations and Their Unrestricted and Combined Use in Crystal Orbital Theories of Hartree-Fock Type

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*Dedicated to Professor Klaus Rüdberg*

**Abstract :** The analysis based on Rüdberg's well-known letter of 1951 which has been outlined for molecules in the preceding contribution now will be transferred to translational periodic systems in one, two, or three dimensions. Again, when applied unrestrictedly to "Linear Combination of Atomic Orbitals" representations (LCAO) of both "Unrestricted" and "Restricted Hartree-Fock" pictures (UHF and RHF), Rüdberg's integral approximations of Mulliken type lead to a thorough interpretation of "Extended Hückel" crystal orbital theories (EHT). Moreover, Rüdberg's ideas provide us with "Unrestricted and Combined" extensions (U&C) of the widely-used approximation schemes "Zero Differential Overlap" (ZDO) and "Neglect of Diatomic Differential Overlap" (NDDO). An improved variant of EHT is also presented. Corresponding "Restricted and Combined" concepts (R&C) which overcome some shortcomings inherent in Rüdberg's original recipes will be sketched.

**Key words :** Unrestricted (and Restricted) Hartree-Fock crystal orbitals - Integral approximations according to Mulliken and Rüdberg - Zero Differential Overlap (ZDO) - Neglect of Diatomic Differential Overlap (NDDO) - Extended Hückel Theory (EHT)

## 1. Introduction

As in the preceding contribution [1], the main topic of this paper is Rüdénberg’s letter of 1951 [2] with its two truncated expansions (symbolized by I and II) of diatomic orbital products. In addition to Rüdénberg’s proper concepts (R) in the sense commonly used, we distinguish three other kinds of Rüdénberg-type approximations which are closely related to the schemes of Mulliken (M) [3], “Zero Differential Overlap” (ZDO) [4], and “Neglect of Diatomic Differential Overlap” (NDDO) [5]. In particular, we consider their application to the crystal-orbital extension of Roothaan’s closed-shell “Restricted Hartree-Fock” theory (RHF) [6] in its generalized “Unrestricted Hartree-Fock” form (UHF) of Pople & Nesbet [7].

Apart from any numerical application which will be the subject of forthcoming investigations, we first of all intend to interpret the consequences of an “Unrestricted and Combined” use (U&C) of Rüdénberg’s approximations in crystal-orbital UHF theory. Within this context, the term “Unrestricted” indicates that the considered approximations will be applied irrespectively of the one-, two-, and multi-index or -center quality of the integrals involved. (Note that “Unrestricted” in this sense has nothing to do with the conceptual particularities of the “Unrestricted Hartree-Fock” picture itself).

As we shall see, the U&C use of Rüdénberg’s Mulliken-type approximations (M.U&C) culminates in a completed understanding of the crystal-orbital analogue of the Wolfsberg-Helmholz formula [8] which is a constituent part of the semi-empirical “Extended Hückel Theory” (EHT) of translationally periodic polymers, surfaces, and solids [9]. Furthermore, an improved Rüdénberg-type variant of M.U&C called R.U&C will be proposed which is appropriate for non-empirical computer implementations, since it fulfills the “rotational invariance requirement” [10] of all *ab-initio* quantum chemical concepts.

Another well-established feature of semi-empirical quantum chemistry is the orthonormality assumption with respect to the predefined atomic orbital basis set. If one supposes this orthonormality property to be valid, our M.U&C and R.U&C frameworks immediately convert into two additional “Zero Integral Overlap” (ZIO) and “Neglect of Diatomic Integral Overlap” (NDIO) pictures, which are partially identical with the widely-used ZDO and NDDO approximation schemes, respectively.

Finally we are going to stress that all these four approximations, which are commonly based on the U&C use of Rüdénberg’s ideas, imply considerable oversimplifications. In order to overcome such shortcomings, another set of four “Restricted and Combined” (R&C) crystal-orbital concepts will be sketched. Here, the attribute “Restricted” indicates the avoidance of particular oversimplifications which is consistent with the corresponding level of approximation.

## 2. Basic equations

Introducing periodic boundary conditions according to Born & v. Kármán [11], we consider a three-dimensional crystal ( $d = 3$ ) as being built up of  $N_{abc} \equiv N_a N_b N_c$  unit cells, connected by  $N_a$ ,  $N_b$ , and  $N_c$  translational symmetry operations along the three crystallographic directions defined through the primitive lattice vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ , respectively.  $N_a = N_b = N_c := 1$  corresponds to the zero-dimensional molecular case ( $d = 0$ ). In one-dimensional systems ( $d = 1$ ) only one of the positive integers  $N_a$ ,  $N_b$ , or  $N_c$  differs from 1 whereas in two-dimensional lattices ( $d = 2$ ) there are two unit-cell numbers greater than one.

Within the Born-Oppenheimer picture [11] of  $N_n$  fixed nuclear positions per unit cell, standard non-empirical quantum chemical methods [11] usually expand the delocalized crystal orbitals of the  $j$ -th energy band  $\{\Psi_j(\mathbf{k}, \mathbf{r}_i) | j = 1, \dots, N_o\}$  as linear combinations of  $N_o$  symmetry adapted Bloch sums [11]  $\{\Phi'_\mu(\mathbf{k}, \mathbf{r}_i) | \mu = 1, \dots, N_o\}$ , constructed from  $N_o$  atomic orbitals per unit cell. Each wavevector  $\mathbf{k} \equiv \{k^a, k^b, k^c\}$  has components that cover the following ranges defining the first Brillouin zone [11]:

$$-\frac{\pi}{|\mathbf{a}|} < k^a \leq +\frac{\pi}{|\mathbf{a}|} \quad ; \quad -\frac{\pi}{|\mathbf{b}|} < k^b \leq +\frac{\pi}{|\mathbf{b}|} \quad ; \quad -\frac{\pi}{|\mathbf{c}|} < k^c \leq +\frac{\pi}{|\mathbf{c}|} . \quad (2.1)$$

In the ‘‘Unrestricted Hartree-Fock’’ theory (UHF) of Pople & Nesbet [7], which is central within the scope of this paper, two different crystal orbital sets have to be determined. The  $\alpha$ -spin ‘‘Linear Combination of Atomic Orbitals’’ (LCAO), for instance, reads:

$$\Psi_j^\alpha(\mathbf{k}, \mathbf{r}_i) := \sum_{\mu=1}^{N_o} \Phi'_\mu(\mathbf{k}, \mathbf{r}_i) C_{\mu j}^{\prime\alpha}(\mathbf{k}), \quad j = 1, \dots, N_o, \quad (2.2)$$

with

$$\Phi'_\mu(\mathbf{k}, \mathbf{r}_i) = N_{abc}^{-\frac{1}{2}} \sum_{\mathbf{m}=\mathbf{N}^-}^{\mathbf{N}^+} \exp(i[k^a m_a |\mathbf{a}| + k^b m_b |\mathbf{b}| + k^c m_c |\mathbf{c}|]) \Phi_\mu(\mathbf{r}_i - \mathbf{R}_\mathbf{m}), \quad (2.3)$$

where we introduced the following abbreviations:

$$\sum_{\mathbf{m}=\mathbf{N}^-}^{\mathbf{N}^+} \equiv \sum_{m_a=N_a^-}^{N_a^+} \sum_{m_b=N_b^-}^{N_b^+} \sum_{m_c=N_c^-}^{N_c^+}, \quad (2.4)$$

$$\mathbf{m} \equiv \{m_a, m_b, m_c\}, \quad \mathbf{N}^- \equiv \{N_a^-, N_b^-, N_c^-\}, \quad \mathbf{N}^+ \equiv \{N_a^+, N_b^+, N_c^+\}, \quad (2.5)$$

and

$$\mathbf{R}_\mathbf{m} \equiv m_a \mathbf{a} + m_b \mathbf{b} + m_c \mathbf{c}. \quad (2.6)$$

The summation limits are defined as follows:

$$N_a^- := \begin{cases} -(N_a - 2)/2, & \text{if } N_a \text{ even,} \\ -(N_a - 1)/2, & \text{if } N_a \text{ odd,} \end{cases} \quad \text{and} \quad N_a^+ := \begin{cases} +N_a/2, & \text{if } N_a \text{ even,} \\ +(N_a - 1)/2, & \text{if } N_a \text{ odd.} \end{cases} \quad (2.7)$$

Analogous definitions hold for the crystallographic  $\mathbf{b}$  and  $\mathbf{c}$  directions.

An equivalent second ansatz has to be made for spin  $\beta$ . If one should find the unrestricted  $\alpha$ - and  $\beta$ -spin orbitals to be identical, they both are of the restricted form according to Roothaan [6]. Hence, Roothaan's "Restricted Hartree-Fock" theory (RHF) is formally included in the more general Pople-Nesbet description. We therefore restrict our discussion to UHF theory. If necessary, all expressions then can be translated easily into the RHF picture.

In order to be more specific, Eqs. (2.2) and (2.3) can be rewritten as follows :

$$\Psi_j^\alpha(\mathbf{k}, \mathbf{r}_i) := \sum_{M=1}^{N_n} \sum_{\mu=1}^{n_o(M)} \Phi'_\mu(\mathbf{k}, \mathbf{r}_i - \mathbf{R}_M) C'_{(M,\mu)j}{}^\alpha(\mathbf{k}), \quad j = 1, \dots, N_o, \quad (2.8)$$

with

$$\begin{aligned} \Phi'_\mu(\mathbf{k}, \mathbf{r}_i - \mathbf{R}_M) = N_{abc}^{-\frac{1}{2}} \sum_{\mathbf{m}=\mathbf{N}^-}^{\mathbf{N}^+} \exp(i[k^a m_a |\mathbf{a}| + k^b m_b |\mathbf{b}| + k^c m_c |\mathbf{c}|]) \\ \times \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M - \mathbf{R}_\mathbf{m}). \end{aligned} \quad (2.9)$$

In contrast to the first notation of Eqs. (2.2) and (2.3), the Eqs. (2.8) and (2.9) explicitly specify the position vector  $\mathbf{R}_M \equiv (x_M, y_M, z_M)$  of the  $M$ -th atom within each unit cell, to which all  $n_o(M)$  basis functions with index  $\mu$  belong. While the first notation will be chosen in discussing the simple approximation recipe of Mulliken [3] and the "Zero Integral Overlap" scheme (ZIO), the second notation will turn out to be particularly appropriate in the context of Rüdberg's more elaborate approximation [2] and the "Neglect of Diatomic Integral Overlap" concept (NDIO).

Four types of integrals can be distinguished within both UHF and RHF theories :

- *Overlap integrals*

$$\begin{aligned} \int \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M) \Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_\mathbf{n}) d\mathbf{r}_i \\ \equiv \begin{cases} (\mathbf{S}_{\mathbf{0n}})_{\mu\nu} & \text{notation 1} \\ \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu \end{pmatrix} & \text{notation 2,} \end{cases} \end{aligned} \quad (2.10)$$

- *kinetic energy integrals*

$$\begin{aligned} \int \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M) [\Delta(\mathbf{r}_i) \Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_\mathbf{n})] d\mathbf{r}_i \\ \equiv \begin{cases} (\mathbf{K}_{\mathbf{0n}})_{\mu\nu} & \text{notation 1} \\ (\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} & \text{notation 2,} \end{cases} \end{aligned} \quad (2.11)$$

with the Laplacian operator  $\Delta(\mathbf{r}_i) = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$ , and

- *nuclear attraction integrals*

$$\begin{aligned}
& -Z_P \int \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M) |\mathbf{r}_i - \mathbf{R}_P - \mathbf{R}_P|^{-1} \Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_n) d\mathbf{r}_i \\
& \equiv \begin{cases} (\mathbf{V}_{0n})_{\mu\nu}[\mathbf{p}P] & \text{notation 1} \\ \left( \begin{array}{c|c} \mathbf{0} & \mathbf{n} \\ M & P \\ \mu & \nu \end{array} \right) & \text{notation 2 ,} \end{cases} \quad (2.12)
\end{aligned}$$

with the atomic number  $Z_P$  of nucleus  $P$ , depend on the three Cartesian coordinates  $\mathbf{r}_i \equiv (x_i, y_i, z_i)$  of one electron only. Using the chemists' notation, the six-dimensional

- *two-electron repulsion integrals* read as follows :

$$\begin{aligned}
& \int \int \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M) \Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_n) |\mathbf{r}_i - \mathbf{r}_j|^{-1} \\
& \times \Phi_\tau(\mathbf{r}_j - \mathbf{R}_T - \mathbf{R}_t) \Phi_\lambda(\mathbf{r}_j - \mathbf{R}_L - \mathbf{R}_l) d\mathbf{r}_i d\mathbf{r}_j \\
& \equiv \begin{cases} \left( \begin{array}{c|c} \mathbf{0} & \mathbf{n} \\ \mu & \nu \end{array} \middle| \begin{array}{c} \mathbf{t} & \mathbf{1} \\ \tau & \lambda \end{array} \right) & \text{notation 1} \\ \left( \begin{array}{c|c} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu \end{array} \middle| \begin{array}{c} \mathbf{t} & \mathbf{1} \\ T & L \\ \tau & \lambda \end{array} \right) & \text{notation 2 .} \end{cases} \quad (2.13)
\end{aligned}$$

Hence, three-index (notation 1) and three-center (notation 2) integrals can be of attraction and repulsion type, whereas all four-index (notation 1) and four-center (notation 2) integrals are exclusively repulsive.

Atomic units (a.u.) are used throughout this paper. For convenience, all atomic functions are taken to be real, normalized, and locally orthogonal.

## 2.1. Pople-Nesbet equations of crystal orbital theory

In crystal orbital theory, the coefficient matrices  $\mathbf{C}'^\alpha(\mathbf{k})$  of Eq. (2.2) or Eq. (2.8) with the property  $\mathbf{C}'^{\alpha\dagger}(\mathbf{k})\mathbf{S}'^\alpha(\mathbf{k})\mathbf{C}'^\alpha(\mathbf{k}) = \mathbf{1}$  are determined by solving the  $\mathbf{k}$ -dependent Pople-Nesbet equations. Their  $\alpha$ -spin part reads as follows :

$$\mathbf{F}'^\alpha(\mathbf{k})\mathbf{C}'^\alpha(\mathbf{k}) = \mathbf{S}'^\alpha(\mathbf{k})\mathbf{C}'^\alpha(\mathbf{k})\mathbf{E}^\alpha(\mathbf{k}) . \quad (2.14)$$

$\mathbf{E}^\alpha(\mathbf{k})$  is the diagonal matrix of crystal-orbital energies :

$$\mathbf{E}^\alpha(\mathbf{k}) = \begin{pmatrix} E_1^\alpha(\mathbf{k}) & 0 & \dots & 0 \\ 0 & E_2^\alpha(\mathbf{k}) & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & E_{N_o}^\alpha(\mathbf{k}) \end{pmatrix} . \quad (2.15)$$

$E_j^\alpha(\mathbf{k})$  belongs to the  $j$ -th column of  $\mathbf{C}'^\alpha(\mathbf{k})$ , where  $j$  is the energy-band index. Density matrices of the Bloch basis are defined through :

$$\mathbf{P}'^\alpha(\mathbf{k}) = \mathbf{C}'^\alpha(\mathbf{k})\mathbf{\Omega}^\alpha(\mathbf{k})\mathbf{C}'^{\alpha\dagger}(\mathbf{k}) . \quad (2.16)$$

The diagonal matrix  $\mathbf{\Omega}^\alpha(\mathbf{k})$  contains the occupation numbers  $\Omega_j^\alpha(\mathbf{k})$  of the crystal orbitals  $\Psi_j^\alpha(\mathbf{k}, \mathbf{r}_i)$  :

$$\mathbf{\Omega}^\alpha(\mathbf{k}) = \begin{pmatrix} \Omega_1^\alpha(\mathbf{k}) & 0 & \dots & 0 \\ 0 & \Omega_2^\alpha(\mathbf{k}) & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \Omega_{N_o}^\alpha(\mathbf{k}) \end{pmatrix}, \quad (2.17)$$

with

$$\Omega_j^\alpha(\mathbf{k}) := \begin{cases} 1 & \text{if } \Psi_j^\alpha(\mathbf{k}, \mathbf{r}_i) \text{ is occupied,} \\ 0 & \text{else.} \end{cases} \quad (2.18)$$

The symmetry adapted complex overlap integrals of the Bloch basis are obtained by summing up all real-space overlap integrals according to

$$\mathbf{S}'(\mathbf{k}) = \sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \exp(i[k^a n_a |\mathbf{a}| + k^b n_b |\mathbf{b}| + k^c n_c |\mathbf{c}|]) \mathbf{S}_{0\mathbf{n}} = \mathbf{S}'^\dagger(\mathbf{k}). \quad (2.19)$$

An equivalent expression holds for the Fock matrix  $\mathbf{F}'^\alpha(\mathbf{k})$  :

$$\mathbf{F}'^\alpha(\mathbf{k}) = \sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \exp(i[k^a n_a |\mathbf{a}| + k^b n_b |\mathbf{b}| + k^c n_c |\mathbf{c}|]) \mathbf{F}'_{0\mathbf{n}} = \mathbf{F}'^{\alpha\dagger}(\mathbf{k}). \quad (2.20)$$

Symmetry properties like  $(\mathbf{S}_{0-\mathbf{n}})_{\mu\nu} = (\mathbf{S}_{0\mathbf{n}})_{\nu\mu}$  and  $(\mathbf{F}'_{0-\mathbf{n}})_{\mu\nu} = (\mathbf{F}'_{0\mathbf{n}})_{\nu\mu}$  can be utilized to accelerate real-space lattice summations from a computational point of view. The summation limits in Eqs. (2.19) and (2.20) have to be chosen in such a way, that the lattice summation includes all non-vanishing contributions. We are going to reconsider this problem below.

## 2.2. Real-space Fock-matrix representations using notation 1

Next, we write down two different but equivalent formulations of the unrestricted  $\alpha$ -spin real-space Fock-matrix representation of Eq. (2.20). Using the first notation we can write :

$$\begin{aligned} (\mathbf{F}'_{0\mathbf{n}})_{\mu\nu} &= (\mathbf{K}_{0\mathbf{n}})_{\mu\nu} \\ &+ \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n} (\mathbf{V}_{0\mathbf{n}})_{\mu\nu} [\mathbf{p}P]}_{\stackrel{\text{def}}{=} (\mathbf{F}'_{0\mathbf{n}})^A_{\mu\nu}} \\ &+ \underbrace{\sum_{\mathbf{t}, \mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau, \lambda=1}^{N_o} (\mathbf{P}_{\mathbf{t}\mathbf{l}}^\oplus)_{\tau\lambda} \begin{pmatrix} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ \mu & \nu & \tau & \lambda \end{pmatrix}}_{\stackrel{\text{def}}{=} (\mathbf{F}'_{0\mathbf{n}})^C_{\mu\nu}} \\ &- \underbrace{\sum_{\mathbf{t}, \mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau, \lambda=1}^{N_o} (\mathbf{P}_{\mathbf{t}\mathbf{l}}^\alpha)_{\tau\lambda} \begin{pmatrix} \mathbf{0} & \mathbf{t} & \mathbf{n} & \mathbf{l} \\ \mu & \tau & \nu & \lambda \end{pmatrix}}_{\stackrel{\text{def}}{=} (\mathbf{F}'_{0\mathbf{n}})^{\alpha E}_{\mu\nu}} \\ &\left\{ \begin{array}{l} \mathbf{n} = \mathbf{N}^-, \dots, \mathbf{N}^+, \\ \mu, \nu = 1, \dots, N_o. \end{array} \right. \end{aligned} \quad (2.21)$$

The symbols  $A$ ,  $C$ , and  $E$  stand for the *Attractive*, *Coulomb*, and *Exchange* parts of the Fock-representation, respectively.

The real-space density-matrix representation  $\mathbf{P}_{\mathbf{t}\mathbf{l}}^\alpha$  is available from the corresponding complex reciprocal-space  $\mathbf{P}'^\alpha(\mathbf{k})$  matrices by means of  $\mathbf{k}$ -space integrations over the Brillouin-zone ranges defined in Eq. (2.1) :

$$\begin{aligned} (\mathbf{P}_{\mathbf{t}\mathbf{l}}^\alpha)_{\tau\lambda} := & \frac{V_d}{(2\pi)^d} \int \int \int \exp\left\{i\left[k^a(t_a - l_a)|\mathbf{a}| \right. \right. \\ & \left. \left. + k^b(t_b - l_b)|\mathbf{b}| \right. \right. \\ & \left. \left. + k^c(t_c - l_c)|\mathbf{c}| \right]\right\} P'_{\tau\lambda}{}^\alpha(\mathbf{k}) dk^a dk^b dk^c . \end{aligned} \quad (2.22)$$

$V_d$  denotes the  $d$ -dimensional volume of the primitive real-space unit cell ( $V_0 := 1$ ). Again, equivalent expressions for  $\beta$ -spin have to be formulated analogously. The total density matrix is defined through :

$$\mathbf{P}_{\mathbf{t}\mathbf{l}}^\oplus = \mathbf{P}_{\mathbf{t}\mathbf{l}}^\alpha + \mathbf{P}_{\mathbf{t}\mathbf{l}}^\beta, \quad \mathbf{t}, \mathbf{l} = \mathbf{N}^-, \dots, \mathbf{N}^+. \quad (2.23)$$

In the RHF theory, however, no second equation for  $\beta$ -spin is needed, since in this case the crystal orbitals are restricted to be doubly occupied in general. Consequently one then finds that  $\mathbf{P}_{\mathbf{t}\mathbf{l}}^\alpha = \mathbf{P}_{\mathbf{t}\mathbf{l}}^\beta = \frac{1}{2}\mathbf{P}_{\mathbf{t}\mathbf{l}}^\oplus$ .

### 2.3. Real-space Fock-matrix representations using notation 2

Choosing the more specific second notation, the formulas of Eqs. (2.21) and (2.22) then read :

$$\begin{aligned} (\mathbf{F}_{\mathbf{0n}}^\alpha)_{(M,\mu)(N,\nu)} &= (\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \\ &+ \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n} \begin{pmatrix} \mathbf{0} & \mathbf{p} & \mathbf{n} \\ M & P & N \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\text{def}}{=} (\mathbf{F}_{\mathbf{0n}}^A)_{(M,\mu)(N,\nu)}} \\ &+ \underbrace{\sum_{\mathbf{t}, \mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T,L=1}^{N_n} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}_{\mathbf{t}\mathbf{l}}^\oplus)_{(T,\tau)(L,\lambda)} \begin{pmatrix} \mathbf{0} & \mathbf{n} & \mathbf{t} & \mathbf{l} \\ M & N & T & L \\ \mu & \nu & \tau & \lambda \end{pmatrix}}_{\stackrel{\text{def}}{=} (\mathbf{F}_{\mathbf{0n}}^C)_{(M,\mu)(N,\nu)}} \\ &- \underbrace{\sum_{\mathbf{t}, \mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T,L=1}^{N_n} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}_{\mathbf{t}\mathbf{l}}^\alpha)_{(T,\tau)(L,\lambda)} \begin{pmatrix} \mathbf{0} & \mathbf{t} & \mathbf{n} & \mathbf{l} \\ M & T & N & L \\ \mu & \tau & \nu & \lambda \end{pmatrix}}_{\stackrel{\text{def}}{=} (\mathbf{F}_{\mathbf{0n}}^{\alpha E})_{(M,\mu)(N,\nu)}} \end{aligned} \quad (2.24)$$

$$\begin{cases} \mathbf{n} = -\mathbf{N}, \dots, +\mathbf{N} , \\ M, N = 1, \dots, N_n , \\ \mu = 1, \dots, n_o(M) , \\ \nu = 1, \dots, n_o(N) , \end{cases}$$

and

$$\begin{aligned}
(\mathbf{P}_{\mathbf{tl}}^\alpha)_{(T,\tau)(L,\lambda)} &:= \frac{V_d}{(2\pi)^d} \int \int \int \exp \left\{ i \left[ k^a(t_a - l_a)|\mathbf{a}| \right. \right. \\
&\quad \left. \left. + k^b(t_b - l_b)|\mathbf{b}| \right. \right. \\
&\quad \left. \left. + k^c(t_c - l_c)|\mathbf{c}| \right] \right\} P'_{(T,\tau)(L,\lambda)}(\mathbf{k}) dk^a dk^b dk^c .
\end{aligned} \tag{2.25}$$

## 2.4. Reciprocal-space integrations

Following Ramírez & Böhm [12] we assume that the integrals of Eq. (2.22) (or equivalently those of Eq. (2.25)) can be approximated by discrete summations within the first Brillouin zone :

$$\begin{aligned}
(\mathbf{P}_{\mathbf{tl}}^\alpha)_{\tau\lambda} &:= (N^{abc})^{-1} \sum_{u=N_-^a}^{N_+^a} \sum_{v=N_-^b}^{N_+^b} \sum_{w=N_-^c}^{N_+^c} W_{uvw} \\
&\quad \times \Re \left\{ \exp \left\{ i \left[ k_u^a(t_a - l_a)|\mathbf{a}| + k_v^b(t_b - l_b)|\mathbf{b}| + k_w^c(t_c - l_c)|\mathbf{c}| \right] \right\} P'_{\tau\lambda}(\mathbf{k}_{uvw}) \right\},
\end{aligned} \tag{2.26}$$

where

$$W_{uvw} := 1 \quad \text{for all } u = N_-^a, \dots, N_+^a; v = N_-^b, \dots, N_+^b; w = N_-^c, \dots, N_+^c. \tag{2.27}$$

The imaginary part of Eq. (2.26) vanishes so that the  $\mathbf{P}_{\mathbf{tl}}^\alpha$  matrices are real.

Furthermore, as recommended in Ref. [12], we consider the  $N^{abc} \equiv N^a N^b N^c$  discrete wavevectors

$$\{\mathbf{k}_{uvw} \equiv \{k_u^a, k_v^b, k_w^c\} | u = N_-^a, \dots, N_+^a; v = N_-^b, \dots, N_+^b; w = N_-^c, \dots, N_+^c\} \tag{2.28}$$

to form a homogeneously distributed grid. Given the positive integers  $N^a$ ,  $N^b$ , and  $N^c$ , we write analogously to Eq. (2.7) :

$$N_-^a := \begin{cases} -(N^a - 2)/2, & \text{if } N^a \text{ even,} \\ -(N^a - 1)/2, & \text{if } N^a \text{ odd,} \end{cases} \quad \text{and} \quad N_+^a := \begin{cases} +N^a/2, & \text{if } N^a \text{ even,} \\ +(N^a - 1)/2, & \text{if } N^a \text{ odd.} \end{cases} \tag{2.29}$$

The equidistant set of wavenumber components now is selected according to

$$k_u^a := \frac{2\pi}{|\mathbf{a}|} \cdot \frac{u}{N^a}, \quad \text{with } u := N_-^a, \dots, N_+^a. \tag{2.30}$$

Equivalent definitions hold for the crystallographic  $\mathbf{b}$  and  $\mathbf{c}$  directions. As in the real space,  $N^a = N^b = N^c := 1$  also corresponds to the zero-dimensional molecular case, for example.

If the summations of Eq. (2.26) run over the full Brillouin-zone ranges, all reciprocal-space  $\mathbf{k}_{uvw}$  points have to be regarded as being equivalent. As indicated above, the



weighting factor  $W_{uvw}$  is always equal to 1 in this case. Utilizing the symmetry property

$$\mathbf{P}'^\alpha(\mathbf{k}) = \mathbf{P}'^{\alpha*}(-\mathbf{k}) \quad (2.31)$$

of the reciprocal-space density matrices, however, we can restrict ourselves to real part summations ranging from  $w = 0$  to  $w = N_+^c$ . All quantities with the exception of those belonging to the two special points  $k_0^c = 0$  and  $k_{+N^c/2}^c = +\pi/|\mathbf{c}|$  have to be counted twice in this case :

$$\begin{aligned} (\mathbf{P}'^\alpha)_{\tau\lambda} &:= (N^{abc})^{-1} \sum_{u=N_-^a}^{N_+^a} \sum_{v=N_-^b}^{N_+^b} \sum_{w=0}^{N_+^c} W_{uvw} \\ &\times \left\{ \cos[k_u^a(t_a - l_a)|\mathbf{a}| + k_v^b(t_b - l_b)|\mathbf{b}| + k_w^c(t_c - l_c)|\mathbf{c}|] \Re \{P'_{\tau\lambda}{}^\alpha(\mathbf{k}_{uvw})\} \right. \\ &\left. - \sin[k_u^a(t_a - l_a)|\mathbf{a}| + k_v^b(t_b - l_b)|\mathbf{b}| + k_w^c(t_c - l_c)|\mathbf{c}|] \Im \{P'_{\tau\lambda}{}^\alpha(\mathbf{k}_{uvw})\} \right\}, \end{aligned} \quad (2.32)$$

with

$$W_{uvw} := \begin{cases} 1, & \text{if } w = 0 \text{ or } w = +N^c/2, \\ 2, & \text{otherwise.} \end{cases} \quad (2.33)$$

Moreover, if one uses the symmetry rules developed by Ramírez & Böhm [12], one finally can even restrict  $\mathbf{k}$ -space summations to the irreducible part of the Brillouin zone. Since the symmetry property of Eq. (2.31) also holds for the matrices

$$\mathbf{F}'^\alpha(\mathbf{k}) = \mathbf{F}'^{\alpha*}(-\mathbf{k}), \quad (2.34)$$

$$\mathbf{S}'(\mathbf{k}) = \mathbf{S}'^*(-\mathbf{k}), \quad (2.35)$$

$$\mathbf{C}'^\alpha(\mathbf{k}) = \mathbf{C}'^{\alpha*}(-\mathbf{k}), \quad (2.36)$$

and

$$\mathbf{E}^\alpha(\mathbf{k}) = \mathbf{E}^\alpha(-\mathbf{k}), \quad (2.37)$$

such techniques may considerably reduce the preselected number of wavevectors for which the generalized eigenvalue problem of Eq. (2.14) has to be solved.

### 3. “Unrestricted and Combined Mulliken” approximations (M.U&C)

We now ask the following question : Under what conditions will the off-diagonal elements  $(\mathbf{F}_{0\mathbf{n}}^A)_{\mu\nu}$ ,  $(\mathbf{F}_{0\mathbf{n}}^C)_{\mu\nu}$ , and  $(\mathbf{F}_{0\mathbf{n}}^{\alpha E})_{\mu\nu}$  of Eq. (2.21) be reduced to their subsequent form ,

$$(\mathbf{F}_{0\mathbf{n}}^A)_{\mu\nu} := \frac{(\mathbf{S}_{0\mathbf{n}})_{\mu\nu}}{2} \left\{ (\mathbf{F}_{00}^A)_{\mu\mu} + \underbrace{(\mathbf{F}_{\mathbf{nn}}^A)_{\nu\nu}}_{=(\mathbf{F}_{00}^A)_{\nu\nu}} \right\}, \quad (3.1)$$

$$(\mathbf{F}_{0\mathbf{n}}^C)_{\mu\nu} := \frac{(\mathbf{S}_{0\mathbf{n}})_{\mu\nu}}{2} \left\{ (\mathbf{F}_{00}^C)_{\mu\mu} + \underbrace{(\mathbf{F}_{\mathbf{nn}}^C)_{\nu\nu}}_{=(\mathbf{F}_{00}^C)_{\nu\nu}} \right\}, \quad (3.2)$$

$$(\mathbf{F}_{0\mathbf{n}}^{\alpha E})_{\mu\nu} := \frac{(\mathbf{S}_{0\mathbf{n}})_{\mu\nu}}{2} \left\{ (\mathbf{F}_{00}^{\alpha E})_{\mu\mu} + \underbrace{(\mathbf{F}_{\mathbf{nn}}^{\alpha E})_{\nu\nu}}_{=(\mathbf{F}_{00}^{\alpha E})_{\nu\nu}} \right\}, \quad (3.3)$$

which is characteristic for semi-empirical crystal orbital theories of “Extended Hückel” type [9] ?

As in the preceding contribution [1] we give the following answer : Applying Mulliken’s well-known approximation [3] of a two-index one-electron density

$$\{\Phi_\mu(\mathbf{r}_i)\Phi_\nu(\mathbf{r}_i - \mathbf{R}_\mathbf{n})\}^{[M_{\mu\nu}^I]} := \frac{(\mathbf{S}_{0\mathbf{n}})_{\mu\nu}}{2} \{ \Phi_\mu(\mathbf{r}_i)\Phi_\mu(\mathbf{r}_i) + \Phi_\nu(\mathbf{r}_i - \mathbf{R}_\mathbf{n})\Phi_\nu(\mathbf{r}_i - \mathbf{R}_\mathbf{n}) \} \quad (3.4)$$

unrestrictedly to the attractive and the Coulomb part of Eq. (2.21), we immediately arrive at Eq. (3.1) and Eq. (3.2), respectively :

$$(\mathbf{F}_{0\mathbf{n}}^A)^{[M^I]}_{\mu\nu} := \frac{(\mathbf{S}_{0\mathbf{n}})_{\mu\nu}}{2} \left\{ \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n} (\mathbf{V}_{00})_{\mu\mu}[\mathbf{p}P]}_{=(\mathbf{F}_{00}^A)_{\mu\mu}} + \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n} (\mathbf{V}_{\mathbf{nn}})_{\nu\nu}[\mathbf{p}P]}_{=(\mathbf{F}_{00}^A)_{\nu\nu}} \right\}, \quad (3.5)$$

and

$$\begin{aligned} (\mathbf{F}_{0\mathbf{n}}^C)^{[M^I M^I]}_{\mu\nu} := & \frac{(\mathbf{S}_{0\mathbf{n}})_{\mu\nu}}{2} \left\{ \underbrace{\sum_{\mathbf{t}, \mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau, \lambda=1}^{N_o} (\mathbf{P}_{\mathbf{tl}}^\oplus)_{\tau\lambda} \begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{1} \\ \mu & \mu & \tau & \lambda \end{pmatrix}^{[M^I_{\tau\lambda}]}}_{=(\mathbf{F}_{00}^C)^{[M^I]}_{\mu\mu}} \right. \\ & \left. + \underbrace{\sum_{\mathbf{t}, \mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau, \lambda=1}^{N_o} (\mathbf{P}_{\mathbf{tl}}^\oplus)_{\tau\lambda} \begin{pmatrix} \mathbf{n} & \mathbf{n} & \mathbf{t} & \mathbf{1} \\ \nu & \nu & \tau & \lambda \end{pmatrix}^{[M^I_{\tau\lambda}]}}_{=(\mathbf{F}_{00}^C)^{[M^I]}_{\nu\nu}} \right\}. \end{aligned} \quad (3.6)$$

The attribute “unrestricted” indicates here that Mulliken’s simple recipe is applied to Eq. (2.21) without making any distinction between one-, two-, three-, or four-index terms. Evidently, oversimplifications with respect to some kinds of two-index integrals are tolerated in such a description. Moreover, as we shall see below, implicit oversimplifications are also inherent in the treatment of some kinds of three-index repulsion integrals as well.

As outlined in the appendix of Ref. [1], Mulliken's approximation of Eq. (3.4) can be regarded as the diagonal term of a Rdenberg-type expansion [2] of a diatomic one-electron density :

$$\begin{aligned} & \{ \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M) \Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_n) \}^{[R_{MN}^I]} \\ & := \frac{1}{2} \left\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M) \Phi_{\mu'}(\mathbf{r}_i - \mathbf{R}_M) \right. \\ & \quad \left. + \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_n) \Phi_{\nu'}(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_n) \right\}. \end{aligned} \quad (3.7)$$

In addition, Rdenberg's letter of 1951 proposes another approximation scheme which refers to an expansion of a two-electron two-center orbital product :

$$\begin{aligned} & \{ \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M) \Phi_\nu(\mathbf{r}_j - \mathbf{R}_N - \mathbf{R}_n) \}^{[R_{MN}^{II}]} \\ & := \frac{1}{2} \left\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \Phi_\mu(\mathbf{r}_i - \mathbf{R}_M) \Phi_{\mu'}(\mathbf{r}_j - \mathbf{R}_M) \right. \\ & \quad \left. + \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_n) \Phi_{\nu'}(\mathbf{r}_j - \mathbf{R}_N - \mathbf{R}_n) \right\}. \end{aligned} \quad (3.8)$$

Similarly, the diagonal term of Eq. (3.8) can be regarded as the two-electron equivalent of Mulliken's simple formula in Eq. (3.4) :

$$\{ \Phi_\mu(\mathbf{r}_i) \Phi_\nu(\mathbf{r}_j - \mathbf{R}_n) \}^{[M^{II} \nu]} := \frac{(\mathbf{S}_{0n})_{\mu\nu}}{2} \{ \Phi_\mu(\mathbf{r}_i) \Phi_\mu(\mathbf{r}_j) + \Phi_\nu(\mathbf{r}_i - \mathbf{R}_n) \Phi_\nu(\mathbf{r}_j - \mathbf{R}_n) \}. \quad (3.9)$$

Inspecting the exchange part of Eq. (2.21), the desired reduction now can be achieved using Eq. (3.9) :

$$\begin{aligned} (\mathbf{F}_{0n}^{\alpha E})_{\mu\nu}^{[M^{II} M^{II}]} & := \frac{(\mathbf{S}_{0n})_{\mu\nu}}{2} \left\{ \underbrace{\sum_{\mathbf{t}, l=N^-}^{N^+} \sum_{\tau, \lambda=1}^{N_o} (\mathbf{P}_{\mathbf{t}l}^\alpha)_{\tau\lambda} \begin{pmatrix} \mathbf{0} & \mathbf{t} & \mathbf{0} & \mathbf{1} \\ \mu & \tau & \mu & \lambda \end{pmatrix}^{[M^{II} \tau\lambda]}}_{=(\mathbf{F}_{00}^{\alpha E})_{\mu\mu}^{[M^{II}]}} \right. \\ & \quad \left. + \underbrace{\sum_{\mathbf{t}, l=N^-}^{N^+} \sum_{\tau, \lambda=1}^{N_o} (\mathbf{P}_{\mathbf{t}l}^\alpha)_{\tau\lambda} \begin{pmatrix} \mathbf{n} & \mathbf{t} & \mathbf{n} & \mathbf{1} \\ \nu & \tau & \nu & \lambda \end{pmatrix}^{[M^{II} \tau\lambda]}}_{=(\mathbf{F}_{00}^{\alpha E})_{\nu\nu}^{[M^{II}]}} \right\}. \end{aligned} \quad (3.10)$$

We therefore conclude : Whenever kinetic energy integrals are considered to be accurately known,

- “Extended Hückel” orbital theories find a rationalization in an “Unrestricted and Combined” use of both Rüdennberg approximations of Mulliken type :

$$\begin{aligned}
(\mathbf{F}_{\mathbf{0n}}^\alpha)^{[\text{M.U\&C}]} &:= (\mathbf{K}_{\mathbf{0n}})_{\mu\nu} + (\mathbf{F}_{\mathbf{0n}}^A)^{[\text{M}^I]} + (\mathbf{F}_{\mathbf{0n}}^C)^{[\text{M}^I\text{M}^I]} - (\mathbf{F}_{\mathbf{0n}}^{\alpha E})^{[\text{M}^{\text{II}}\text{M}^{\text{II}}]} \\
&:= (\mathbf{K}_{\mathbf{0n}})_{\mu\nu} + \frac{(\mathbf{S}_{\mathbf{0n}})_{\mu\nu}}{2} \left\{ (\mathbf{F}_{\mathbf{00}}^A)_{\mu\mu} + (\mathbf{F}_{\mathbf{00}}^C)_{\mu\mu}^{[\text{M}^I]} - (\mathbf{F}_{\mathbf{00}}^{\alpha E})_{\mu\mu}^{[\text{M}^{\text{II}}]} \right. \\
&\quad \left. + (\mathbf{F}_{\mathbf{00}}^A)_{\nu\nu} + (\mathbf{F}_{\mathbf{00}}^C)_{\nu\nu}^{[\text{M}^I]} - (\mathbf{F}_{\mathbf{00}}^{\alpha E})_{\nu\nu}^{[\text{M}^{\text{II}}]} \right\}.
\end{aligned} \tag{3.11}$$

- All what we need besides the overlap integrals are the diagonal elements which have to be calculated according to Eqs. (3.5), (3.12), and (3.13) :

$$\begin{aligned}
(\mathbf{F}_{\mathbf{00}}^C)_{\mu\mu}^{[\text{M}^I]} &:= \frac{1}{2} \left\{ \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau=1}^{N_o} \begin{pmatrix} \mathbf{0} & \mathbf{0} & | & \mathbf{t} & \mathbf{t} \\ \mu & \mu & | & \tau & \tau \end{pmatrix} \sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\lambda=1}^{N_o} (\mathbf{P}_{\mathbf{tl}}^\oplus)_{\tau\lambda} (\mathbf{S}_{\mathbf{tl}})_{\tau\lambda} \right. \\
&\quad \left. + \sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\lambda=1}^{N_o} \begin{pmatrix} \mathbf{0} & \mathbf{0} & | & \mathbf{l} & \mathbf{l} \\ \mu & \mu & | & \lambda & \lambda \end{pmatrix} \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau=1}^{N_o} (\mathbf{P}_{\mathbf{tl}}^\oplus)_{\tau\lambda} (\mathbf{S}_{\mathbf{tl}})_{\tau\lambda} \right\} \\
&= \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau=1}^{N_o} \begin{pmatrix} \mathbf{0} & \mathbf{0} & | & \mathbf{t} & \mathbf{t} \\ \mu & \mu & | & \tau & \tau \end{pmatrix} ((\mathbf{P}^\oplus \mathbf{S})_{\mathbf{tt}})_{\tau\tau} = \sum_{\tau=1}^{N_o} ((\mathbf{P}^\oplus \mathbf{S})_{\mathbf{00}})_{\tau\tau} \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \begin{pmatrix} \mathbf{0} & \mathbf{0} & | & \mathbf{t} & \mathbf{t} \\ \mu & \mu & | & \tau & \tau \end{pmatrix},
\end{aligned} \tag{3.12}$$

and

$$\begin{aligned}
(\mathbf{F}_{\mathbf{00}}^{\alpha E})_{\mu\mu}^{[\text{M}^{\text{II}}]} &:= \frac{1}{2} \left\{ \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau=1}^{N_o} \begin{pmatrix} \mathbf{0} & \mathbf{t} & | & \mathbf{0} & \mathbf{t} \\ \mu & \tau & | & \mu & \tau \end{pmatrix} \sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\lambda=1}^{N_o} (\mathbf{P}_{\mathbf{tl}}^\alpha)_{\tau\lambda} (\mathbf{S}_{\mathbf{tl}})_{\tau\lambda} \right. \\
&\quad \left. + \sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\lambda=1}^{N_o} \begin{pmatrix} \mathbf{0} & \mathbf{l} & | & \mathbf{0} & \mathbf{l} \\ \mu & \lambda & | & \mu & \lambda \end{pmatrix} \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau=1}^{N_o} (\mathbf{P}_{\mathbf{tl}}^\alpha)_{\tau\lambda} (\mathbf{S}_{\mathbf{tl}})_{\tau\lambda} \right\} \\
&= \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{\tau=1}^{N_o} \begin{pmatrix} \mathbf{0} & \mathbf{t} & | & \mathbf{0} & \mathbf{t} \\ \mu & \tau & | & \mu & \tau \end{pmatrix} ((\mathbf{P}^\alpha \mathbf{S})_{\mathbf{tt}})_{\tau\tau} = \sum_{\tau=1}^{N_o} ((\mathbf{P}^\alpha \mathbf{S})_{\mathbf{00}})_{\tau\tau} \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \begin{pmatrix} \mathbf{0} & \mathbf{t} & | & \mathbf{0} & \mathbf{t} \\ \mu & \tau & | & \mu & \tau \end{pmatrix},
\end{aligned} \tag{3.13}$$

- Within such an “Unrestricted and Combined Mulliken” picture (M.U&C) multi-index integral computations can be avoided. Only the one- and two-index integrals occuring in Eqs. (3.5), (3.12), and (3.13) have to be evaluated completely.

#### 4. “Unrestricted and Combined ZIO” approximations (ZIO.U&C)

Another well-established feature of semi-empirical quantum chemistry is the assumption of a globally orthonormal atomic orbital basis set. If one supposes this orthonormality property to be valid, the M.U&C picture outlined above immediately converts into a corresponding “Zero Integral Overlap” approximation (ZIO.U&C), the one-electron part of which is identical with the “Zero Differential Overlap” scheme (ZDO) originally introduced by Parr [4] :

$$\{\Phi_\mu(\mathbf{r}_i)\Phi_\nu(\mathbf{r}_i - \mathbf{R}_n)\}^{[\text{ZIO}^{\text{I}}_{\mu\nu}]} := \{\Phi_\mu(\mathbf{r}_i)\Phi_\nu(\mathbf{r}_i - \mathbf{R}_n)\}^{[\text{ZDO}_{\mu\nu}]} := \delta_{\mathbf{0n}}\delta_{\mu\nu}\Phi_\mu(\mathbf{r}_i)\Phi_\mu(\mathbf{r}_i), \quad (4.1)$$

where  $\delta_{\mathbf{0n}} \equiv \delta_{0n_a}\delta_{0n_b}\delta_{0n_c}$ . Following Rüdénberg’s two-electron route of approximation the two-electron analog of Eq. (4.1) then reads :

$$\{\Phi_\mu(\mathbf{r}_i)\Phi_\nu(\mathbf{r}_j - \mathbf{R}_n)\}^{[\text{ZIO}^{\text{II}}_{\mu\nu}]} := \delta_{\mathbf{0n}}\delta_{\mu\nu}\Phi_\mu(\mathbf{r}_i)\Phi_\mu(\mathbf{r}_j). \quad (4.2)$$

In order to deduce the close relationship between the M.U&C and the “Unrestricted and Combined ZIO” picture (ZIO.U&C) one only has to substitute all overlap integrals of the last section by an equivalent Kronecker symbol.

- Consequently, we then define :

$$(\mathbf{F}_{\mathbf{0n}}^\alpha)^{[\text{ZIO.U\&C}]}_{\mu\nu} := (\mathbf{K}_{\mathbf{0n}})_{\mu\nu} + \delta_{\mathbf{0n}}\delta_{\mu\nu} \left\{ (\mathbf{F}_{\mathbf{00}}^A)_{\mu\mu} + (\mathbf{F}_{\mathbf{00}}^C)^{[\text{ZIO}^{\text{I}}]}_{\mu\mu} - (\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\text{ZIO}^{\text{II}}]}_{\mu\mu} \right\}, \quad (4.3)$$

with

$$(\mathbf{F}_{\mathbf{00}}^C)^{[\text{ZIO}^{\text{I}}]}_{\mu\mu} := \sum_{\tau=1}^{N_o} (\mathbf{P}_{\mathbf{00}}^\oplus)_{\tau\tau} \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ \mu & \mu & \tau & \tau \end{pmatrix}, \quad (4.4)$$

and

$$(\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\text{ZIO}^{\text{II}}]}_{\mu\mu} := \sum_{\tau=1}^{N_o} (\mathbf{P}_{\mathbf{00}}^\alpha)_{\tau\tau} \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \begin{pmatrix} \mathbf{0} & \mathbf{t} & \mathbf{0} & \mathbf{t} \\ \mu & \tau & \mu & \tau \end{pmatrix}. \quad (4.5)$$

- The ZIO.U&C scheme introduced in this way is completely compatible with Rüdénberg’s approximations of Mulliken type, together with the additional assumption  $(\mathbf{S}_{\mathbf{0n}})_{\mu\nu} := \delta_{\mathbf{0n}}\delta_{\mu\nu}$ .

It should be emphasized that the ZIO equations of this section can only be valid non-empirically if all the integrals involved have been correctly transferred into the globally orthonormalized basis as well. Alternatively, one could try to introduce empirical parametrizations like in the “Complete Neglect of Differential Overlap” (CNDO) or “Intermediate Neglect of Differential Overlap” (INDO) treatment [5,13], for instance.

## 5. “Unrestricted and Combined Rüdberg” approximations (R.U&C)

Mulliken- and ZDO-type simplifications are not invariant with respect to rotations of local coordinate axes [10]. Although they offer considerable advantages due to their conceptual simplicity, neither the M.U&C nor the ZIO.U&C approach can be considered as an approximate non-empirical orbital theory without imposing additional assumptions.

Rüdberg’s more elaborate expansions of Eqs. (3.7) and (3.8), on the other hand, as well as the “Neglect of Diatomic Differential Overlap” concept (NDDO) of Pople, Santry & Segal [5], to be discussed in the next section, fulfil this rotational invariance requirement automatically [10].

In analogy to the corresponding M.U&C ansatz of Eq. (3.11) we now write :

$$\begin{aligned}
 (\mathbf{F}_{\mathbf{0n}}^\alpha)^{[\text{R.U\&C}]} &:= (\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + (\mathbf{F}_{\mathbf{0n}}^A)^{[\text{R}^I]} \\
 &+ (\mathbf{F}_{\mathbf{0n}}^C)^{[\text{R}^I\text{R}^I]} - (\mathbf{F}_{\mathbf{0n}}^{\alpha E})^{[\text{R}^{II}\text{R}^{II}]} .
 \end{aligned} \tag{5.1}$$

In the “Unrestricted and Combined Rüdberg” picture (R.U&C) defined in this way, both approximation routes are considered to be applied exhaustively. Consequently, oversimplifications are generally tolerated here, not only for certain three-center repulsion integrals, as we shall see later, but even for some kinds of two-center repulsion and attraction integrals as well.

Using Eq. (3.7), we get for the attractive part of the Fock matrix defined in Eq. (5.1) :

$$\begin{aligned}
 (\mathbf{F}_{\mathbf{0n}}^A)^{[\text{R}^I]} &:= \frac{1}{2} \left\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n} \begin{pmatrix} \mathbf{0} & \mathbf{p} & \mathbf{0} \\ M & P & M \\ \mu & & \mu' \end{pmatrix}}_{=(\mathbf{F}_{\mathbf{00}}^A)_{(M,\mu)(M,\mu')}}} \right. \\
 &+ \left. \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \underbrace{\sum_{\mathbf{p}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{P=1}^{N_n} \begin{pmatrix} \mathbf{n} & \mathbf{p} & \mathbf{n} \\ N & P & N \\ \nu' & & \nu \end{pmatrix}}_{=(\mathbf{F}_{\mathbf{00}}^A)_{(N,\nu')(N,\nu)}}} \right\} .
 \end{aligned} \tag{5.2}$$

Along the same lines, an application of Eq. (3.7) to the Coulomb part of Eq. (5.1)

yields :

$$\begin{aligned}
(\mathbf{F}_{\mathbf{0n}}^C)^{[\mathbf{R}^I \mathbf{R}^I]}_{(M,\mu)(N,\nu)} &:= \frac{1}{2} \left\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \right. \\
&\times \underbrace{\sum_{\mathbf{t}, \mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T,L=1}^{N_n} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}_{\mathbf{tl}}^\oplus)_{(T,\tau)(L,\lambda)} \begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{1} \\ M & M & T & L \\ \mu & \mu' & \tau & \lambda \end{pmatrix}}_{=(\mathbf{F}_{\mathbf{00}}^C)^{[\mathbf{R}^I]}_{(M,\mu)(M,\mu')}}}^{[\mathbf{R}_{TL}^I]} \\
&+ \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \\
&\times \underbrace{\sum_{\mathbf{t}, \mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T,L=1}^{N_n} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}_{\mathbf{tl}}^\oplus)_{(T,\tau)(L,\lambda)} \begin{pmatrix} \mathbf{n} & \mathbf{n} & \mathbf{t} & \mathbf{1} \\ N & N & T & L \\ \nu' & \nu & \tau & \lambda \end{pmatrix}}_{=(\mathbf{F}_{\mathbf{00}}^C)^{[\mathbf{R}^I]}_{(N,\nu')(N,\nu)}}}^{[\mathbf{R}_{TL}^I]} \left. \right\}. \tag{5.3}
\end{aligned}$$

Finally, using Rdenberg's two-electron approximation of Eq. (3.8) for the exchange part of Eq. (5.1), we achieve an analogous expression :

$$\begin{aligned}
(\mathbf{F}_{\mathbf{0n}}^{\alpha E})^{[\mathbf{R}^{II} \mathbf{R}^{II}]}_{(M,\mu)(N,\nu)} &:= \frac{1}{2} \left\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \right. \\
&\times \underbrace{\sum_{\mathbf{t}, \mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T,L=1}^{N_n} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}_{\mathbf{tl}}^\alpha)_{(T,\tau)(L,\lambda)} \begin{pmatrix} \mathbf{0} & \mathbf{t} & \mathbf{0} & \mathbf{1} \\ M & T & M & L \\ \mu & \tau & \mu' & \lambda \end{pmatrix}}_{=(\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\mathbf{R}^{II}]}_{(M,\mu)(M,\mu')}}}^{[\mathbf{R}_{TL}^{II}]} \\
&+ \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \\
&\times \underbrace{\sum_{\mathbf{t}, \mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T,L=1}^{N_n} \sum_{\tau=1}^{n_o(T)} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}_{\mathbf{tl}}^\alpha)_{(T,\tau)(L,\lambda)} \begin{pmatrix} \mathbf{n} & \mathbf{t} & \mathbf{n} & \mathbf{1} \\ N & T & N & L \\ \nu' & \tau & \nu & \lambda \end{pmatrix}}_{=(\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\mathbf{R}^{II}]}_{(N,\nu')(N,\nu)}}}^{[\mathbf{R}_{TL}^{II}]} \left. \right\}. \tag{5.4}
\end{aligned}$$

Conclusion :

- Disregarding the kinetic energy integrals of the first term of Eq. (5.1), the most appealing feature of Eqs. (5.2), (5.3), and (5.4) is that off-blockdiagonal elements

can be fully led back to a determination of related blockdiagonal elements :

$$\begin{aligned}
(\mathbf{F}_{\mathbf{0n}}^\alpha)^{[\text{R.U\&C}]}_{(M,\mu)(N,\nu)} &:= (\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \\
&+ \frac{1}{2} \left\{ \sum_{\mu'=1}^{n_o(M)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \left[ (\mathbf{F}_{\mathbf{00}}^A)_{(M,\mu)(M,\mu')} + (\mathbf{F}_{\mathbf{00}}^C)^{[\text{R}^I]}_{(M,\mu)(M,\mu')} - (\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\text{R}^{\text{II}}]}_{(M,\mu)(M,\mu')} \right] \right. \\
&\quad \left. + \sum_{\nu'=1}^{n_o(N)} \begin{pmatrix} \mathbf{0} & \mathbf{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \left[ (\mathbf{F}_{\mathbf{00}}^A)_{(N,\nu')(N,\nu)} + (\mathbf{F}_{\mathbf{00}}^C)^{[\text{R}^I]}_{(N,\nu')(N,\nu)} - (\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\text{R}^{\text{II}}]}_{(N,\nu')(N,\nu)} \right] \right\}.
\end{aligned} \tag{5.5}$$

- The “Unrestricted and Combined Rüdberg” picture defined in this way, can thus be regarded as a rotational invariant extension of the “Unrestricted and Combined Mulliken” approximation.
- Multi-center integrations can be avoided. Only those one- and two-center integrals have to be evaluated completely which occur in the following blockdiagonal expressions :

$$\begin{aligned}
(\mathbf{F}_{\mathbf{00}}^C)^{[\text{R}^I]}_{(M,\mu)(M,\mu')} &:= \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n} \sum_{\tau,\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{0} & \mathbf{0} & | & \mathbf{t} & \mathbf{t} \\ M & M & | & T & T \\ \mu & \mu' & | & \tau & \tau' \end{pmatrix} \\
&\quad \times \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{L=1}^{N_n} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}_{\mathbf{tl}}^\oplus)_{(T,\tau)(L,\lambda)} \begin{pmatrix} \mathbf{t} & \mathbf{1} \\ T & L \\ \tau' & \lambda \end{pmatrix}}_{=((\mathbf{P}^\oplus \mathbf{S})_{\mathbf{tt}})_{(T,\tau)(T,\tau')}}} \\
&= \sum_{T=1}^{N_n} \sum_{\tau,\tau'=1}^{n_o(T)} ((\mathbf{P}^\oplus \mathbf{S})_{\mathbf{00}})_{(T,\tau)(T,\tau')} \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \begin{pmatrix} \mathbf{0} & \mathbf{0} & | & \mathbf{t} & \mathbf{t} \\ M & M & | & T & T \\ \mu & \mu' & | & \tau & \tau' \end{pmatrix},
\end{aligned} \tag{5.6}$$

and

$$\begin{aligned}
(\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\text{R}^{\text{II}}]}_{(M,\mu)(M,\mu')} &:= \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{T=1}^{N_n} \sum_{\tau,\tau'=1}^{n_o(T)} \begin{pmatrix} \mathbf{0} & \mathbf{t} & | & \mathbf{0} & \mathbf{t} \\ M & T & | & M & T \\ \mu & \tau & | & \mu' & \tau' \end{pmatrix} \\
&\quad \times \frac{1}{2} \left\{ \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{L=1}^{N_n} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}_{\mathbf{tl}}^\alpha)_{(T,\tau)(L,\lambda)} \begin{pmatrix} \mathbf{t} & \mathbf{1} \\ T & L \\ \tau' & \lambda \end{pmatrix}}_{=((\mathbf{P}^\alpha \mathbf{S})_{\mathbf{tt}})_{(T,\tau)(T,\tau')}}} \right. \\
&\quad \left. + \underbrace{\sum_{\mathbf{l}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{L=1}^{N_n} \sum_{\lambda=1}^{n_o(L)} (\mathbf{P}_{\mathbf{tl}}^\alpha)_{(T,\tau')(L,\lambda)} \begin{pmatrix} \mathbf{t} & \mathbf{1} \\ T & L \\ \tau & \lambda \end{pmatrix}}_{=((\mathbf{P}^\alpha \mathbf{S})_{\mathbf{tt}})_{(T,\tau')(T,\tau)}}} \right\} \\
&= \sum_{T=1}^{N_n} \sum_{\tau,\tau'=1}^{n_o(T)} \frac{1}{2} \left\{ ((\mathbf{P}^\alpha \mathbf{S})_{\mathbf{00}})_{(T,\tau)(T,\tau')} + ((\mathbf{P}^\alpha \mathbf{S})_{\mathbf{00}})_{(T,\tau')(T,\tau)} \right\} \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \begin{pmatrix} \mathbf{0} & \mathbf{t} & | & \mathbf{0} & \mathbf{t} \\ M & T & | & M & T \\ \mu & \tau & | & \mu' & \tau' \end{pmatrix}.
\end{aligned} \tag{5.7}$$



## 6. “Unrestricted and Combined NDIO” approximations (NDIO.U&C)

As in the “Unrestricted and Combined ZIO” section, we finally assume the atomic orbital basis set to be globally orthogonalized. The R.U&C picture outlined above then immediately converts into an “Unrestricted and Combined” variant of the “Neglect of Diatomic Integral Overlap” scheme (NDIO), the one-electron part of which is identical with the “Neglect of Diatomic Differential Overlap” scheme (NDDO) originally introduced by Pople, Santry, & Segal [5] :

$$\begin{aligned} \{\Phi_\mu(\mathbf{r}_i - \mathbf{R}_M)\Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_n)\}^{[\text{NDIO}_{MN}^I]} &:= \\ \{\Phi_\mu(\mathbf{r}_i - \mathbf{R}_M)\Phi_\nu(\mathbf{r}_i - \mathbf{R}_N - \mathbf{R}_n)\}^{[\text{NDDO}_{MN}]} &:= \delta_{\mathbf{0n}}\delta_{MN}\Phi_\mu(\mathbf{r}_i - \mathbf{R}_M)\Phi_\nu(\mathbf{r}_i - \mathbf{R}_M), \end{aligned} \quad (6.1)$$

where again  $\delta_{\mathbf{0n}} \equiv \delta_{0n_a}\delta_{0n_b}\delta_{0n_c}$ . Following Rüdénberg’s two-electron route of approximation the two-electron analog of Eq. (6.1) then reads :

$$\{\Phi_\mu(\mathbf{r}_i - \mathbf{R}_M)\Phi_\nu(\mathbf{r}_j - \mathbf{R}_N - \mathbf{R}_n)\}^{[\text{NDIO}_{MN}^{\text{II}}]} := \delta_{\mathbf{0n}}\delta_{MN}\Phi_\mu(\mathbf{r}_i - \mathbf{R}_M)\Phi_\nu(\mathbf{r}_j - \mathbf{R}_M). \quad (6.2)$$

In order to deduce the close relationship between the R.U&C and the “Unrestricted and Combined NDIO” picture (NDIO.U&C), one only has to substitute all diatomic overlap integrals of the last section by an equivalent diatomic Kronecker symbol.

- Consequently, we then define :

$$\begin{aligned} (\mathbf{F}_{\mathbf{0n}}^\alpha)_{(M,\mu)(N,\nu)}^{[\text{NDIO.U\&C}]} &:= (\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} \\ &+ \delta_{\mathbf{0n}}\delta_{MN} \left\{ (\mathbf{F}_{\mathbf{00}}^A)_{(M,\mu)(M,\nu)} + (\mathbf{F}_{\mathbf{00}}^C)_{(M,\mu)(M,\nu)}^{[\text{NDIO}^I]} - (\mathbf{F}_{\mathbf{00}}^{\alpha E})_{(M,\mu)(M,\nu)}^{[\text{NDIO}^{\text{II}}]} \right\}, \end{aligned} \quad (6.3)$$

with

$$(\mathbf{F}_{\mathbf{00}}^C)_{(M,\mu)(M,\nu)}^{[\text{NDIO}^I]} := \sum_{T=1}^{N_n} \sum_{\tau,\lambda=1}^{n_o(T)} (\mathbf{P}_{\mathbf{00}}^\oplus)_{(T,\tau)(T,\lambda)} \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \left( \begin{array}{cc|cc} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \nu & \tau & \lambda \end{array} \right), \quad (6.4)$$

and

$$(\mathbf{F}_{\mathbf{00}}^{\alpha E})_{(M,\mu)(M,\nu)}^{[\text{NDIO}^{\text{II}}]} := \sum_{T=1}^{N_n} \sum_{\tau,\lambda=1}^{n_o(T)} (\mathbf{P}_{\mathbf{00}}^\alpha)_{(T,\tau)(T,\lambda)} \sum_{\mathbf{t}=\mathbf{N}^-}^{\mathbf{N}^+} \left( \begin{array}{cc|cc} \mathbf{0} & \mathbf{t} & \mathbf{0} & \mathbf{t} \\ M & T & M & T \\ \mu & \tau & \nu & \lambda \end{array} \right). \quad (6.5)$$

- The NDIO.U&C picture constructed in this way can be completely understood within the R.U&C framework together with the additional assumption of zero diatomic integral overlap.

Again, it should be emphasized that the NDIO equations of this section can only be valid non-empirically if all the integrals involved have been correctly transferred into the globally orthonormalized basis as well. Alternatively, one could try to introduce empirical parametrizations like in the standard NDDO treatment [5,13], for instance.

## 7. Real-space lattice summations including long-range interactions

### 7.1. Long-range correction of the Fock matrix

We now return to the problem mentioned above in connection with the Eqs. (2.19) and (2.20) concerning real-space lattice sums. In these two cases, the choice of unit-cell numbers  $N_a$ ,  $N_b$ , and  $N_c$ , which governs the expense of real-space lattice summations in general, can be kept rather small, since the matrices  $(\mathbf{S}_{\mathbf{0n}})$  and  $(\mathbf{K}_{\mathbf{0n}})$  occurring in the Fock-matrix representations

$$(\mathbf{F}_{\mathbf{0n}}^\alpha)^{[\text{M.U\&C}]} \text{ (Eq. (3.11))}, (\mathbf{F}_{\mathbf{0n}}^\alpha)^{[\text{ZIO.U\&C}]} \text{ (Eq. (4.3))}, (\mathbf{F}_{\mathbf{0n}}^\alpha)^{[\text{R.U\&C}]} \text{ (Eq. (5.5))}, \text{ and } (\mathbf{F}_{\mathbf{0n}}^\alpha)^{[\text{NDIO.U\&C}]} \text{ (Eq. (6.3))}$$

decay rather quickly with increasing intercellular distances  $|\mathbf{R}_0 - \mathbf{R}_n|$ .

Due to an equally rapid fall-off of the two-center exchange integrals, even the matrices  $(\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\text{M}^{\text{II}}]} \text{ (Eq. (3.13))}, (\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\text{ZIO}^{\text{II}}]} \text{ (Eq. (4.5))}, (\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\text{R}^{\text{II}}]} \text{ (Eq. (5.7))}, (\mathbf{F}_{\mathbf{00}}^{\alpha E})^{[\text{NDIO}^{\text{II}}]} \text{ (Eq. (6.5))},$

can get along with small  $N_a$ ,  $N_b$ , and  $N_c$  parameters.

Only the attractive and repulsive matrix representations

$$(\mathbf{F}_{\mathbf{00}}^A) \text{ (Eqs. (2.21) or (2.24)) and } (\mathbf{F}_{\mathbf{00}}^C)^{[\text{M}^{\text{I}}]} \text{ (Eq. (3.12))}, (\mathbf{F}_{\mathbf{00}}^C)^{[\text{ZIO}^{\text{I}}]} \text{ (Eq. (4.4))}, (\mathbf{F}_{\mathbf{00}}^C)^{[\text{R}^{\text{I}}]} \text{ (Eq. (5.6))}, (\mathbf{F}_{\mathbf{00}}^C)^{[\text{NDIO}^{\text{I}}]} \text{ (Eq. (6.4))}$$

contain long-ranging two-center integrals of Coulomb-type.

For large internuclear distances, however, these Coulomb-type attraction and repulsion integrals can be identified approximately with classical Coulomb interaction energies :

$$\begin{pmatrix} \mathbf{0} & \mathbf{t} & \mathbf{0} \\ M & T & M \\ \mu & \mu & \mu \end{pmatrix}_\infty := -Z_T |\mathbf{R}_M - [\mathbf{R}_T - \mathbf{R}_t]|^{-1} \quad \text{for all } \mu, \quad (7.1)$$

$$\begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \mu & \tau & \tau \end{pmatrix}_\infty := |\mathbf{R}_M - [\mathbf{R}_T - \mathbf{R}_t]|^{-1} \quad \text{for all } \mu, \tau. \quad (7.2)$$

Therefore, instead of choosing extremely large unit-cell parameters, we propose the following real-space summation technique. Assuming that all integrals except those of Eqs. (7.1) and (7.2) have decayed sufficiently, if

$$(\mathbf{S}_{\mathbf{0}\{N_a^+, 0, 0\}}) \approx (\mathbf{S}_{\mathbf{0}\{0, N_b^+, 0\}}) \approx (\mathbf{S}_{\mathbf{0}\{0, 0, N_c^+\}}) \approx \mathbf{0}, \quad (7.3)$$

we introduce the following long-range correction :



We now conclude : To allow a choice of small integers for the unit-cell parameters  $N_a$ ,  $N_b$ , and  $N_c$ , which control the expense of real-space lattice summations, Eq. (3.11), (4.3), (5.5), and (6.3) have to be replaced by the corresponding expression of Eq. (7.6).

Since long-range interactions now are approximately included, real-space lattice summations can be restricted to cover only few unit cells.

## 7.2. Long-range correction of the total energy per unit cell

Finally, we discuss real-space lattice summations in the computation of the total energy per unit cell :

$$\begin{aligned}
\mathcal{E}_t^{[X.U\&C]} := & \frac{1}{2} \sum_{\mathbf{n}=\mathbf{N}^-}^{\mathbf{N}^+} \sum_{M,N=1}^{N_n} \sum_{\mu=1}^{n_o(M)} \sum_{\nu=1}^{n_o(N)} \left\{ (\mathbf{P}_{\mathbf{0n}}^\oplus)_{(M,\mu)(N,\nu)} \right. \\
& \times \left[ (\mathbf{K}_{\mathbf{0n}})_{(M,\mu)(N,\nu)} + (\mathbf{F}_{\mathbf{0n}}^A)_{(M,\mu)(N,\nu)}^{[X.U\&C]} \right] \\
& + (\mathbf{P}_{\mathbf{0n}}^\alpha)_{(M,\mu)(N,\nu)} (\mathbf{F}_{\mathbf{0n}}^\alpha)_{(M,\mu)(N,\nu)}^{[X.U\&C]} + (\mathbf{P}_{\mathbf{0n}}^\beta)_{(M,\mu)(N,\nu)} (\mathbf{F}_{\mathbf{0n}}^\beta)_{(M,\mu)(N,\nu)}^{[X.U\&C]} \left. \right\} \\
& + \frac{1}{2} \left\{ \underbrace{\sum_{M,N=1}^{N_n}}_{N \neq M} (Z_M Z_N) |\mathbf{R}_M - \mathbf{R}_N|^{-1} \right. \\
& \left. + \sum_{M,N=1}^{N_n} (Z_M Z_N) \sum_{\substack{\mathbf{n}=\mathbf{N}^- \\ \mathbf{n} \neq \mathbf{0}}}^{\mathbf{N}^+} |\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_\mathbf{n}]|^{-1} \right\}, \quad X = M, ZIO, R, NDIO .
\end{aligned} \tag{7.8}$$

As before,  $N_a$ ,  $N_b$ , and  $N_c$  can be kept small, if we include long-range Coulomb contributions by means of classical Madelung energies, which again can be evaluated by means of Ewald-summation techniques [14] :

$$\mathcal{E}_t^\infty := \frac{1}{2} \left\{ \underbrace{\sum_{M,N=1}^{N_n}}_{N \neq M} q_M q_N |\mathbf{R}_M - \mathbf{R}_N|^{-1} + \sum_{M,N=1}^{N_n} q_M q_N \underbrace{\sum_{\substack{\mathbf{n}=-\infty \\ \mathbf{n} \neq \mathbf{0}}}^{+\infty}} |\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_\mathbf{n}]|^{-1} \right\}. \tag{7.9}$$

Again, the part of the non-classical domain has to be resubstituted :

$$\mathcal{E}_t^{\infty[X.U\&C]} := \mathcal{E}_t^\infty - \mathcal{E}_t^\circ + \mathcal{E}_t^{[X.U\&C]}, \quad X = M, ZIO, R, NDIO, \tag{7.10}$$

where

$$\mathcal{E}_t^\circ := \frac{1}{2} \left\{ \underbrace{\sum_{M,N=1}^{N_n}}_{N \neq M} q_M q_N |\mathbf{R}_M - \mathbf{R}_N|^{-1} + \sum_{M,N=1}^{N_n} q_M q_N \sum_{\substack{\mathbf{n}=\mathbf{N}^- \\ \mathbf{n} \neq \mathbf{0}}}^{\mathbf{N}^+} |\mathbf{R}_M - [\mathbf{R}_N - \mathbf{R}_\mathbf{n}]|^{-1} \right\}. \tag{7.11}$$

## 8. Oversimplifications in the “unrestricted” modes of approximation

The title of Rüdénberg’s short paper (“On the Three- and Four-Center Integrals in Molecular Quantum Mechanics”) shows us that its author does not recommend his approximation for an application to all kinds of two-center integrals. Only all two-index and two-center integrals of Coulomb type like

$$(\mathbf{V}_{\mathbf{mm}})_{\mu\mu}[\mathbf{p}P] \quad \text{and} \quad \left( \begin{array}{c|c} \mathbf{m} & \mathbf{p} \\ M & P \\ \mu & \nu \end{array} \right) \quad \text{as well as} \quad \left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ \mu & \mu \end{array} \middle| \begin{array}{c} \mathbf{t} & \mathbf{t} \\ \tau & \tau \end{array} \right) \quad \text{and} \quad \left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ M & M \\ \mu & \nu \end{array} \middle| \begin{array}{c} \mathbf{t} & \mathbf{t} \\ T & T \\ \tau & \lambda \end{array} \right)$$

remain unaffected by the one-electron approximation route of Mulliken and Rüdénberg, respectively, while all two-index and two-center integrals of exchange type

$$\left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} & \mathbf{t} \\ \mu & \tau \end{array} \right) \quad \text{and} \quad \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ M & T \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} & \mathbf{t} \\ M & T \\ \nu & \lambda \end{array} \right)$$

remain unchanged by the corresponding two-electron branch. One-index Coulomb integrals can always be reproduced within the Mulliken scheme, and one-center Coulomb integrals are generally reproduced by Rüdénberg’s approximation.

The “Unrestricted and Combined” use of Mulliken- and Rüdénberg-type approximations as well as their ZIO and NDIO variants described above, however, intentionally tolerated such obvious oversimplifications. But it is clear, that a less radical approximation scheme has to avoid such conceptional shortcomings, though the beauty and simplicity of the U&C approaches of the last sections is lost in this case.

“Restricted” approximation procedures, on the other hand, which intend to avoid some or all kinds of oversimplifications, have to take care of additional inconsistencies that are not explicitly discussed in Rüdénberg’s letter. Our question now is : How do both approximation schemes operate on the following two types of three-index and three-center repulsion integrals :

$$\left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ \mu & \mu \end{array} \middle| \begin{array}{c} \mathbf{t} & \mathbf{1} \\ \tau & \lambda \end{array} \right) \quad \text{and} \quad \left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ M & M \\ \mu & \nu \end{array} \middle| \begin{array}{c} \mathbf{t} & \mathbf{1} \\ T & L \\ \tau & \lambda \end{array} \right)$$

as well as

$$\left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} & \mathbf{1} \\ \mu & \lambda \end{array} \right) \quad \text{and} \quad \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ M & T \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} & \mathbf{1} \\ M & L \\ \nu & \lambda \end{array} \right)?$$

While the double application of Rüdénberg’s one-electron route is particularly appropriate for all four-index and four-center integrals in the Coulomb part of the Fock matrix representation, the exchange-part four-index and four-center integrals generally can be regarded as being favourable for the two-electron approximation branch. Double applications, however, are always unnecessary in both three-index and three-center cases. The “restricted” modes of the four approximation recipes based on Rüdénberg’s ideas therefore can be postulated as follows :

- Within a “Restricted and Combined Mulliken” picture (M.R&C)

- $M^I$  will be used for three-index exchange part integrals of type

$$\begin{aligned} \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \mu \end{array} \middle| \begin{array}{c} \mathbf{1} \\ \tau \end{array} \right)^{[M_{\mu\mu}^I M_{\tau\lambda}^I]} &:= \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \mu \end{array} \middle| \begin{array}{c} \mathbf{1} \\ \tau \end{array} \right)^{[M_{\tau\lambda}^I]} \\ &:= \frac{(\mathbf{S}_{\mathbf{t}\mathbf{1}})_{\tau\lambda}}{2} \left\{ \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \mu \end{array} \middle| \begin{array}{c} \mathbf{t} \\ \tau \end{array} \right) + \left( \begin{array}{c|c} \mathbf{m} & \mathbf{1} \\ \mu & \mu \end{array} \middle| \begin{array}{c} \mathbf{1} \\ \lambda \end{array} \right) \right\}, \end{aligned} \quad (8.1)$$

too, and

- $M^{II}$  will also be used for three-index Coulomb part integrals of type

$$\begin{aligned} \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} \\ \mu \end{array} \right)^{[M_{\mu\mu}^{II} M_{\tau\lambda}^{II}]} &:= \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} \\ \mu \end{array} \right)^{[M_{\tau\lambda}^{II}]} \\ &:= \frac{(\mathbf{S}_{\mathbf{t}\mathbf{1}})_{\tau\lambda}}{2} \left\{ \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} \\ \mu \end{array} \right) + \left( \begin{array}{c|c} \mathbf{m} & \mathbf{1} \\ \mu & \lambda \end{array} \middle| \begin{array}{c} \mathbf{m} \\ \mu \end{array} \right) \right\}. \end{aligned} \quad (8.2)$$

- Within a “Restricted and Combined ZIO” picture (ZIO.R&C)

- $ZIO^I$  will be used for three-index exchange part integrals of type

$$\left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ \mu & \mu \end{array} \middle| \begin{array}{c} \mathbf{t} \\ \tau \end{array} \right)^{[ZIO_{\mu\mu}^I ZIO_{\tau\lambda}^I]} := \left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ \mu & \mu \end{array} \middle| \begin{array}{c} \mathbf{t} \\ \tau \end{array} \right)^{[ZIO_{\tau\lambda}^I]} := \delta_{\mathbf{t}\mathbf{1}} \delta_{\tau\lambda} \left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ \mu & \mu \end{array} \middle| \begin{array}{c} \mathbf{t} \\ \tau \end{array} \right), \quad (8.3)$$

too, and

- $ZIO^{II}$  will also be used for three-index Coulomb part integrals of type

$$\left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} \\ \mu \end{array} \right)^{[ZIO_{\mu\mu}^{II} ZIO_{\tau\lambda}^{II}]} := \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} \\ \mu \end{array} \right)^{[ZIO_{\tau\lambda}^{II}]} := \delta_{\mathbf{t}\mathbf{1}} \delta_{\tau\lambda} \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} \\ \mu \end{array} \right). \quad (8.4)$$

- Within a “Restricted and Combined Rüdberg” picture (R.R&C)

- $R^I$  will be used for three-center exchange part integrals of type

$$\begin{aligned} \left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ M & M \end{array} \middle| \begin{array}{c} \mathbf{t} \\ T \end{array} \right)^{[R_{MM}^I R_{TL}^I]} &:= \left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ M & M \end{array} \middle| \begin{array}{c} \mathbf{t} \\ T \end{array} \right)^{[R_{TL}^I]} \\ &:= \frac{1}{2} \left\{ \sum_{\tau'=1}^{n_o(T)} \left( \begin{array}{c|c} \mathbf{t} & \mathbf{1} \\ T & L \end{array} \right) \left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ \mu & \nu \end{array} \middle| \begin{array}{c} \mathbf{t} \\ \tau \end{array} \right) + \sum_{\lambda'=1}^{n_o(L)} \left( \begin{array}{c|c} \mathbf{t} & \mathbf{1} \\ T & L \end{array} \right) \left( \begin{array}{c|c} \mathbf{m} & \mathbf{m} \\ \mu & \nu \end{array} \middle| \begin{array}{c} \mathbf{1} \\ \lambda' \end{array} \right) \right\}, \end{aligned} \quad (8.5)$$

too, and

- $R^{II}$  will also be used for three-center Coulomb part integrals of type

$$\begin{aligned} \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ M & T \end{array} \middle| \begin{array}{c} \mathbf{m} \\ M \end{array} \right)^{[R_{MM}^{II} R_{TL}^{II}]} &:= \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ M & T \end{array} \middle| \begin{array}{c} \mathbf{m} \\ M \end{array} \right)^{[R_{TL}^{II}]} \\ &:= \frac{1}{2} \left\{ \sum_{\tau'=1}^{n_o(T)} \left( \begin{array}{c|c} \mathbf{t} & \mathbf{1} \\ T & L \end{array} \right) \left( \begin{array}{c|c} \mathbf{m} & \mathbf{t} \\ \mu & \tau \end{array} \middle| \begin{array}{c} \mathbf{m} \\ \nu \end{array} \right) + \sum_{\lambda'=1}^{n_o(L)} \left( \begin{array}{c|c} \mathbf{t} & \mathbf{1} \\ T & L \end{array} \right) \left( \begin{array}{c|c} \mathbf{m} & \mathbf{1} \\ \mu & \lambda' \end{array} \middle| \begin{array}{c} \mathbf{m} \\ \nu \end{array} \right) \right\}. \end{aligned} \quad (8.6)$$

- Within a “Restricted and Combined NDIO” picture (NDIO.R&C)

- NDIO<sup>I</sup> will be used for three-center exchange part integrals of type

$$\begin{aligned}
\left( \begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \nu & \tau & \lambda \end{array} \right)^{[\text{NDIO}_{MM}^I \text{NDIO}_{TL}^I]} &:= \left( \begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{l} \\ M & M & T & L \\ \mu & \nu & \tau & \lambda \end{array} \right)^{[\text{NDIO}_{TL}^I]} \\
&:= \delta_{\mathbf{t}\mathbf{l}} \delta_{TL} \left( \begin{array}{cc|cc} \mathbf{m} & \mathbf{m} & \mathbf{t} & \mathbf{t} \\ M & M & T & T \\ \mu & \nu & \tau & \lambda \end{array} \right),
\end{aligned} \tag{8.7}$$

too, and

- NDIO<sup>II</sup> will also be used for three-center Coulomb part integrals of type

$$\begin{aligned}
\left( \begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{array} \right)^{[\text{NDIO}_{MM}^{II} \text{NDIO}_{TL}^{II}]} &:= \left( \begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{l} \\ M & T & M & L \\ \mu & \tau & \nu & \lambda \end{array} \right)^{[\text{NDIO}_{TL}^{II}]} \\
&:= \delta_{\mathbf{t}\mathbf{l}} \delta_{TL} \left( \begin{array}{cc|cc} \mathbf{m} & \mathbf{t} & \mathbf{m} & \mathbf{t} \\ M & T & M & T \\ \mu & \tau & \nu & \lambda \end{array} \right).
\end{aligned} \tag{8.8}$$

Although the formulation of “restricted” treatments sketched in this way turns out to be quite extensive, the application of these rules is straightforward. As in the molecular case [15], the “Restricted and Combined” use of Rüdénberg’s approximations in crystal orbital theories of Hartree-Fock type will thus be presented in a forthcoming paper [16].

Finally, it should be stressed, that such “restricted” routes of approximations do not improve the quality of all multi-index and multi-center integrals, in general [17]. Improvements, however, can be expected from the fact that conceptual shortcomings are minimized in a way, which is designed to be well-balanced in both attractive and repulsive energy contributions.

## 9. Concluding remarks

The present contribution shows that the insights of the preceding paper obtained for the molecular case can be extended to a related quantum chemical solid-state formalism.

Within a picture gained by an “Unrestricted and Combined” application (U&C), the four approximations

- of Mulliken type (M),
- of “Zero Integral Overlap” type (ZIO),
- of Rüdénberg type (R), and
- of “Neglect of Diatomic Integral Overlap” type (NDIO)

considered here are interconnected in the following way :

Rotational invariance	Globally orthogonal atomic orbital basis	Locally orthogonal atomic orbital basis
violated	ZIO.U&C	M.U&C
fulfilled	NDIO.U&C	R.U&C

All the oversimplifications tolerated in these four U&C approximating approaches can be avoided within the corresponding “Restricted and Combined” description (R&C), where all types of one- and two-index integrals (first row) or one- and two-center integrals (second row), respectively, are calculated accurately.

Rotational invariance	Globally orthogonal atomic orbital basis	Locally orthogonal atomic orbital basis
violated	ZIO.R&C	M.R&C
fulfilled	NDIO.R&C	R.R&C

Two-electron extensions of ZDO and NDDO like ZIO.U&C, NDIO.U&C, ZIO.R&C, and NDIO.R&C, as well as M.U&C and M.R&C might prove to be useful as modifications of numerous computational concepts in semi-empirical quantum chemistry. For a non-empirical orbital theory, however, only those concepts can be important, which neither assume a globally orthogonal basis set, nor violate the rotational invariance condition. Hence, for practical purposes, we are particularly interested in the R.R&C and R.U&C branches which require a computational procedure for the accurate evaluation of all or a major part of all two-center integrals, respectively.

Due to their dependence on a single geometric parameter, all types of two-center integrals can be calculated in advance for about one hundred fixed interatomic distances at the desired level of sophistication [18] and stored once and for all. A cubic spline algorithm [19] may be taken to interpolate the actual integral value from each pre-computed list. Such techniques, particularly appropriate for minimal basis sets, have been incorporated in a non-empirical crystal orbital procedure based on Rüdénberg’s ideas.

From a common point of view, these ideas offer an extension together with an interpretation of some fundamental concepts, such as the “Neglect of Differential Overlap” schemes ZDO and NDDO or the “Extended Hückel” theory. The present paper shows, that the last statement also holds for crystal orbital concepts of Hartree-Fock type.



Finally it should be stressed, that numerical problems arising from incomplete or unbalanced real-space lattice summations possibly can be overcome here, due to the common footing of all “Unrestricted & Combined” schemes on Rüdénberg’s fundamental approximations.

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As the preceding contribution, this paper is dedicated to Professor Klaus Rüdénberg, whose famous two approximations of 1951 still lead to interesting insights, not only “in Molecular Quantum Mechanics”, but also in crystal orbital theory.

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