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

Wolfhard Koch[a,b], Bastian Frey[b], Juan Francisco Sánchez Ruiz[a], and Thomas Scior[c]

[a] Universidad Nacional Autónoma de México, Facultad de Estudios Superiores Zaragoza, Av. Guelatao No. 66, Col. Ejercito de Oriente, Del. Iztapalapa, 09230 México, D.F., Mexico.
[b] Institut für Physikalische und Theoretische Chemie der Universität Tübingen, Auf der Morgenstelle 8, D-72076 Tübingen, Germany.
[c] Benemérita Universidad Autónoma de Puebla, Facultad de Ciencias Químicas y de Farmacia, 14 Sur con Av. San Claudio, Col. San Miguel, 72570 Puebla, Pue., Mexico.

Reprint requests to Dr. W. K.; Fax: +52 55 5773 6310; E-mail: koch@puma2.zaragoza.unam.mx

Z. Naturforsch. **58a,** 785 – 800 (2003); received May 24, 2003

Dedicated to Prof. Dr. Otto E. Rössler

The analysis based on Rüdenberg's well-known letter of 1951, which has been outlined for molecules in a preceding contribution, now will be transfered 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), Rüdenberg's integral approximations of Mulliken type lead to a thorough interpretation of "Extended Hückel" crystal orbital theories (EHT). Moreover, Rüdenberg'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 Rüdenberg's original recipes, will be sketched.

Key words: Unrestricted (and Restricted) Hartree-Fock Crystal Orbitals; Integral Approximations According to Mulliken and Rüdenberg; 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 the present paper is Rüdenberg's letter of 1951 [2] with its two truncated expansions (symbolized by I and II) of diatomic orbital products. In addition to Rüdenberg's proper concepts (R) in the sense commonly used, we distinguish three other kinds of Rüdenberg-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 and Nesbet [7].

Apart from any numerical application, which will be the subject of forthcoming investigations, we first of all intend to interprete the consequences of an "Unrestricted and Combined" use (U&C) of Rüdenberg'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 Rüdenberg'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 Rüdenberg-type variant of M.U&C, called R.U&C, will be proposed, which is appropriate for non-empirical computer implementations, since it

0932–0784 / 03 / 1200–0785 $ 06.00 © 2003 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

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 Rüdenberg'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 and 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 a, b, and 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 $\{\Psi_j(\boldsymbol{k},\boldsymbol{r}_i)|j = 1,\ldots,N_\mathrm{o}\}$ as linear combinations of N_o symmetry adapted Bloch sums [11] $\{\Phi'_\mu(\boldsymbol{k},\boldsymbol{r}_i)|\mu = 1,\ldots,N_\mathrm{o}\}$, constructed from N_o atomic orbitals per unit cell. Each wavevector $\boldsymbol{k} \equiv \{k^a,k^b,k^c\}$ has components that cover the following ranges defining the first Brillouin zone [11]:

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

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

$$\Psi_j^\alpha(\boldsymbol{k},\boldsymbol{r}_i) := \sum_{\mu=1}^{N_\mathrm{o}} \Phi'_\mu(\boldsymbol{k},\boldsymbol{r}_i) C'^\alpha_{\mu j}(\boldsymbol{k}),\ j = 1,\ldots,N_\mathrm{o}, \tag{2.2}$$

with

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

where we introduced the following abbreviations:

$$\sum_{\boldsymbol{m}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \equiv \sum_{m_a=N_a^-}^{N_a^+} \sum_{m_b=N_b^-}^{N_b^+} \sum_{m_c=N_c^-}^{N_c^+}, \tag{2.4}$$

$$\boldsymbol{m} \equiv \{m_a,m_b,m_c\}, \quad \boldsymbol{N}^- \equiv \{N_a^-,N_b^-,N_c^-\},\ \boldsymbol{N}^+ \equiv \{N_a^+,N_b^+,N_c^+\}, \tag{2.5}$$

and

$$\boldsymbol{R}_{\boldsymbol{m}} \equiv m_a\boldsymbol{a} + m_b\boldsymbol{b} + m_c\boldsymbol{c}. \tag{2.6}$$

The summation limits are defined as:

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

and

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

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

An equivalent second ansatz has to be made for spin β. If one should find the unrestricted α- and β-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, (2.2) and (2.3) can be rewritten as follows:

$$\Psi_j^\alpha(\boldsymbol{k},\boldsymbol{r}_i) := \sum_{M=1}^{N_\mathrm{n}} \sum_{\mu=1}^{n_\mathrm{o}(M)} \Phi'_\mu(\boldsymbol{k},\boldsymbol{r}_i-\boldsymbol{R}_M) C'^\alpha_{(M,\mu)j}(\boldsymbol{k}), \quad j=1,\ldots,N_\mathrm{o}, \tag{2.8}$$

with

$$\Phi'_\mu(\boldsymbol{k},\boldsymbol{r}_i-\boldsymbol{R}_M) = N_{abc}^{-\frac{1}{2}} \tag{2.9}$$

$$\cdot \sum_{m=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \exp + k^b m_b |\boldsymbol{b}| + k^c m_c |\boldsymbol{c}|]) \Phi_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M-\boldsymbol{R}_{\boldsymbol{m}}).$$

In contrast to the first notation of (2.2) and (2.3), the (2.8) and (2.9) explicitely specify the position vector $\boldsymbol{R}_M \equiv (x_M, y_M, z_M)$ of the M-th atom within each unit cell, to which all $n_\mathrm{o}(M)$ basis functions with index μ 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 Rüdenberg'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*

$$\int \Phi_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\Phi_\nu(\boldsymbol{r}_i-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\mathrm{d}\boldsymbol{r}_i \equiv \begin{cases} (\boldsymbol{S}_{\boldsymbol{On}})_{\mu\nu} & \text{notation 1} \\ \begin{pmatrix} \boldsymbol{O} & \boldsymbol{n} \\ M & N \\ \mu & \nu \end{pmatrix} & \text{notation 2,} \end{cases} \tag{2.10}$$

• *kinetic energy integrals*

$$\int \Phi_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\left[\Delta(\boldsymbol{r}_i)\Phi_\nu(\boldsymbol{r}_i-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\right]\mathrm{d}\boldsymbol{r}_i \equiv \begin{cases} (\boldsymbol{K}_{\boldsymbol{On}})_{\mu\nu} & \text{notation 1} \\ (\boldsymbol{K}_{\boldsymbol{On}})_{(M,\mu)(N,\nu)} & \text{notation 2,} \end{cases} \tag{2.11}$$

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

• *nuclear attraction integrals*

$$-Z_P \int \Phi_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)|\boldsymbol{r}_i-\boldsymbol{R}_P-\boldsymbol{R}_{\boldsymbol{p}}|^{-1}\Phi_\nu(\boldsymbol{r}_i-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\mathrm{d}\boldsymbol{r}_i \equiv \begin{cases} (\boldsymbol{V}_{\boldsymbol{On}})_{\mu\nu}[_{\boldsymbol{p}}P] & \text{notation 1} \\ \begin{pmatrix} \boldsymbol{O} & & \boldsymbol{n} \\ & \boldsymbol{P} & \\ M & P & N \\ \mu & & \nu \end{pmatrix} & \text{notation 2,} \end{cases} \tag{2.12}$$

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

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

$$\int\int \Phi_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\Phi_\nu(\boldsymbol{r}_i-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})|\boldsymbol{r}_i-\boldsymbol{r}_j|^{-1} \cdot \Phi_\tau(\boldsymbol{r}_j-\boldsymbol{R}_T-\boldsymbol{R}_{\boldsymbol{t}})\Phi_\lambda(\boldsymbol{r}_j-\boldsymbol{R}_L-\boldsymbol{R}_{\boldsymbol{l}})\mathrm{d}\boldsymbol{r}_i\mathrm{d}\boldsymbol{r}_j \equiv \begin{cases} \left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{n} & \boldsymbol{t} & \boldsymbol{l} \\ \mu & \nu & \tau & \lambda \end{array}\right) & \text{notation 1,} \\ \left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{n} & \boldsymbol{t} & \boldsymbol{l} \\ M & N & T & L \\ \mu & \nu & \tau & \lambda \end{array}\right) & \text{notation 2.} \end{cases} \tag{2.13}$$

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 $\boldsymbol{C}'^\alpha(\boldsymbol{k})$ of (2.2) or (2.8) with the property $\boldsymbol{C}'^{\alpha\dagger}(\boldsymbol{k})\boldsymbol{S}'^\alpha(\boldsymbol{k})\boldsymbol{C}'^\alpha(\boldsymbol{k}) = \boldsymbol{1}$ are determined by solving the $\boldsymbol{k}$-dependent Pople-Nesbet equations. Their α-spin part reads as follows:

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

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

$$\boldsymbol{E}^\alpha(\boldsymbol{k}) = \begin{pmatrix} E_1^\alpha(\boldsymbol{k}) & 0 & \ldots & 0 \\ 0 & E_2^\alpha(\boldsymbol{k}) & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \ldots & E_{N_\mathrm{o}}^\alpha(\boldsymbol{k}) \end{pmatrix}. \tag{2.15}$$

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

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

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

$$\boldsymbol{\Omega}^\alpha(\boldsymbol{k}) = \begin{pmatrix} \Omega_1^\alpha(\boldsymbol{k}) & 0 & \dots & 0 \\ 0 & \Omega_2^\alpha(\boldsymbol{k}) & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \Omega_{N_\mathrm{o}}^\alpha(\boldsymbol{k}) \end{pmatrix}, \tag{2.17}$$

with

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

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

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

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

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

Symmetry properties like $(\boldsymbol{S}_{\boldsymbol{O-n}})_{\mu\nu} = (\boldsymbol{S}_{\boldsymbol{On}})_{\nu\mu}$ and $(\boldsymbol{F}_{\boldsymbol{O-n}}^\alpha)_{\mu\nu} = (\boldsymbol{F}_{\boldsymbol{On}}^\alpha)_{\nu\mu}$ can be utilized to accelerate real-space lattice summations from a computational point of view. The summation limits in (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 α-spin real-space Fock-matrix representation of (2.20). Using the first notation we can write:

$$\begin{aligned}(\boldsymbol{F}_{\boldsymbol{On}}^\alpha)_{\mu\nu} = (\boldsymbol{K}_{\boldsymbol{On}})_{\mu\nu} &+ \underbrace{\sum_{\boldsymbol{p}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{P=1}^{N_\mathrm{n}} (\boldsymbol{V}_{\boldsymbol{On}})_{\mu\nu}[\boldsymbol{p}P]}_{\stackrel{\mathrm{def}}{=}(\boldsymbol{F}_{\boldsymbol{On}}^A)_{\mu\nu}} \\ &+ \underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{\tau,\lambda=1}^{N_\mathrm{o}} (\boldsymbol{P}_{\boldsymbol{tl}}^\oplus)_{\tau\lambda}\left(\begin{matrix}\boldsymbol{O} & \boldsymbol{n} \\ \mu & \nu\end{matrix}\middle|\begin{matrix}\boldsymbol{t} & \boldsymbol{l} \\ \tau & \lambda\end{matrix}\right)}_{\stackrel{\mathrm{def}}{=}(\boldsymbol{F}_{\boldsymbol{On}}^C)_{\mu\nu}} \\ &- \underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{\tau,\lambda=1}^{N_\mathrm{o}} (\boldsymbol{P}_{\boldsymbol{tl}}^\alpha)_{\tau\lambda}\left(\begin{matrix}\boldsymbol{O} & \boldsymbol{t} \\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{n} & \boldsymbol{l} \\ \nu & \lambda\end{matrix}\right)}_{\stackrel{\mathrm{def}}{=}(\boldsymbol{F}_{\boldsymbol{On}}^{\alpha E})_{\mu\nu}} \\ &\begin{cases} \boldsymbol{n} = \boldsymbol{N}^-,\dots,\boldsymbol{N}^+, \\ \mu,\nu = 1,\dots,N_\mathrm{o}. \end{cases}\end{aligned} \tag{2.21}$$

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 $\boldsymbol{P}_{\boldsymbol{tl}}^\alpha$ is available from the corresponding complex reciprocal-space $\boldsymbol{P}'^\alpha(\boldsymbol{k})$ matrices by means of $\boldsymbol{k}$-space integrations over the Brillouin-zone ranges defined in (2.1):

$$(\boldsymbol{P}_{\boldsymbol{tl}}^\alpha)_{\tau\lambda} := \frac{V_\mathrm{d}}{(2\pi)^\mathrm{d}}\int\int\int \exp\Big\{i\Big[k^a(t_a-l_a)|\boldsymbol{a}| + k^b(t_b-l_b)|\boldsymbol{b}| + k^c(t_c-l_c)|\boldsymbol{c}|\Big]\Big\}P_{\tau\lambda}'^\alpha(\boldsymbol{k})\mathrm{d}k^a\mathrm{d}k^b\mathrm{d}k^c. \tag{2.22}$$

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

$$\boldsymbol{P}_{\boldsymbol{tl}}^\oplus = \boldsymbol{P}_{\boldsymbol{tl}}^\alpha + \boldsymbol{P}_{\boldsymbol{tl}}^\beta, \quad \boldsymbol{t},\boldsymbol{l} = \boldsymbol{N}^-,\dots,\boldsymbol{N}^+. \tag{2.23}$$

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

2.3. Real-space Fock-matrix Representations Using Notation 2

Choosing the more specific second notation, (2.21) and (2.22) read:

$$(\boldsymbol{F}^{\alpha}_{\boldsymbol{On}})_{(M,\mu)(N,\nu)} = (\boldsymbol{K}_{\boldsymbol{On}})_{(M,\mu)(N,\nu)} + \underbrace{\sum_{\boldsymbol{P}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{P=1}^{N_\mathrm{n}} \begin{pmatrix} \boldsymbol{O} & \boldsymbol{p} & \boldsymbol{n} \\ M & P & N \\ \mu & & \nu \end{pmatrix}}_{\stackrel{\mathrm{def}}{=}(\boldsymbol{F}^{\mathrm{A}}_{\boldsymbol{On}})_{(M,\mu)(N,\nu)}} + \underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{T,L=1}^{N_\mathrm{n}}\sum_{\tau=1}^{n_\mathrm{o}(T)}\sum_{\lambda=1}^{n_\mathrm{o}(L)} (\boldsymbol{P}^{\oplus}_{\boldsymbol{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{ccc|cc} \boldsymbol{O} & \boldsymbol{n} & & \boldsymbol{t} & \boldsymbol{l} \\ M & N & & T & L \\ \mu & \nu & & \tau & \lambda \end{array}\right)}_{\stackrel{\mathrm{def}}{=}(\boldsymbol{F}^{\mathrm{C}}_{\boldsymbol{On}})_{(M,\mu)(N,\nu)}}$$

$$- \underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{T,L=1}^{N_\mathrm{n}}\sum_{\tau=1}^{n_\mathrm{o}(T)}\sum_{\lambda=1}^{n_\mathrm{o}(L)} (\boldsymbol{P}^{\alpha}_{\boldsymbol{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{ccc|cc} \boldsymbol{O} & \boldsymbol{t} & & \boldsymbol{n} & \boldsymbol{l} \\ M & T & & N & L \\ \mu & \tau & & \nu & \lambda \end{array}\right)}_{\stackrel{\mathrm{def}}{=}(\boldsymbol{F}^{\alpha\mathrm{E}}_{\boldsymbol{On}})_{(M,\mu)(N,\nu)}}, \tag{2.24}$$

$\boldsymbol{n} = -\boldsymbol{N},\ldots,+\boldsymbol{N};\ M,N = 1,\ldots,N_\mathrm{n};\ \mu = 1,\ldots,n_\mathrm{o}(M);\ \nu = 1,\ldots,n_\mathrm{o}(N),$

and

$$(\boldsymbol{P}^{\alpha}_{\boldsymbol{tl}})_{(T,\tau)(L,\lambda)} :=$$

$$\frac{V_\mathrm{d}}{(2\pi)^\mathrm{d}} \int\int\int \exp\left\{ i\left[k^a(t_a - l_a)|\boldsymbol{a}| + k^b(t_b - l_b)|\boldsymbol{b}| + k^c(t_c - l_c)|\boldsymbol{c}|\right]\right\} P'^{\alpha}_{(T,\tau)(L,\lambda)}(\boldsymbol{k})\mathrm{d}k^a\mathrm{d}k^b\mathrm{d}k^c. \tag{2.25}$$

2.4. Reciprocal-space Integrations

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

$$(\boldsymbol{P}^{\alpha}_{\boldsymbol{tl}})_{\tau\lambda} := (N^{abc})^{-1} \sum_{u=N^a_-}^{N^a_+}\sum_{v=N^b_-}^{N^b_+}\sum_{w=N^c_-}^{N^c_+} W_{uvw}\Re\left\{\exp\left\{ i\left[k^a_u(t_a - l_a)|\boldsymbol{a}| + k^b_v(t_b - l_b)|\boldsymbol{b}| + k^c_w(t_c - l_c)|\boldsymbol{c}|\right]\right\} P'^{\alpha}_{\tau\lambda}(\boldsymbol{k}_{uvw})\right\}, \tag{2.26}$$

where

$$\begin{aligned} &W_{uvw} := 1 \quad \text{for all} \quad u = N^a_-,\ldots,N^a_+; \\ &v = N^b_-,\ldots,N^b_+; w = N^c_-,\ldots,N^c_+. \end{aligned} \tag{2.27}$$

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

Furthermore, as recommended in [12], we consider the $N^{abc} \equiv N^aN^bN^c$ discrete wavevectors

$$\begin{aligned} \{\boldsymbol{k}_{uvw} \equiv \{k^a_u, k^b_v, k^c_w\} | u = N^a_-,\ldots,N^a_+; \\ v = N^b_-,\ldots,N^b_+; w = N^c_-,\ldots,N^c_+\} \end{aligned} \tag{2.28}$$

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

$$N^a_- := \begin{cases} -(N^a - 2)/2, & \text{if } N^a \text{ even}, \\ -(N^a - 1)/2, & \text{if } N^a \text{ odd}, \end{cases}$$

and

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

The equidistant set of wavenumber components is now selected according to

$$k^a_u := \frac{2\pi}{|\boldsymbol{a}|} \cdot \frac{u}{N^a}, \text{ with } u := N^a_-,\ldots,N^a_+. \tag{2.30}$$

Equivalent definitions hold for the crystallographic $\boldsymbol{b}$ and $\boldsymbol{c}$ 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 (2.26) run over the full Brillouin-zone ranges, all reciprocal-space $\boldsymbol{k}_{uvw}$ 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

$$\boldsymbol{P}'^{\alpha}(\boldsymbol{k}) = \boldsymbol{P}'^{\alpha *}(-\boldsymbol{k}) \tag{2.31}$$

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 $k_{+N^c/2}^c = +\pi/|\boldsymbol{c}|$ have to be counted twice in this case:

$$(\boldsymbol{P}_{\boldsymbol{tl}}^{\alpha})_{\tau\lambda} := (N^{abc})^{-1} \sum_{u=N_-^a}^{N_+^a} \sum_{v=N_-^b}^{N_+^b} \sum_{w=0}^{N_+^c} W_{uvw}$$
$$\cdot \Big\{ \cos\big[k_u^a(t_a - l_a)|\boldsymbol{a}| + k_v^b(t_b - l_b)|\boldsymbol{b}| + k_w^c(t_c - l_c)|\boldsymbol{c}|\big] \Re\big\{P_{\tau\lambda}'^{\alpha}(\boldsymbol{k}_{uvw})\big\} - \sin\big[k_u^a(t_a - l_a)|\boldsymbol{a}| + k_v^b(t_b - l_b)|\boldsymbol{b}| + k_w^c(t_c - l_c)|\boldsymbol{c}|\big] \Im\big\{P_{\tau\lambda}'^{\alpha}(\boldsymbol{k}_{uvw})\big\}\Big\}, \quad (2.32)$$

with

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

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

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

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

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

and

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

such techniques may considerably reduce the preselected number of wavevectors for which the generalized eigenvalue problem of (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 $(\boldsymbol{F}_{\boldsymbol{On}}^{\mathrm{A}})_{\mu\nu}$, $(\boldsymbol{F}_{\boldsymbol{On}}^{\mathrm{C}})_{\mu\nu}$, and $(\boldsymbol{F}_{\boldsymbol{On}}^{\alpha\mathrm{E}})_{\mu\nu}$ of (2.21) be reduced to their subsequent form

$$(\boldsymbol{F}_{\boldsymbol{On}}^{\mathrm{A}})_{\mu\nu} := \frac{(\boldsymbol{S}_{\boldsymbol{On}})_{\mu\nu}}{2}\big\{(\boldsymbol{F}_{\boldsymbol{OO}}^{\mathrm{A}})_{\mu\mu} + \underbrace{(\boldsymbol{F}_{\boldsymbol{nn}}^{\mathrm{A}})_{\nu\nu}}_{=(\boldsymbol{F}_{\boldsymbol{OO}}^{\mathrm{A}})_{\nu\nu}}\big\}, \quad (3.1)$$

$$(\boldsymbol{F}_{\boldsymbol{On}}^{\mathrm{C}})_{\mu\nu} := \frac{(\boldsymbol{S}_{\boldsymbol{On}})_{\mu\nu}}{2}\big\{(\boldsymbol{F}_{\boldsymbol{OO}}^{\mathrm{C}})_{\mu\mu} + \underbrace{(\boldsymbol{F}_{\boldsymbol{nn}}^{\mathrm{C}})_{\nu\nu}}_{=(\boldsymbol{F}_{\boldsymbol{OO}}^{C})_{\nu\nu}}\big\}, \quad (3.2)$$

$$(\boldsymbol{F}_{\boldsymbol{On}}^{\alpha\mathrm{E}})_{\mu\nu} := \frac{(\boldsymbol{S}_{\boldsymbol{On}})_{\mu\nu}}{2}\big\{(\boldsymbol{F}_{\boldsymbol{OO}}^{\alpha\mathrm{E}})_{\mu\mu} + \underbrace{(\boldsymbol{F}_{nn}^{\alpha E})_{\nu\nu}}_{=(\boldsymbol{F}_{\boldsymbol{OO}}^{\alpha\mathrm{E}})_{\nu\nu}}\big\}, \quad (3.3)$$

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

$$\big\{\Phi_\mu(\boldsymbol{r}_i)\Phi_\nu(\boldsymbol{r}_i - \boldsymbol{R}_{\boldsymbol{n}})\big\}^{[\mathrm{M}_{\mu\nu}^{\mathrm{I}}]} := \quad (3.4)$$
$$\frac{(\boldsymbol{S}_{\boldsymbol{On}})_{\mu\nu}}{2}\big\{\Phi_\mu(\boldsymbol{r}_i)\Phi_\mu(\boldsymbol{r}_i) + \Phi_\nu(\boldsymbol{r}_i - \boldsymbol{R}_{\boldsymbol{n}})\Phi_\nu(\boldsymbol{r}_i - \boldsymbol{R}_{\boldsymbol{n}})\big\}$$

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

$$(\boldsymbol{F}_{\boldsymbol{On}}^{\mathrm{A}})_{\mu\nu}^{[\mathrm{M}^{\mathrm{I}}]} := \frac{(\boldsymbol{S}_{\boldsymbol{On}})_{\mu\nu}}{2}\Bigg\{\underbrace{\sum_{\boldsymbol{p}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{P=1}^{N_{\mathrm{n}}}(\boldsymbol{V}_{\boldsymbol{OO}})_{\mu\mu}[\boldsymbol{p}P]}_{=(\boldsymbol{F}_{\boldsymbol{OO}}^{\mathrm{A}})_{\mu\mu}} + \underbrace{\sum_{\boldsymbol{p}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{P=1}^{N_{\mathrm{n}}}(\boldsymbol{V}_{\boldsymbol{nn}})_{\nu\nu}[\boldsymbol{p}P]}_{=(\boldsymbol{F}_{\boldsymbol{OO}}^{\mathrm{A}})_{\nu\nu}}\Bigg\} \quad (3.5)$$

and

$$(\boldsymbol{F}_{\boldsymbol{On}}^{\mathrm{C}})_{\mu\nu}^{[\mathrm{M}^{\mathrm{I}}\mathrm{M}^{\mathrm{I}}]} := \frac{(\boldsymbol{S}_{\boldsymbol{On}})_{\mu\nu}}{2}\Bigg\{\underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{\tau,\lambda=1}^{N_{\mathrm{o}}}(\boldsymbol{P}_{\boldsymbol{tl}}^{\oplus})_{\tau\lambda}\left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{l} \\ \mu & \mu & \tau & \lambda \end{array}\right)^{[\mathrm{M}_{\tau\lambda}^{\mathrm{I}}]}}_{=(\boldsymbol{F}_{\boldsymbol{OO}}^{\mathrm{C}})_{\mu\mu}^{[\mathrm{M}^{\mathrm{I}}]}} + \underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{\tau,\lambda=1}^{N_{\mathrm{o}}}(\boldsymbol{P}_{\boldsymbol{tl}}^{\oplus})_{\tau\lambda}\left(\begin{array}{c|cc} \boldsymbol{n} & \boldsymbol{t} & \boldsymbol{l} \\ \nu & \tau & \lambda \end{array}\right)^{[\mathrm{M}^{\mathrm{I}\tau\lambda}]}}_{=(\boldsymbol{F}_{\boldsymbol{OO}}^{\mathrm{C}})_{\nu\nu}^{[\mathrm{M}^{\mathrm{I}}]}}\Bigg\}. \quad (3.6)$$

The attribute "unrestricted" indicates here that Mulliken's simple recipe is applied to (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 [1], Mulliken's approximation of (3.4) can be regarded as the diagonal term of a Rüdenberg-type expansion [2] of a diatomic one-electron density:

$$\left\{\Phi_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\Phi_\nu(\boldsymbol{r}_i-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\right\}^{[\mathrm{R}^{\mathrm{I}}_{MN}]} := \frac{1}{2}\left\{\sum_{\mu'=1}^{n_{\mathrm{o}}(M)}\begin{pmatrix}\boldsymbol{O} & \boldsymbol{n}\\ M & N\\ \mu' & \nu\end{pmatrix}\Phi_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\Phi_{\mu'}(\boldsymbol{r}_i-\boldsymbol{R}_M)\right. \tag{3.7}$$
$$\left.+\sum_{\nu'=1}^{n_{\mathrm{o}}(N)}\begin{pmatrix}\boldsymbol{O} & \boldsymbol{n}\\ M & N\\ \mu & \nu'\end{pmatrix}\Phi_\nu(\boldsymbol{r}_i-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\Phi_{\nu'}(\boldsymbol{r}_i-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\right\}.$$

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

$$\left\{\Phi_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\Phi_\nu(\boldsymbol{r}_j-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\right\}^{[\mathrm{R}^{\mathrm{II}}_{MN}]} := \frac{1}{2}\left\{\sum_{\mu'=1}^{n_{\mathrm{o}}(M)}\begin{pmatrix}\boldsymbol{O} & \boldsymbol{n}\\ M & N\\ \mu' & \nu\end{pmatrix}\Phi_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\Phi_{\mu'}(\boldsymbol{r}_j-\boldsymbol{R}_M)\right.$$
$$\left.+\sum_{\nu'=1}^{n_{\mathrm{o}}(N)}\begin{pmatrix}\boldsymbol{O} & \boldsymbol{n}\\ M & N\\ \mu & \nu'\end{pmatrix}\Phi_\nu(\boldsymbol{r}_i-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\Phi_{\nu'}(\boldsymbol{r}_j-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\right\}. \tag{3.8}$$

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

$$\left\{\Phi_\mu(\boldsymbol{r}_i)\Phi_\nu(\boldsymbol{r}_j-\boldsymbol{R}_{\boldsymbol{n}})\right\}^{[\mathrm{M}^{\mathrm{II}}_{\mu\nu}]} := \frac{(\boldsymbol{S}_{\boldsymbol{O}\boldsymbol{n}})_{\mu\nu}}{2}\left\{\Phi_\mu(\boldsymbol{r}_i)\Phi_\mu(\boldsymbol{r}_j)+\Phi_\nu(\boldsymbol{r}_i-\boldsymbol{R}_{\boldsymbol{n}})\Phi_\nu(\boldsymbol{r}_j-\boldsymbol{R}_{\boldsymbol{n}})\right\}. \tag{3.9}$$

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

$$(\boldsymbol{F}^{\alpha\mathrm{E}}_{\boldsymbol{O}\boldsymbol{n}})^{[\mathrm{M}^{\mathrm{II}}\mathrm{M}^{\mathrm{II}}]}_{\mu\nu} := \frac{(\boldsymbol{S}_{\boldsymbol{O}\boldsymbol{n}})_{\mu\nu}}{2}\left\{\underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{n}^-}^{\boldsymbol{N}^+}\sum_{\tau,\lambda=1}^{N_{\mathrm{o}}}(\boldsymbol{P}^{\alpha}_{\boldsymbol{t}\boldsymbol{l}})_{\tau\lambda}\left(\begin{matrix}\boldsymbol{O} & \boldsymbol{t}\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{O} & \boldsymbol{l}\\ \mu & \lambda\end{matrix}\right)^{[\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]}}_{=(\boldsymbol{F}^{\alpha\mathrm{E}}_{\boldsymbol{O}\boldsymbol{O}})^{[\mathrm{M}^{\mathrm{II}}]}_{\mu\mu}}+\underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{n}^-}^{\boldsymbol{N}^+}\sum_{\tau,\lambda=1}^{N_{\mathrm{o}}}(\boldsymbol{P}^{\alpha}_{\boldsymbol{t}\boldsymbol{l}})_{\tau\lambda}\left(\begin{matrix}\boldsymbol{n} & \boldsymbol{t}\\ \nu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{n} & \boldsymbol{l}\\ \nu & \lambda\end{matrix}\right)^{[\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]}}_{=(\boldsymbol{F}^{\alpha\mathrm{E}}_{\boldsymbol{O}\boldsymbol{O}})^{[\mathrm{M}^{\mathrm{II}}]}_{\nu\nu}}\right\}. \tag{3.10}$$

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 Rüdenberg approximations of Mulliken type:

$$(\boldsymbol{F}^{\alpha}_{\boldsymbol{O}\boldsymbol{n}})^{[\mathrm{M.U\&C}]}_{\mu\nu} := (\boldsymbol{K}_{\boldsymbol{O}\boldsymbol{n}})_{\mu\nu}+(\boldsymbol{F}^{\mathrm{A}}_{\boldsymbol{O}\boldsymbol{n}})^{[\mathrm{M}^{\mathrm{I}}]}_{\mu\nu}+(\boldsymbol{F}^{\mathrm{C}}_{\boldsymbol{O}\boldsymbol{n}})^{[\mathrm{M}^{\mathrm{I}}\mathrm{M}^{\mathrm{I}}]}_{\mu\nu}-(\boldsymbol{F}^{\alpha\mathrm{E}}_{\boldsymbol{O}\boldsymbol{n}})^{[\mathrm{M}^{\mathrm{II}}\mathrm{M}^{\mathrm{II}}]}_{\mu\nu} \tag{3.11}$$
$$:= (\boldsymbol{K}_{\boldsymbol{O}\boldsymbol{n}})_{\mu\nu}+\frac{(\boldsymbol{S}_{\boldsymbol{O}\boldsymbol{n}})_{\mu\nu}}{2}\left\{(\boldsymbol{F}^{\mathrm{A}}_{\boldsymbol{O}\boldsymbol{O}})_{\mu\mu}+(\boldsymbol{F}^{\mathrm{C}}_{\boldsymbol{O}\boldsymbol{O}})^{[\mathrm{M}^{\mathrm{I}}]}_{\mu\mu}-(\boldsymbol{F}^{\alpha\mathrm{E}}_{\boldsymbol{O}\boldsymbol{O}})^{[\mathrm{M}^{\mathrm{II}}]}_{\mu\mu}+(\boldsymbol{F}^{\mathrm{A}}_{\boldsymbol{O}\boldsymbol{O}})_{\nu\nu}+(\boldsymbol{F}^{\mathrm{C}}_{\boldsymbol{O}\boldsymbol{O}})^{[\mathrm{M}^{\mathrm{I}}]}_{\nu\nu}-(\boldsymbol{F}^{\alpha\mathrm{E}}_{\boldsymbol{O}\boldsymbol{O}})^{[\mathrm{M}^{\mathrm{II}}]}_{\nu\nu}\right\}.$$

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

$$(\boldsymbol{F}^{\mathrm{C}}_{\boldsymbol{O}\boldsymbol{O}})^{[\mathrm{M}^{\mathrm{I}}]}_{\mu\mu} := \frac{1}{2}\left\{\sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{\tau=1}^{N_{\mathrm{o}}}\left(\begin{matrix}\boldsymbol{O} & \boldsymbol{O}\\ \mu & \mu\end{matrix}\middle|\begin{matrix}\boldsymbol{t} & \boldsymbol{t}\\ \tau & \tau\end{matrix}\right)\sum_{\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{\lambda=1}^{N_{\mathrm{o}}}(\boldsymbol{P}^{\oplus}_{\boldsymbol{t}\boldsymbol{l}})_{\tau\lambda}(\boldsymbol{S}_{\boldsymbol{t}\boldsymbol{l}})_{\tau\lambda}+\sum_{\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{\lambda=1}^{N_{\mathrm{o}}}\left(\begin{matrix}\boldsymbol{O} & \boldsymbol{O}\\ \mu & \mu\end{matrix}\middle|\begin{matrix}\boldsymbol{l} & \boldsymbol{l}\\ \lambda & \lambda\end{matrix}\right)\sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{\tau=1}^{N_{\mathrm{o}}}(\boldsymbol{P}^{\oplus}_{\boldsymbol{t}\boldsymbol{l}})_{\tau\lambda}(\boldsymbol{S}_{\boldsymbol{t}\boldsymbol{l}})_{\tau\lambda}\right\}$$
$$=\sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{\tau=1}^{N_{\mathrm{o}}}\left(\begin{matrix}\boldsymbol{O} & \boldsymbol{O}\\ \mu & \mu\end{matrix}\middle|\begin{matrix}\boldsymbol{t} & \boldsymbol{t}\\ \tau & \tau\end{matrix}\right)((\boldsymbol{P}^{\oplus}\boldsymbol{S})_{\boldsymbol{t}\boldsymbol{t}})_{\tau\tau}=\sum_{\tau=1}^{N_{\mathrm{o}}}((\boldsymbol{P}^{\oplus}\boldsymbol{S})_{\boldsymbol{O}\boldsymbol{O}})_{\tau\tau}\sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\left(\begin{matrix}\boldsymbol{O} & \boldsymbol{O}\\ \mu & \mu\end{matrix}\middle|\begin{matrix}\boldsymbol{t} & \boldsymbol{t}\\ \tau & \tau\end{matrix}\right), \tag{3.12}$$

and

$$(\boldsymbol{F}^{\alpha\mathrm{E}}_{\boldsymbol{OO}})^{[\mathrm{M^{II}}]}_{\mu\mu} := \frac{1}{2}\left\{ \sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{\tau=1}^{N_\mathrm{o}} \left(\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{t} \\ \mu & \tau \end{smallmatrix}\middle|\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{t} \\ \mu & \tau \end{smallmatrix}\right) \sum_{\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{\lambda=1}^{N_\mathrm{o}} (\boldsymbol{P}^{\alpha}_{\boldsymbol{tl}})_{\tau\lambda} (\boldsymbol{S}_{\boldsymbol{tl}})_{\tau\lambda} + \sum_{\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{\lambda=1}^{N_\mathrm{o}} \left(\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{l} \\ \mu & \lambda \end{smallmatrix}\middle|\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{l} \\ \mu & \lambda \end{smallmatrix}\right) \sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{\tau=1}^{N_\mathrm{o}} (\boldsymbol{P}^{\alpha}_{\boldsymbol{tl}})_{\tau\lambda} (\boldsymbol{S}_{\boldsymbol{tl}})_{\tau\lambda} \right\}$$

$$= \sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{\tau=1}^{N_\mathrm{o}} \left(\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{t} \\ \mu & \tau \end{smallmatrix}\middle|\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{t} \\ \mu & \tau \end{smallmatrix}\right) ((\boldsymbol{P}^{\alpha}\boldsymbol{S})_{\boldsymbol{tt}})_{\tau\tau} = \sum_{\tau=1}^{N_\mathrm{o}} ((\boldsymbol{P}^{\alpha}\boldsymbol{S})_{\boldsymbol{OO}})_{\tau\tau} \sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \left(\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{t} \\ \mu & \tau \end{smallmatrix}\middle|\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{t} \\ \mu & \tau \end{smallmatrix}\right). \tag{3.13}$$

• 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 (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]:

$$\begin{aligned} &\left\{\Phi_\mu(\boldsymbol{r}_i)\Phi_\nu(\boldsymbol{r}_i-\boldsymbol{R}_{\boldsymbol{n}})\right\}^{[\mathrm{ZIO}^{\mathrm{I}}_{\mu\nu}]} \\ &\quad := \left\{\Phi_\mu(\boldsymbol{r}_i)\Phi_\nu(\boldsymbol{r}_i-\boldsymbol{R}_{\boldsymbol{n}})\right\}^{[\mathrm{ZDO}_{\mu\nu}]} \\ &\quad := \delta_{\boldsymbol{On}}\delta_{\mu\nu}\Phi_\mu(\boldsymbol{r}_i)\Phi_\mu(\boldsymbol{r}_i), \end{aligned} \tag{4.1}$$

where $\delta_{\boldsymbol{On}} \equiv \delta_{0n_a}\delta_{0n_b}\delta_{0n_c}$. Following Rüdenberg's two-electron route of approximation the two-electron analog of (4.1) then reads

$$\left\{\Phi_\mu(\boldsymbol{r}_i)\Phi_\nu(\boldsymbol{r}_j-\boldsymbol{R}_{\boldsymbol{n}})\right\}^{[\mathrm{ZIO}^{\mathrm{II}}_{\mu\nu}]} := \delta_{\boldsymbol{On}}\delta_{\mu\nu}\Phi_\mu(\boldsymbol{r}_i)\Phi_\mu(\boldsymbol{r}_j). \tag{4.2}$$

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:

$$\begin{aligned} (\boldsymbol{F}^{\alpha}_{\boldsymbol{On}})^{[\mathrm{ZIO.U\&C}]}_{\mu\nu} &:= (\boldsymbol{K}_{\boldsymbol{On}})_{\mu\nu} + \delta_{\boldsymbol{On}}\delta_{\mu\nu} \\ &\quad + \delta_{\boldsymbol{On}}\delta_{\mu\nu}\left\{(\boldsymbol{F}^{A}_{\boldsymbol{OO}})_{\mu\mu} + (\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{ZIO}^{\mathrm{I}}]}_{\mu\mu} - (\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{ZIO}^{\mathrm{II}}]}_{\mu\mu}\right\}, \end{aligned} \tag{4.3}$$

with

$$(\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{ZIO}^{\mathrm{I}}]}_{\mu\mu} := \sum_{\tau=1}^{N_\mathrm{o}} (\boldsymbol{P}^{\oplus}_{\boldsymbol{OO}})_{\tau\tau} \sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \left(\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{O} \\ \mu & \mu \end{smallmatrix}\middle|\begin{smallmatrix} \boldsymbol{t} & \boldsymbol{t} \\ \tau & \tau \end{smallmatrix}\right), \tag{4.4}$$

and

$$(\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{ZIO}^{\mathrm{II}}]}_{\mu\mu} := \sum_{\tau=1}^{N_\mathrm{o}} (\boldsymbol{P}^{\alpha}_{\boldsymbol{OO}})_{\tau\tau} \sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \left(\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{t} \\ \mu & \tau \end{smallmatrix}\middle|\begin{smallmatrix} \boldsymbol{O} & \boldsymbol{t} \\ \mu & \tau \end{smallmatrix}\right). \tag{4.5}$$

• The ZIO.U&C scheme introduced in this way is completely compatible with Rüdenberg's approximations of Mulliken type, together with the additional assumption $(\mathbf{S}_{\boldsymbol{On}})_{\mu\nu} := \delta_{\boldsymbol{On}}\delta_{\mu\nu}$.

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 Rüdenberg" 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.

Rüdenberg's more elaborate expansions of (3.7) and (3.8), on the other hand, as well as the "Neglect of Diatomic Differential Overlap" concept (NDDO) of Pople, Santry and 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 (3.11) we now write

$$(\boldsymbol{F}^{\alpha}_{\boldsymbol{On}})^{[\mathrm{R.U\&C}]}_{(M,\mu)(N,\nu)} := (\boldsymbol{K}_{\boldsymbol{On}})_{(M,\mu)(N,\nu)} + (\boldsymbol{F}^{A}_{\boldsymbol{On}})^{[\mathrm{R^I}]}_{(M,\mu)(N,\nu)} + (\boldsymbol{F}^{C}_{\boldsymbol{On}})^{[\mathrm{R^I R^I}]}_{(M,\mu)(N,\nu)} - (\boldsymbol{F}^{\alpha E}_{\boldsymbol{On}})^{[\mathrm{R^{II} R^{II}}]}_{(M,\mu)(N,\nu)}. \tag{5.1}$$

In the "Unrestricted and Combined Rüdenberg" 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 (3.7), we get for the attractive part of the Fock matrix defined in (5.1):

$$(\boldsymbol{F}^{A}_{\boldsymbol{On}})^{[\mathrm{R^I}]}_{(M,\mu)(N,\nu)} := \frac{1}{2}\left\{ \sum_{\mu'=1}^{n_\mathrm{o}(M)} \begin{pmatrix} \boldsymbol{O} & \boldsymbol{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \underbrace{\sum_{\boldsymbol{p}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{P=1}^{N_\mathrm{n}} \begin{pmatrix} \boldsymbol{O} & & \boldsymbol{O} \\ & \boldsymbol{p} & \\ M & P & M \\ \mu & & \mu' \end{pmatrix}}_{=(\boldsymbol{F}^{A}_{\boldsymbol{OO}})_{(M,\mu)(M,\mu')}} + \sum_{\nu'=1}^{n_\mathrm{o}(N)} \begin{pmatrix} \boldsymbol{O} & \boldsymbol{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \underbrace{\sum_{\boldsymbol{p}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{P=1}^{N_\mathrm{n}} \begin{pmatrix} \boldsymbol{n} & & \boldsymbol{n} \\ & \boldsymbol{p} & \\ N & P & N \\ \nu' & & \nu \end{pmatrix}}_{=(\boldsymbol{F}^{A}_{\boldsymbol{OO}})_{(N,\nu')(N,\nu)}} \right\}. \tag{5.2}$$

Along the same lines, an application of (3.7) to the Coulomb part of (5.1) yields:

$$\begin{aligned} (\boldsymbol{F}^{C}_{\boldsymbol{On}})^{[\mathrm{R^I R^I}]}_{(M,\mu)(N,\nu)} := \frac{1}{2}\Bigg\{ & \sum_{\mu'=1}^{n_\mathrm{o}(M)} \begin{pmatrix} \boldsymbol{O} & \boldsymbol{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{T,L=1}^{N_\mathrm{n}} \sum_{\tau=1}^{n_\mathrm{o}(T)} \sum_{\lambda=1}^{n_\mathrm{o}(L)} (\boldsymbol{P}^{\oplus}_{\boldsymbol{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{l} \\ M & M & T & L \\ \mu & \mu' & \tau & \lambda \end{array}\right)^{[\mathrm{R^I}_{TL}]}}_{=(\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{R^I}]}_{(M,\mu)(M,\mu')}} \\ & + \sum_{\nu'=1}^{n_\mathrm{o}(N)} \begin{pmatrix} \boldsymbol{O} & \boldsymbol{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{T,L=1}^{N_\mathrm{n}} \sum_{\tau=1}^{n_\mathrm{o}(T)} \sum_{\lambda=1}^{n_\mathrm{o}(L)} (\boldsymbol{P}^{\oplus}_{\boldsymbol{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc} \boldsymbol{n} & \boldsymbol{n} & \boldsymbol{t} & \boldsymbol{l} \\ N & N & T & L \\ \nu' & \nu & \tau & \lambda \end{array}\right)^{[\mathrm{R^I}_{TL}]}}_{=(\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{R^I}]}_{(N,\nu')(N,\nu)}} \Bigg\}. \end{aligned} \tag{5.3}$$

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

$$\begin{aligned} (\boldsymbol{F}^{\alpha E}_{\boldsymbol{On}})^{[\mathrm{R^{II} R^{II}}]}_{(M,\mu)(N,\nu)} := \frac{1}{2}\Bigg\{ & \sum_{\mu'=1}^{n_\mathrm{o}(M)} \begin{pmatrix} \boldsymbol{O} & \boldsymbol{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{T,L=1}^{N_\mathrm{n}} \sum_{\tau=1}^{n_\mathrm{o}(T)} \sum_{\lambda=1}^{n_\mathrm{o}(L)} (\boldsymbol{P}^{\alpha}_{\boldsymbol{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{O} & \boldsymbol{l} \\ M & T & M & L \\ \mu & \tau & \mu' & \lambda \end{array}\right)^{[\mathrm{R^{II}}_{TL}]}}_{=(\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{R^{II}}]}_{(M,\mu)(M,\mu')}} \\ & + \sum_{\nu'=1}^{n_\mathrm{o}(N)} \begin{pmatrix} \boldsymbol{O} & \boldsymbol{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \underbrace{\sum_{\boldsymbol{t},\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{T,L=1}^{N_\mathrm{n}} \sum_{\tau=1}^{n_\mathrm{o}(T)} \sum_{\lambda=1}^{n_\mathrm{o}(L)} (\boldsymbol{P}^{\alpha}_{\boldsymbol{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc|cc} \boldsymbol{n} & \boldsymbol{t} & \boldsymbol{n} & \boldsymbol{l} \\ N & T & N & L \\ \nu' & \tau & \nu & \lambda \end{array}\right)^{[\mathrm{R^{II}}_{TL}]}}_{=(\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{R^{II}}]}_{(N,\nu')(N,\nu)}} \Bigg\}. \end{aligned} \tag{5.4}$$

Conclusion:

• Disregarding the kinetic energy integrals of the first term of (5.1), the most appealing feature of (5.2), (5.3), and (5.4) is that off-blockdiagonal elements can be fully led back to a determination of related blockdiagonal elements:

$$\begin{aligned} (\boldsymbol{F}^{\alpha}_{\boldsymbol{On}})^{[\mathrm{R.U\&C}]}_{(M,\mu)(N,\nu)} := (\boldsymbol{K}_{\boldsymbol{On}})_{(M,\mu)(N,\nu)} + \frac{1}{2}\Bigg\{ & \sum_{\mu'=1}^{n_\mathrm{o}(M)} \begin{pmatrix} \boldsymbol{O} & \boldsymbol{n} \\ M & N \\ \mu' & \nu \end{pmatrix} \left[(\boldsymbol{F}^{A}_{\boldsymbol{OO}})_{(M,\mu)(M,\mu')} + (\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{R^I}]}_{(M,\mu)(M,\mu')} - (\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{R^{II}}]}_{(M,\mu)(M,\mu')} \right] \\ & + \sum_{\nu'=1}^{n_\mathrm{o}(N)} \begin{pmatrix} \boldsymbol{O} & \boldsymbol{n} \\ M & N \\ \mu & \nu' \end{pmatrix} \left[(\boldsymbol{F}^{A}_{\boldsymbol{OO}})_{(N,\nu')(N,\nu)} + (\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{R^I}]}_{(N,\nu')(N,\nu)} - (\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{R^{II}}]}_{(N,\nu')(N,\nu)} \right] \Bigg\}. \end{aligned} \tag{5.5}$$

• The "Unrestricted and Combined Rüdenberg" 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:

$$
\begin{aligned}
(\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{R^I}]}_{(M,\mu)(M,\mu')} &:= \sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{T=1}^{N_\mathrm{n}}\sum_{\tau,\tau'=1}^{n_\mathrm{o}(T)} \left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{t} \\ M & M & T & T \\ \mu & \mu' & \tau & \tau' \end{array}\right) \underbrace{\sum_{\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{L=1}^{N_\mathrm{n}}\sum_{\lambda=1}^{n_\mathrm{o}(L)} (\boldsymbol{P}^{\oplus}_{\boldsymbol{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc} \boldsymbol{t} & \boldsymbol{l} \\ T & L \\ \tau' & \lambda \end{array}\right)}_{=((\boldsymbol{P}^{\oplus}\mathbf{S})_{\boldsymbol{tt}})_{(T,\tau)(T,\tau')}} \\
&= \sum_{T=1}^{N_\mathrm{n}}\sum_{\tau,\tau'=1}^{n_\mathrm{o}(T)} ((\boldsymbol{P}^{\oplus}\mathbf{S})_{\boldsymbol{OO}})_{(T,\tau)(T,\tau')} \sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{t} \\ M & M & T & T \\ \mu & \mu' & \tau & \tau' \end{array}\right),
\end{aligned}
\tag{5.6}
$$

and

$$
\begin{aligned}
(\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{R^{II}}]}_{(M,\mu)(M,\mu')} &:= \sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{T=1}^{N_\mathrm{n}}\sum_{\tau,\tau'=1}^{n_\mathrm{o}(T)} \left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{O} & \boldsymbol{t} \\ M & T & M & T \\ \mu & \tau & \mu' & \tau' \end{array}\right) \frac{1}{2} \Bigg\{ \underbrace{\sum_{\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{L=1}^{N_\mathrm{n}}\sum_{\lambda=1}^{n_\mathrm{o}(L)} (\boldsymbol{P}^{\alpha}_{\boldsymbol{tl}})_{(T,\tau)(L,\lambda)} \left(\begin{array}{cc} \boldsymbol{t} & \boldsymbol{l} \\ T & L \\ \tau' & \lambda \end{array}\right)}_{=((\boldsymbol{P}^{\alpha}\mathbf{S})_{\boldsymbol{tt}})_{(T,\tau)(T,\tau')}} \\
&\qquad + \underbrace{\sum_{\boldsymbol{l}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}\sum_{L=1}^{N_\mathrm{n}}\sum_{\lambda=1}^{n_\mathrm{o}(L)} (\boldsymbol{P}^{\alpha}_{\boldsymbol{tl}})_{(T,\tau')(L,\lambda)} \left(\begin{array}{cc} \boldsymbol{t} & \boldsymbol{l} \\ T & L \\ \tau & \lambda \end{array}\right)}_{=((\boldsymbol{P}^{\alpha}\mathbf{S})_{\boldsymbol{tt}})_{(T,\tau')(T,\tau)}} \Bigg\} \\
&= \sum_{T=1}^{N_\mathrm{n}}\sum_{\tau,\tau'=1}^{n_\mathrm{o}(T)} \frac{1}{2} \Big\{ ((\boldsymbol{P}^{\alpha}\mathbf{S})_{\boldsymbol{OO}})_{(T,\tau)(T,\tau')} + ((\boldsymbol{P}^{\alpha}\mathbf{S})_{\boldsymbol{OO}})_{(T,\tau')(T,\tau)} \Big\} \sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{O} & \boldsymbol{t} \\ M & T & M & T \\ \mu & \tau & \mu' & \tau' \end{array}\right).
\end{aligned}
\tag{5.7}
$$

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, and Segal [5]:

$$
\begin{aligned}
&\big\{\boldsymbol{\Phi}_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\boldsymbol{\Phi}_\nu(\boldsymbol{r}_i-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\big\}^{[\mathrm{NDIO}^{\mathrm{I}}_{MN}]} := \\
&\big\{\boldsymbol{\Phi}_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\boldsymbol{\Phi}_\nu(\boldsymbol{r}_i-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\big\}^{[\mathrm{NDDO}_{MN}]} := \\
&\qquad \delta_{\boldsymbol{On}}\delta_{MN}\boldsymbol{\Phi}_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\boldsymbol{\Phi}_\nu(\boldsymbol{r}_i-\boldsymbol{R}_M),
\end{aligned}
\tag{6.1}
$$

where again $\delta_{\boldsymbol{On}} \equiv \delta_{0n_a}\delta_{0n_b}\delta_{0n_c}$. Following Rüdenberg's two-electron route of approximation, the two-electron analog of (6.1) then reads

$$
\begin{aligned}
&\big\{\boldsymbol{\Phi}_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\boldsymbol{\Phi}_\nu(\boldsymbol{r}_j-\boldsymbol{R}_N-\boldsymbol{R}_{\boldsymbol{n}})\big\}^{[\mathrm{NDIO}^{\mathrm{II}}_{MN}]} := \\
&\qquad \delta_{\boldsymbol{On}}\delta_{MN}\boldsymbol{\Phi}_\mu(\boldsymbol{r}_i-\boldsymbol{R}_M)\boldsymbol{\Phi}_\nu(\boldsymbol{r}_j-\boldsymbol{R}_M).
\end{aligned}
\tag{6.2}
$$

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:

$$
\begin{aligned}
(\boldsymbol{F}^{\alpha}_{\boldsymbol{On}})^{[\mathrm{NDIO.U\&C}]}_{(M,\mu)(N,\nu)} &:= (\boldsymbol{K}_{\boldsymbol{On}})_{(M,\mu)(N,\nu)} \\
&+ \delta_{\boldsymbol{On}}\delta_{MN}\Big\{(\boldsymbol{F}^{A}_{\boldsymbol{OO}})_{(M,\mu)(M,\nu)} + (\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{NDIO^I}]}_{(M,\mu)(M,\nu)} \\
&\qquad - (\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(M,\nu)}\Big\},
\end{aligned}
\tag{6.3}
$$

with

$$(\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{NDIO^{I}}]}_{(M,\mu)(M,\nu)} := \tag{6.4}$$

$$\sum_{T=1}^{N_{\mathrm{n}}} \sum_{\tau,\lambda=1}^{n_{\mathrm{o}}(T)} (\boldsymbol{P}^{\oplus}_{\boldsymbol{OO}})_{(T,\tau)(T,\lambda)} \sum_{\boldsymbol{t}=\boldsymbol{N}^{-}}^{\boldsymbol{N}^{+}} \left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{t} \\ M & M & T & T \\ \mu & \nu & \tau & \lambda \end{array} \right)$$

and

$$(\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{NDIO^{II}}]}_{(M,\mu)(M,\nu)} := \tag{6.5}$$

$$\sum_{T=1}^{N_{\mathrm{n}}} \sum_{\tau,\lambda=1}^{n_{\mathrm{o}}(T)} (\boldsymbol{P}^{\alpha}_{\boldsymbol{OO}})_{(T,\tau)(T,\lambda)} \sum_{\boldsymbol{t}=\boldsymbol{N}^{-}}^{\boldsymbol{N}^{+}} \left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{O} & \boldsymbol{t} \\ M & T & M & T \\ \mu & \tau & \nu & \lambda \end{array} \right).$$

• 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 (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 $(\mathbf{S}_{\boldsymbol{On}})$ and $(\boldsymbol{K}_{\boldsymbol{On}})$ occuring in the Fock-matrix representations $(\boldsymbol{F}^{\alpha}_{\boldsymbol{On}})^{[\mathrm{M.U\&C}]}$ (3.11), $(\boldsymbol{F}^{\alpha}_{\boldsymbol{On}})^{[\mathrm{ZIO.U\&C}]}$ (4.3), $(\boldsymbol{F}^{\alpha}_{\boldsymbol{On}})^{[\mathrm{R.U\&C}]}$ (5.5), and $(\boldsymbol{F}^{\alpha}_{\boldsymbol{On}})^{[\mathrm{NDIO.U\&C}]}$ (6.3) decay rather quickly with increasing intercellular distances $|\boldsymbol{R}_{\boldsymbol{O}} - \boldsymbol{R}_{\boldsymbol{n}}|$.

Due to an equally rapid fall-off of the two-center exchange integrals, even the matrices $(\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{M^{II}}]}$ (3.13), $(\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{ZIO^{II}}]}$ (4.5), $(\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{R^{II}}]}$ (5.7), $(\boldsymbol{F}^{\alpha E}_{\boldsymbol{OO}})^{[\mathrm{NDIO^{II}}]}$ (6.5), can get along with small N_a, N_b, and N_c parameters.

Only the attractive and repulsive matrix representations $(\boldsymbol{F}^{A}_{\boldsymbol{OO}})$ (2.21) or (2.24) and $(\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{M^{I}}]}$ (3.12), $(\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{ZIO^{I}}]}$ (4.4), $(\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{R^{I}}]}$ (5.6), $(\boldsymbol{F}^{C}_{\boldsymbol{OO}})^{[\mathrm{NDIO^{I}}]}$ (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:

$$\left(\begin{array}{ccc} \boldsymbol{O} & & \boldsymbol{O} \\ & \boldsymbol{t} & \\ M & T & M \\ \mu & & \mu \end{array} \right)_{\infty} := -Z_T |\boldsymbol{R}_M - [\boldsymbol{R}_T - \boldsymbol{R}_{\boldsymbol{t}}]|^{-1} \text{ for all } \mu, \tag{7.1}$$

$$\left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{t} \\ M & M & T & T \\ \mu & \mu & \tau & \tau \end{array} \right)_{\infty} := |\boldsymbol{R}_M - [\boldsymbol{R}_T - \boldsymbol{R}_{\boldsymbol{t}}]|^{-1} \text{ for all } \mu, \tau. \tag{7.2}$$

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

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

we introduce the following long-range correction:

$$\begin{aligned} F^{\infty}_{(M,\mu)(M,\mu)} &\stackrel{\mathrm{def}}{=} \underbrace{\sum_{\boldsymbol{t}=-\infty}^{+\infty} \sum_{T=1}^{N_{\mathrm{n}}}}_{\boldsymbol{t}T \neq \boldsymbol{O}M} \left\{ \underbrace{\left(\begin{array}{ccc} \boldsymbol{O} & & \boldsymbol{O} \\ & \boldsymbol{t} & \\ M & T & M \\ \mu & & \mu \end{array} \right)_{\infty}}_{:=-Z_T|\boldsymbol{R}_M-[\boldsymbol{R}_T-\boldsymbol{R}_{\boldsymbol{t}}]|^{-1}} + \underbrace{\sum_{\tau=1}^{n_{\mathrm{o}}(T)} (\boldsymbol{P}^{\oplus}_{\boldsymbol{OO}})_{(T,\tau)(T,\tau)}}_{:=Z_T-q_T^{\infty}} \underbrace{\left(\begin{array}{cc|cc} \boldsymbol{O} & \boldsymbol{O} & \boldsymbol{t} & \boldsymbol{t} \\ M & M & T & T \\ \mu & \mu & \tau & \tau \end{array} \right)_{\infty}}_{:=|\boldsymbol{R}_M-[\boldsymbol{R}_T-\boldsymbol{R}_{\boldsymbol{t}}]|^{-1}} \right\} \\ &= \underbrace{\sum_{\boldsymbol{t}=-\infty}^{+\infty} \sum_{T=1}^{N_{\mathrm{n}}}}_{\boldsymbol{t}T \neq \boldsymbol{O}M} (-q_T^{\infty}) |\boldsymbol{R}_M - [\boldsymbol{R}_T - \boldsymbol{R}_{\boldsymbol{t}}]|^{-1} \text{ for all } \mu, \end{aligned} \tag{7.4}$$

where we used the definition of an atomic point charge q_T^∞ at center T with respect to a locally orthonormalized basis set [11]:

$$q_T^\infty \stackrel{\text{def}}{=} Z_T - \sum_{\tau=1}^{n_\text{o}(T)} (\boldsymbol{P}_{\boldsymbol{OO}}^{\oplus})_{(T,\tau)(T,\tau)}. \tag{7.5}$$

Equation (7.4) contains all the long-range terms of (3.11), (4.3), (5.5), and (6.3) for the M.U&C, the ZIO.U&C, the R.U&C, and the NDIO.U&C variant, respectively.

Following Ramírez and Böhm [12], (7.4) can be interpreted as follows: For large internuclear distances each non-zero Fock-matrix element $F^\infty_{(M,\mu)(M,\mu)}$ belonging to an atom M represents the Madelung potential of an electronic point charge at the center M of the reference cell. Such Madelung potentials can be evaluated using Ewald-summation techniques [14].

The infinite summation of (7.4), however, includes also the non-classical domain, which is defined through the conditions of (7.3). Therefore, the final Madelung correction formula has to resubstitute the Madelung terms $F^\circ_{(M,\mu)(M,\mu)}$ of the non-classical domain by the correct Fock-matrix representation:

$$\begin{aligned}(\boldsymbol{F}_{\boldsymbol{OO}}^\infty)^{[\mathrm{X^I}]}_{(M,\mu)(M,\mu)} &\stackrel{\text{def}}{=} F^\infty_{(M,\mu)(M,\mu)} - F^\circ_{(M,\mu)(M,\mu)} \\ &\quad + (\boldsymbol{F}_{\boldsymbol{OO}})^{[\mathrm{X^I}]}_{(M,\mu)(M,\mu)}, \\ &\mathrm{X} = \mathrm{M, ZIO, R, NDIO},\end{aligned} \tag{7.6}$$

where

$$F^\circ_{(M,\mu)(M,\mu)} \stackrel{\text{def}}{=} \underbrace{\sum_{T=1}^{N_\text{n}}}_{T\neq M} (-q_T^\infty)|\boldsymbol{R}_M - \boldsymbol{R}_T|^{-1} + \sum_{T=1}^{N_\text{n}} (-q_T^\infty) \underbrace{\sum_{\boldsymbol{t}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}}_{\boldsymbol{t}\neq\boldsymbol{O}} |\boldsymbol{R}_M - [\boldsymbol{R}_T - \boldsymbol{R}_{\boldsymbol{t}}]|^{-1} \text{ for all } \mu. \tag{7.7}$$

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

$$\begin{aligned}\mathcal{E}_t^{[\mathrm{X.U\&C}]} := \frac{1}{2} \sum_{\boldsymbol{n}=\boldsymbol{N}^-}^{\boldsymbol{N}^+} \sum_{M,N=1}^{N_\text{n}} \sum_{\mu=1}^{n_\text{o}(M)} \sum_{\nu=1}^{n_\text{o}(N)} \Bigg\{ &(\boldsymbol{P}_{\boldsymbol{On}}^{\oplus})_{(M,\mu)(N,\nu)} \cdot \Big[(\boldsymbol{K}_{\boldsymbol{On}})_{(M,\mu)(N,\nu)} + (\boldsymbol{F}_{\boldsymbol{On}}^{A})^{[\mathrm{X.U\&C}]}_{(M,\mu)(N,\nu)} \Big] \\ &+ (\boldsymbol{P}_{\boldsymbol{On}}^{\alpha})_{(M,\mu)(N,\nu)} (\boldsymbol{F}_{\boldsymbol{On}}^{\alpha})^{[\mathrm{X.U\&C}]}_{(M,\mu)(N,\nu)} + (\boldsymbol{P}_{\boldsymbol{On}}^{\beta})_{(M,\mu)(N,\nu)} (\boldsymbol{F}_{\boldsymbol{On}}^{\beta})^{[\mathrm{X.U\&C}]}_{(M,\mu)(N,\nu)} \Bigg\} \\ &+ \frac{1}{2} \Bigg\{ \underbrace{\sum_{M,N=1}^{N_\text{n}}}_{N\neq M} (Z_M Z_N)|\boldsymbol{R}_M - \boldsymbol{R}_N|^{-1} + \sum_{M,N=1}^{N_\text{n}} (Z_M Z_N) \underbrace{\sum_{\boldsymbol{n}=\boldsymbol{N}^-}^{\boldsymbol{N}^+}}_{\boldsymbol{n}\neq\boldsymbol{O}} |\boldsymbol{R}_M - [\boldsymbol{R}_N - \boldsymbol{R}_{\boldsymbol{n}}]|^{-1} \Bigg\}, \\ &\mathrm{X} = \mathrm{M, ZIO, R, NDIO}.\end{aligned} \tag{7.8}$$

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]:

$$\mathcal{E}_t^\infty := \frac{1}{2} \Bigg\{ \underbrace{\sum_{M,N=1}^{N_\text{n}}}_{N\neq M} q_M q_N |\boldsymbol{R}_M - \boldsymbol{R}_N|^{-1} + \sum_{M,N=1}^{N_\text{n}} q_M q_N \underbrace{\sum_{\boldsymbol{n}=-\infty}^{+\infty}}_{\boldsymbol{n}\neq\boldsymbol{O}} |\boldsymbol{R}_M - [\boldsymbol{R}_N - \boldsymbol{R}_{\boldsymbol{n}}]|^{-1} \Bigg\}. \tag{7.9}$$

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

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

where

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

8. Oversimplifications in the "Unrestricted" Modes of Approximation

The title of Rüdenberg'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

$$(\mathbf{V}_{\mathbf{mm}})_{\mu\mu}[\boldsymbol{p}P] \text{ and } \begin{pmatrix} \boldsymbol{m} & \boldsymbol{p} & \boldsymbol{m} \\ M & P & M \\ \mu & & \nu \end{pmatrix}, \quad \text{as well as}$$

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

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

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

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 Rüdenberg's approximation.

The "Unrestricted and Combined" use of Mulliken- and Rüdenberg-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 explicitely discussed in Rüdenberg's letter. Our question now is: How do both approximation schemes operate on the two types of three-index and three-center repulsion integrals

$$\left(\begin{matrix} \boldsymbol{m} & \boldsymbol{m} \\ \mu & \mu \end{matrix} \middle| \begin{matrix} \boldsymbol{t} & \boldsymbol{l} \\ \tau & \lambda \end{matrix}\right) \quad \text{and} \quad \left(\begin{matrix} \boldsymbol{m} & \boldsymbol{m} \\ M & M \\ \mu & \nu \end{matrix} \middle| \begin{matrix} \boldsymbol{t} & \boldsymbol{l} \\ T & L \\ \tau & \lambda \end{matrix}\right) \quad \text{as well as}$$

$$\left(\begin{matrix} \boldsymbol{m} & \boldsymbol{t} \\ \mu & \tau \end{matrix} \middle| \begin{matrix} \boldsymbol{m} & \boldsymbol{l} \\ \mu & \lambda \end{matrix}\right) \quad \text{and} \quad \left(\begin{matrix} \boldsymbol{m} & \boldsymbol{t} \\ M & T \\ \mu & \tau \end{matrix} \middle| \begin{matrix} \boldsymbol{m} & \boldsymbol{l} \\ M & L \\ \nu & \lambda \end{matrix}\right)?$$

While the double application of Rüdenberg'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 three-index and three-center cases. The "restricted" modes of the four approximation recipes based on Rüdenberg'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

$$\left(\begin{matrix} \boldsymbol{m} & \boldsymbol{m} \\ \mu & \mu \end{matrix} \middle| \begin{matrix} \boldsymbol{t} & \boldsymbol{l} \\ \tau & \lambda \end{matrix}\right)^{[\mathrm{M}^{\mathrm{I}}_{\mu\mu}\mathrm{M}^{\mathrm{I}}_{\tau\lambda}]} := \left(\begin{matrix} \boldsymbol{m} & \boldsymbol{m} \\ \mu & \mu \end{matrix} \middle| \begin{matrix} \boldsymbol{t} & \boldsymbol{l} \\ \tau & \lambda \end{matrix}\right)^{[\mathrm{M}^{\mathrm{I}}_{\tau\lambda}]} := \frac{(\mathbf{S}_{\mathbf{tl}})_{\tau\lambda}}{2}\left\{\left(\begin{matrix} \boldsymbol{m} & \boldsymbol{m} \\ \mu & \mu \end{matrix} \middle| \begin{matrix} \boldsymbol{t} & \boldsymbol{t} \\ \tau & \tau \end{matrix}\right) + \left(\begin{matrix} \boldsymbol{m} & \boldsymbol{m} \\ \mu & \mu \end{matrix} \middle| \begin{matrix} \boldsymbol{l} & \boldsymbol{l} \\ \lambda & \lambda \end{matrix}\right)\right\}, \tag{8.1}$$

too, and

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

$$\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{l}\\ \mu & \lambda\end{matrix}\right)^{[\mathrm{M}^{\mathrm{II}}_{\mu\mu}\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]} := \left(\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{l}\\ \mu & \lambda\end{matrix}\right)^{[\mathrm{M}^{\mathrm{II}}_{\tau\lambda}]} := \frac{(\mathbf{S}_{\mathbf{tl}})_{\tau\lambda}}{2}\left\{\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ \mu & \tau\end{matrix}\right) + \left(\begin{matrix}\boldsymbol{m} & \boldsymbol{l}\\ \mu & \lambda\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{l}\\ \mu & \lambda\end{matrix}\right)\right\}. \tag{8.2}$$

• Within a "Restricted and Combined ZIO" picture (ZIO.R&C)
○ $\mathrm{ZIO}^{\mathrm{I}}$ will be used for three-index exchange part integrals of type

$$\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{m}\\ \mu & \mu\end{matrix}\middle|\begin{matrix}\boldsymbol{t} & \boldsymbol{l}\\ \tau & \lambda\end{matrix}\right)^{[\mathrm{ZIO}^{\mathrm{I}}_{\mu\mu}\mathrm{ZIO}^{\mathrm{I}}_{\tau\lambda}]} := \left(\begin{matrix}\boldsymbol{m} & \boldsymbol{m}\\ \mu & \mu\end{matrix}\middle|\begin{matrix}\boldsymbol{t} & \boldsymbol{l}\\ \tau & \lambda\end{matrix}\right)^{[\mathrm{ZIO}^{\mathrm{I}}_{\tau\lambda}]} := \delta_{\mathbf{tl}}\delta_{\tau\lambda}\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{m}\\ \mu & \mu\end{matrix}\middle|\begin{matrix}\boldsymbol{t} & \boldsymbol{t}\\ \tau & \tau\end{matrix}\right), \tag{8.3}$$

too, and
○ $\mathrm{ZIO}^{\mathrm{II}}$ will also be used for three-index Coulomb part integrals of type

$$\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{l}\\ \mu & \lambda\end{matrix}\right)^{[\mathrm{ZIO}^{\mathrm{II}}_{\mu\mu}\mathrm{ZIO}^{\mathrm{II}}_{\tau\lambda}]} := \left(\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{l}\\ \mu & \lambda\end{matrix}\right)^{[\mathrm{ZIO}^{\mathrm{II}}_{\tau\lambda}]} := \delta_{\mathbf{tl}}\delta_{\tau\lambda}\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ \mu & \tau\end{matrix}\right). \tag{8.4}$$

• Within a "Restricted and Combined Rüdenberg" picture (R.R&C)
○ R^{I} will be used for three-center exchange part integrals of type

$$\begin{aligned}\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{m}\\ M & M\\ \mu & \nu\end{matrix}\middle|\begin{matrix}\boldsymbol{t} & \boldsymbol{l}\\ T & L\\ \tau & \lambda\end{matrix}\right)^{[\mathrm{R}^{\mathrm{I}}_{MM}\mathrm{R}^{\mathrm{I}}_{TL}]} &:= \left(\begin{matrix}\boldsymbol{m} & \boldsymbol{m}\\ M & M\\ \mu & \nu\end{matrix}\middle|\begin{matrix}\boldsymbol{t} & \boldsymbol{l}\\ T & L\\ \tau & \lambda\end{matrix}\right)^{[\mathrm{R}^{\mathrm{I}}_{TL}]}\\ &:= \frac{1}{2}\left\{\sum_{\tau'=1}^{n_{\mathrm{o}}(T)}\left(\begin{matrix}\boldsymbol{t} & \boldsymbol{l}\\ T & L\\ \tau' & \lambda\end{matrix}\right)\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{m}\\ M & M\\ \mu & \nu\end{matrix}\middle|\begin{matrix}\boldsymbol{t} & \boldsymbol{t}\\ T & T\\ \tau & \tau'\end{matrix}\right) + \sum_{\lambda'=1}^{n_{\mathrm{o}}(L)}\left(\begin{matrix}\boldsymbol{t} & \boldsymbol{l}\\ T & L\\ \tau & \lambda'\end{matrix}\right)\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{m}\\ M & M\\ \mu & \nu\end{matrix}\middle|\begin{matrix}\boldsymbol{l} & \boldsymbol{l}\\ L & L\\ \lambda' & \lambda\end{matrix}\right)\right\},\end{aligned} \tag{8.5}$$

too, and
○ R^{II} will also be used for three-center Coulomb part integrals of type

$$\begin{aligned}\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ M & T\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{l}\\ M & L\\ \nu & \lambda\end{matrix}\right)^{[\mathrm{R}^{\mathrm{II}}_{MM}\mathrm{R}^{\mathrm{II}}_{TL}]} &:= \left(\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ M & T\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{l}\\ M & L\\ \nu & \lambda\end{matrix}\right)^{[\mathrm{R}^{\mathrm{II}}_{TL}]}\\ &:= \frac{1}{2}\left\{\sum_{\tau'=1}^{n_{\mathrm{o}}(T)}\left(\begin{matrix}\boldsymbol{t} & \boldsymbol{l}\\ T & L\\ \tau' & \lambda\end{matrix}\right)\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ M & T\\ \mu & \tau\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{t}\\ M & T\\ \nu & \tau'\end{matrix}\right) + \sum_{\lambda'=1}^{n_{\mathrm{o}}(L)}\left(\begin{matrix}\boldsymbol{t} & \boldsymbol{l}\\ T & L\\ \tau & \lambda'\end{matrix}\right)\left(\begin{matrix}\boldsymbol{m} & \boldsymbol{l}\\ M & L\\ \mu & \lambda'\end{matrix}\middle|\begin{matrix}\boldsymbol{m} & \boldsymbol{l}\\ M & L\\ \nu & \lambda\end{matrix}\right)\right\}.\end{aligned} \tag{8.6}$$

• Within a "Restricted and Combined NDIO" picture (NDIO.R&C)
○ $\mathrm{NDIO}^{\mathrm{I}}$ will be used for three-center exchange part integrals of type

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

too, and
○ $\mathrm{NDIO}^{\mathrm{II}}$ will also be used for three-center Coulomb part integrals of type

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

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 Rüdenberg's approximations in crystal orbital theories of Hartree-Fock type will thus be presented in a forthcoming paper.

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 [16]. 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 Rüdenberg 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 [17] and stored once and for all. A cubic spline algorithm [18] may be taken to interpolate the actual integral value from each precomputed list. Such techniques, particularly appropriate for minimal basis sets, have been incorporated in a non-empirical crystal orbital procedure based on Rüdenberg'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 Rüdenberg's fundamental approximations.

Acknowledgements

Many thanks to Juliette Ruddy for improving the English manuscript, and to Dr. Dietrich Hoffmann for clarifying discussions.

[1] W. Koch, On Rüdenberg's Approximations and Their Unrestricted and Combined Use in Molecular Orbital Theories of Hartree-Fock Type, Int. J. Quantum Chem. **76**, 148 (2000).
[2] K. Rüdenberg, J. Chem. Phys. **19**, 1433 (1951).
[3] R. S. Mulliken, J. Chim. Phys. **46**, 500 and 521 (1949).
[4] R. G. Parr, J. Chem. Phys. **20**, 1499 (1952).
[5] J. A. Pople, D. P. Santry, and G. A. Segal,

J. Chem. Phys. **43**, S 129 (1965). J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory (McGraw-Hill, New York, 1970), and references therein.

[6] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

[7] J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954).

[8] M. Wolfsberg and L. Helmholz, J. Chem. Phys. **20**, 837 (1952).

[9] R. Hoffmann, Solids and Surfaces: A Chemist' View of Bonding in Extended Structures (VCH Publisher, New York, 1988) and references therein.

[10] P. J. A. Ruttink, Theoret. chim. Acta (Berl.) **6**, 83 (1966).

[11] M. C. Böhm, One-Dimensional Organometallic Materials (Springer, Berlin, 1987). C. Pisani, R. Dovesi, and C. Roetti, Hartree-Fock Ab-Initio Treatment of Crystalline Systems (Springer, Berlin, 1988). J. J. Ladik, Quantum Theory of Polymers as Solids (Plenum Press, New York, 1988). J.-M. André, J. Delhalle, and J.-L. Brédas, Quantum Chemistry Aided Design of Organic Polymers (World Scientific, Singapore, 1991). C. Pisani (Ed.), Quantum-Mechanical Ab-Initio Calculation of the Properties of Crystalline Materials (Springer, Berlin, 1996).

[12] R. Ramírez and M. C. Böhm, Int. J. Quantum Chem. **30**, 391 (1986). R. Ramírez and M. C. Böhm, Int. J. Quantum Chem. **34**, 47 (1988). R. Ramírez and M. C. Böhm, Int. J. Quantum Chem. **34**, 571 (1988).

[13] M. C. Zerner, Semiempirical Molecular Orbital Methods, in: K. B. Lipkowitz and D. B. Boyd (Eds.), Reviews in Computational Chemistry, Vol. 2, 313 (VCH Publishers, New York, 1991), and references therein. W. Thiel, Perspectives on Semiempirical Molecular Orbital Theory, in: I. Prigogine and S. A. Rice (Eds.), Advances in Chemical Physics, Vol. 93, 703 (John Wiley & Sons, London, New York, Sydney, 1996), and references therein.

[14] M. P. Tosi, Solid State Phys. **16**, 1 (1964).

[15] W. Koch, On the Restricted and Combined Use of Rüdenberg's Approximations in Molecular Orbital Theories of Hartree-Fock Type, Z. Naturforsch. **a**, this issue.

[16] Improvements of Rüdenberg's truncated one-electron expansion have already been described in a paper entitled "Limited Expansion of Diatomic Overlap (LEDO): A Near-Accurate Approximate Ab Initio LCAO MO Method" of F. P. Billingsley II and J. E. Bloor, Chem. Phys. Letters **4**, 48 (1969), and F. P. Billingsley II and J. E. Bloor, J. Chem. Phys. **55**, 5178 (1971). The LEDO technique has many points of similarity with the "Projection of Diatomic Differential Overlap" method (PDDO) of M. D. Newton, N. S. Ostlund, and J. A. Pople, J. Chem. Phys. **49**, 5192 (1968), M. D. Newton, J. Chem. Phys. **51**, 3917 (1969), and M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Chem. Phys. **51**, 3927 (1969). Another starting point for the LEDO procedure were the integral approximations of F. E. Harris and R. Rein, Theoret. Chim. Acta (Berl.) **6**, 73 (1966).

[17] The interest in using Slater-type orbitals (STO) also in non-empirical calculations has been reanimated through "STOP: A Slater-Type Orbital Package for Molecular Electronic Structure Determination" by A. Bouferguene, M. Fares, and P. E. Hoggan, Int. J. Quantum Chem. **57**, 801 (1996).

[18] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, Numerical Recipes (Cambridge University Press, Cambridge, 1986).