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# Hermitian “Chemical” Hamiltonian: an Alternative *ab Initio* Method\*

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## Abstract

Some previous results of the present author are combined in order to develop a Hermitian version of the “Chemical Hamiltonian Approach”. In this framework the second quantized Born-Oppenheimer Hamiltonian is decomposed into one- and two-center components, if some finite basis corrections are omitted. (No changes are introduced into the one- and two-center integrals, while projective expansions are used for the three- and four-center ones, which become exact only in the limit of complete basis sets.) The total molecular energy calculated with this Hamiltonian can then be presented as a sum of the intraatomic and diatomic energy terms which were introduced in our previous “Chemical Energy Component Analysis” scheme. The corresponding modified Hartree-Fock-Roothaan equations are also derived; they do not contain any three- and four-center integrals, while the non-empirical character of the theory is conserved. This scheme may be useful also as a “layer” in approaches like ONIOM.

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\*Dedicated to the 60-th birthday of Professor Péter R. Surján.

## 1. Introduction

Three decades ago the present author studied the apparent contradiction that one has one- and two-electron integrals up to four-center ones in the *ab initio* quantum chemical theory, while the empirical chemical facts indicate that the intramolecular interactions are basically of atomic and diatomic character [1]. In chemical practice one needs not to assume the existence of any *primary* three- and four-atom effects in a molecule, while the presence of the three- and four-center integrals in the theory would indicate the opposite. The problem was approached by introducing a “projected” integral approximation scheme [1], permitting to present each three- and four-center integral as a sum of a leading “physical” term containing only one- and two-center integrals, and a finite basis correction to it. (This integral approximation scheme has some resemblance with Ruedenberg classical proposition [2].) Combined with a special “mixed” second quantized formalism for non-orthogonal basis orbitals, this permitted to present the finite basis version of the Born-Oppenheimer Hamiltonian as a sum of atomic and diatomic “physical” terms and finite basis correction ones. An interesting theoretical property of these atomic Hamiltonians was that—despite the interatomic overlap of the basis functions—the antisymmetrized product of atomic full CI solutions was an eigenfunction of the respective sum of the atomic Hamiltonians, and the eigenvalues were the sums of the atomic full CI energies [1]. (No analogous property could be proved, however, for the Hartree-Fock wave functions.) The diatomic terms of the Hamiltonian have been also decomposed into terms of different physical nature, like electrostatic and overlap effects...

These properties motivated us to call this formalism as “Chemical Hamiltonian Approach” (CHA). The disadvantage of the formalism was the non-Hermiticity of the “physical” terms [1], obviously causing complications in the practical applications. This non-Hermiticity originated from the asymmetric treatment of “bra”-s and “ket”-s constituting the different one- and two-electron integrals, as different functions in the integrands were analyzed by assuming that every operator acts “to right”.

The intramolecular CHA formalism received no direct numerical applications. However, the application of the same philosophy to the BSSE problem of intermolecular interactions has been found rather useful [1,3,4]. An energy decomposition formalism has also been developed [1], in which the different energy components were defined as the expectation values of the corresponding ‘physical’ terms of the Hamiltonian; the analysis of one of them (that of the diatomic electrostatic interactions in a point-charge approximation) had lead to the definition of the bond order index [5–8], that has been widely

applied in studying different chemical problems.

Later a somewhat different energy decomposition scheme – called “chemical energy component analysis” (CECA) – has been introduced [9,10]. It differed from the scheme in [1] in two aspects. First all two-center integrals were conserved, including those that in [1] were considered as finite basis correction terms with respect to the intraatomic Hamiltonians, and were omitted from the “physical terms”. Second, the projective integral approximations were symmetrized with respect the “bra”-s and “ket”-s. Although for the energy decomposition this symmetrization probably would have a true significance only if one admitted the use of complex basis functions, it is the conceptual starting point for our present analysis, because it permits to build up a Hermitian version of the “chemical” Hamiltonian.

In the CECA scheme the energy of a molecule calculated at the SCF level is expressed *approximately but to a good accuracy* as a sum of atomic and diatomic contributions, the computation of which requires the use of *one- and two-center integrals only* [9]. It seems important that the error of this approximation apparently has the character of a “white noise” and does not reflect any actual intramolecular effects of physical or chemical significance.

For the CECA scheme several (more or less successful) improvements and refinements have been developed (see *e.g.*, [11–14]; we are not going to discuss them here in any detail. All of them (including, of course, CECA itself) are *a posteriori* means of analysis, that is they can be applied *after* a conventional *ab initio* SCF calculation has been performed, in order to elucidate the results of the latter. The aim of the present paper is to use the same integral approximation scheme in order to develop an approximate *ab initio* scheme of *a priori* calculations, in which one needs not to calculate any three- and four-center integrals. In this respect the scheme could be put in parallel with the semiempirical quantum chemical methods. However, the projective integral approximations are improving with increasing basis sets, thus one may expect that the proposed scheme will exhibit convergence to the conventional Hartree-Fock limit. (The proposed scheme may be useful also as a “layer” in schemes like ONIOM [15].)

## 2. Integral approximation

Let us first consider the three-center one-electron integral  $\langle \chi_\mu^A | \frac{Z_C}{r_C} | \chi_\nu^B \rangle$ , where  $A$ ,  $B$  and  $C$  represent three *different* atoms. Here the superscripts  $A$  and  $B$  indicate that the basis orbitals  $\chi_\mu$  and  $\chi_\nu$  are centered on the atoms  $A$  and  $B$ , respectively. Thus the integral describes the interaction of the diatomic overlap population  $\chi_\mu^{A*}(\vec{r})\chi_\nu^B(\vec{r})$  with the nucleus of atom  $C$ . This integral

can also be written in the symmetrized form

$$\langle \chi_\mu^A | \frac{Z_C}{r_C} | \chi_\nu^B \rangle = \frac{1}{2} \left[ \langle \chi_\mu^A | \frac{Z_C}{r_C} | \chi_\nu^B \rangle + \langle \chi_\nu^B | \frac{Z_C}{r_C} | \chi_\mu^A \rangle^* \right] . \quad (1)$$

(All the one- and two-electron integrals, if the opposite is not stated, include also summations over the spin variables.) Considering the “bra”  $\frac{Z_C}{r_C} | \chi_\nu^B \rangle$  in the first integral, one may pictorially consider it as describing the “scattering” of the electron occupying orbital  $\chi_\nu^B$  on the nucleus of atom  $C$ ; it is a function that may be considered a diatomic entity related to the atoms  $B$  and  $C$ . By writing a resolution of identity in the form

$$1 \equiv \hat{P}_{BC} + (1 - \hat{P}_{BC}) , \quad (2)$$

where  $\hat{P}_{BC}$  is the projector on the subspace of orbitals centered on atoms  $B$  and  $C$ , this function can be written as a sum of two components: one which is in the subspace  $BC$  of the basis orbitals centered on atoms  $B$  and  $C$ , and another which is orthogonal to that subspace. The first component appears always when atoms  $B$  and  $C$  are at the given configuration with respect to each other, while the question whether the second plays any role in the molecular problem depends on the particular configuration of the other atoms of the molecule. (That term is simply neglected in any calculations of the diatomic molecule  $BC$ .) As the basis set on atoms  $B$  and  $C$  improves, the term in the orthogonal complement becomes smaller and smaller; experience shows that for reasonable basis sets—but not for the minimal ones—one may neglect these terms without causing serious problems [9,11].

According to the above discussion, we shall replace the function  $\frac{Z_C}{r_C} | \chi_\nu^B \rangle$  in the first integral by its projection  $\hat{P}_{BC} \frac{Z_C}{r_C} | \chi_\nu^B \rangle$ , and analogously, the function  $\frac{Z_C}{r_C} | \chi_\mu^A \rangle$  in the second integral by its projection  $\hat{P}_{AC} \frac{Z_C}{r_C} | \chi_\mu^A \rangle$  on the subspace of the basis orbitals centered on atoms  $A$  and  $C$ :

$$\langle \chi_\mu^A | \frac{Z_C}{r_C} | \chi_\nu^B \rangle \implies \frac{1}{2} \left[ \langle \chi_\mu^A | \hat{P}_{BC} \frac{Z_C}{r_C} | \chi_\nu^B \rangle + \langle \chi_\nu^B | \hat{P}_{AC} \frac{Z_C}{r_C} | \chi_\mu^A \rangle^* \right] . \quad (3)$$

Here and further on we use the symbol  $\implies$  to indicate the replacements caused by the projective integral approximations of the type discussed. We recall in this connection, that in the case of an overlapping basis, the projection on the subspace of orbitals centered on some subunit  $X$  can be presented as

$$\hat{P}_X = \sum_{\kappa, \lambda \in X} | \chi_\kappa \rangle S_{(X)\kappa\lambda}^{-1} \langle \chi_\lambda | . \quad (4)$$

Here and further on we use the shorthand  $S_{(X)\kappa\lambda}^{-1}$  for the elements of the *inverse* overlap matrix of the subunit  $X$ :

$$S_{(X)\kappa\lambda}^{-1} = (\mathbf{S}_{(X)}^{-1})_{\kappa\lambda} . \quad (5)$$

One should proceed analogously with the three- and four-center two-electron integrals. The two-electron function  $\frac{1}{r_{12}}\chi_\kappa^C(1)\chi_\rho^D(2)$  can be considered as belonging primarily to the diatomic fragment  $CD$  where the basis orbitals are centered; accordingly, we introduce projectors on the  $CD$  subspace *for both electrons*. We shall again perform the symmetrization, thus we obtain the projective integral approximation for the two-electron integral

$$\begin{aligned} & \langle \chi_\gamma^A(1)\chi_\nu^B(2) | \frac{1}{r_{12}} | \chi_\kappa^C(1)\chi_\rho^D(2) \rangle \\ & \implies \frac{1}{2} \left[ \langle \chi_\gamma^A(1)\chi_\nu^B(2) | \hat{P}_{CD}(1)\hat{P}_{CD}(2) \frac{1}{r_{12}} \chi_\kappa^C(1)\chi_\rho^D(2) \rangle \right. \\ & \quad \left. + \langle \chi_\kappa^C(1)\chi_\rho^D(2) | \hat{P}_{AB}(1)\hat{P}_{AB}(2) \frac{1}{r_{12}} \chi_\gamma^A(1)\chi_\nu^B(2) \rangle^* \right]. \end{aligned} \quad (6)$$

It is assumed that at least three of the four atoms  $A$ ,  $B$ ,  $C$  and  $D$  are different. (If it happens that for a three-center integral  $A=B$  or  $C=D$ , then the projector  $\hat{P}_{AB}$  or  $\hat{P}_{CD}$  obviously reduces to  $\hat{P}_A$  or  $\hat{P}_C$ , respectively.)

We introduce the matrices  $\mathbf{A}^X$  closely related to the projectors, with the elements

$$A_{\mu\nu}^X = \sum_{\rho \in X} S_{\mu\rho} S_{(X)\rho\nu}^{-1}. \quad (7)$$

Note that the intra-fragment block of matrix  $\mathbf{A}^X$  (*i.e.*, that corresponding to both  $\mu, \nu \in X$ ) is a unit matrix, according to the definition.

Utilizing the definition (7) when substituting the expression (4) of the projection operators in the integral approximation formulae (3) and (6), the latter become

$$\begin{aligned} \langle \chi_\mu^A | \frac{Z_C}{r_C} | \chi_\nu^B \rangle & \implies \frac{1}{2} \left[ \sum_{\rho \in BC} A_{\mu\rho}^{BC} \langle \chi_\rho | \frac{Z_C}{r_C} | \chi_\nu \rangle + \sum_{\rho \in AC} \left( A_{\nu\rho}^{AC} \langle \chi_\rho | \frac{Z_C}{r_C} | \chi_\mu \rangle \right)^* \right] \\ & = \frac{1}{2} \left[ \sum_{\rho \in BC} A_{\mu\rho}^{BC} \langle \rho | \frac{Z_C}{r_C} | \nu \rangle + \sum_{\rho \in AC} \langle \mu | \frac{Z_C}{r_C} | \rho \rangle A_{\rho\nu}^{AC\dagger} \right], \end{aligned} \quad (8)$$

and

$$\begin{aligned} & \langle \chi_\gamma^A(1)\chi_\nu^B(2) | \frac{1}{r_{12}} | \chi_\kappa^C(1)\chi_\rho^D(2) \rangle \\ & \implies \frac{1}{2} \left[ \sum_{\lambda, \tau \in CD} A_{\gamma\lambda}^{CD} A_{\nu\tau}^{CD} \langle \chi_\lambda(1)\chi_\tau(2) | \frac{1}{r_{12}} | \chi_\kappa(1)\chi_\rho(2) \rangle \right. \\ & \quad \left. + \left( \sum_{\lambda, \tau \in AB} A_{\kappa\lambda}^{AB} A_{\rho\tau}^{AB} \langle \chi_\lambda(1)\chi_\tau(2) | \frac{1}{r_{12}} | \chi_\gamma(1)\chi_\nu(2) \rangle \right)^* \right] \\ & = \frac{1}{2} \left[ \sum_{\lambda, \tau \in CD} A_{\gamma\lambda}^{CD} A_{\nu\tau}^{CD} [\lambda\tau | \kappa\rho] + \sum_{\lambda, \tau \in AB} [\gamma\nu | \lambda\tau] A_{\lambda\kappa}^{AB\dagger} A_{\tau\rho}^{AB\dagger} \right]. \end{aligned} \quad (9)$$

respectively. Here, and further on, † denotes the adjoint, and we have introduced the short-hand notations for the one- and two-electron integrals

$$\langle \mu | \frac{Z_C}{r_C} | \nu \rangle = \langle \chi_\mu | \frac{Z_C}{r_C} | \chi_\nu \rangle ; \quad [\mu\nu | \rho\tau] = \langle \chi_\mu(1)\chi_\nu(2) | \frac{1}{r_{12}} | \chi_\rho(1)\chi_\tau(2) \rangle , \quad (10)$$

which, in general, include also summations over the spin variables.

The integral approximations (8) and (9) are the same as were used in the energy decomposition scheme [9]; we hope that here we succeeded to present them in a more compact and transparent manner.

The accuracy of the integral approximations introduced may be guessed on the basis of comparing the exact SCF energies and the sum of the CECA one- and two-center energy components of a given molecule. In Ref. 9 such a comparison was done for ethane molecule, by using a wide variety of basis sets from 6-31G to 6-311++G\*\* and cc-pVDZ, and it was found that the total energy of about  $-79.2$  Hartree-s of this molecule in all cases was approximated within 15 *milli*Hartree-s, and the deviation was less than 20 *mH* even for 4-31G. Considering the refined version of the CECA scheme [11] in which these remaining three- and four-electron effects were distributed among the one- and two-center components by using a special scheme, one could conclude that this error is scattered in a random fashion among the numerous energy components, so it does not carry any physical or chemical significance. (This conclusion was drawn not only for ethane molecule, but for every system considered as yet.)

### 3. The LCAO Hamiltonian

In the followings we shall use, besides the non-orthogonal set of original basis orbitals  $\{\chi_\mu\}$ , also the respective *Löwdin-orthogonalized* set  $\{\psi_\nu\}$  of orbitals:

$$\psi_\nu = \sum_\mu S_{\mu\nu}^{-\frac{1}{2}} \chi_\mu , \quad (11)$$

where  $S_{\mu\nu}^{-\frac{1}{2}}$  is an element of the  $-\frac{1}{2}$ -th power of the overlap matrix, as well as the biorthogonal set  $\{\varphi_\rho\}$ :

$$\varphi_\rho = \sum_\mu S_{\mu\rho}^{-1} \chi_\mu . \quad (12)$$

All the three sets span the same subspace of the one-electron functions.

We introduce creation and annihilation operators corresponding to each set of these orbitals. In order to distinguish to what type of orbitals the given creation or annihilation orbital is pertinent, we shall use Longuet-Higgins' [16] notations  $\hat{\psi}_\nu^+$ ,  $\hat{\chi}_\mu^+$  and  $\hat{\varphi}_\rho^+$  for the creation operators and  $\hat{\psi}_\nu^-$ ,  $\hat{\chi}_\mu^-$  and

$\hat{\varphi}_\rho^-$  for the annihilation ones. The annihilation operators are defined as the adjoints of the respective creation operators:

$$\hat{\psi}_\nu^- = (\hat{\psi}_\nu^+)^\dagger ; \quad \hat{\chi}_\mu^- = (\hat{\chi}_\mu^+)^\dagger ; \quad \hat{\varphi}_\rho^- = (\hat{\varphi}_\rho^+)^\dagger . \quad (13)$$

The creation operators transform in the same manner as the respective orbitals do, *i.e.*, according to Eq.s (11) and (12). However, standard Fermion anticommutation rules hold only for the creation and annihilation operators defined for the orthonormalized set  $\{\psi_\nu\}$

$$\{\hat{\psi}_\nu^+; \hat{\psi}_\mu^-\} = \hat{\psi}_\nu^+ \hat{\psi}_\mu^- + \hat{\psi}_\mu^+ \hat{\psi}_\nu^- = \delta_{\mu\nu} , \quad (14)$$

while

$$\{\hat{\chi}_\nu^+; \hat{\chi}_\mu^-\} = \hat{\chi}_\nu^+ \hat{\chi}_\mu^- + \hat{\chi}_\mu^+ \hat{\chi}_\nu^- = S_{\mu\nu} , \quad (15)$$

and

$$\{\hat{\varphi}_\nu^+; \hat{\varphi}_\mu^-\} = \hat{\varphi}_\nu^+ \hat{\varphi}_\mu^- + \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^- = S_{\mu\nu}^{-1} , \quad (16)$$

respectively. Owing to the presence of the (inverse) overlap matrix elements in the anticommutators (15) and (16), Fermion anticommutation rules hold for the *mixed* anticommutators

$$\{\hat{\chi}_\nu^+; \hat{\varphi}_\mu^-\} = \delta_{\mu\nu} . \quad (17)$$

and

$$\{\hat{\varphi}_\nu^+; \hat{\chi}_\mu^-\} = \delta_{\mu\nu} . \quad (18)$$

This means that when acting *to right* on a string of creation operators  $\hat{\chi}_\mu^+$  in a “ket”, operator  $\hat{\varphi}_\mu^-$  behaves as a conventional annihilation operator does, and analogously, when acting *to left* on a string of annihilation operators  $\hat{\chi}_\mu^- = (\hat{\chi}_\mu^+)^\dagger$  in a “bra”, operator  $\hat{\varphi}_\mu^+$  behaves as a conventional creation operator.

The LCAO version of the Born-Oppenheimer Hamiltonian has a standard form in terms of the creation and annihilation operators referring to the Löwdin-orthogonalized basis [16,17]:

$$\hat{H} = \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} + \sum_{\mu,\nu} h_{\mu\nu}^\lambda \hat{\psi}_\mu^+ \hat{\psi}_\nu^- + \frac{1}{2} \sum_{\mu,\nu,\rho,\tau} [\psi_\mu \psi_\nu | \psi_\rho \psi_\tau] \hat{\psi}_\mu^+ \hat{\psi}_\nu^+ \hat{\psi}_\tau^- \hat{\psi}_\rho^- . \quad (19)$$

Here the first sum describes the internuclear repulsion,  $h_{\mu\nu}^\lambda = \langle \psi_\mu | \hat{h} | \psi_\nu \rangle$  is the matrix element of the one-electron Hamiltonian

$$\hat{h} = -\frac{1}{2}\Delta - \sum_A \frac{Z_A}{r_A} , \quad (20)$$



in the Löwdin-orthogonalized basis, and  $[\psi_\mu\psi_\nu|\psi_\rho\psi_\tau]$  is a two-electron integral in that basis and the [12|12] convention.

Using the transformations (11), (12) connecting the different sets of the orbitals (and thus also the respective creation and annihilation operators,) one can transform the Hamiltonian (19) into several equivalent forms. We shall present here two of them.

*Using “biorthogonal” operators*

In one version we collect pairs of matrices  $\mathbf{S}^{-\frac{1}{2}}$  into matrices  $\mathbf{S}^{-1}$ , and express the Hamiltonian in terms of the one- and two-electron integrals over the original *overlapping* basis orbitals and of the “biorthogonal” creation and annihilation operators  $\hat{\varphi}_\mu^+$ ,  $\hat{\varphi}_\nu^-$ :

$$\hat{H} = \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} + \sum_{\mu,\nu} h_{\mu\nu} \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^- + \frac{1}{2} \sum_{\mu,\nu,\kappa,\rho} [\mu\nu|\kappa\rho] \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^+ \hat{\varphi}_\rho^- \hat{\varphi}_\kappa^- . \quad (21)$$

where  $h_{\mu\nu}$  and  $[\mu\nu|\kappa\rho]$  are the one- and two-electron integrals calculated for the overlapping set of basis orbitals  $\{\chi_\mu\}$ .

As it is known [17], the expectation value  $E$  of operator  $\hat{H}$  can be expressed through the matrix-representations  $\mathbf{P}$  and  $\mathbf{\Gamma}$  of the first and second order density matrices, respectively:

$$E = \langle \hat{H} \rangle = \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} + \sum_{\mu,\nu} h_{\mu\nu} P_{\nu\mu} + \frac{1}{2} \sum_{\mu,\nu,\kappa,\rho} [\mu\nu|\kappa\rho] \Gamma_{\kappa\rho\mu\nu} . \quad (22)$$

Comparison with Eq. (21) indicates that in *overlapping basis* the elements of the spin-dependent first and second order density matrix can be obtained as expectation values of operator strings constructed from “biorthogonal” creation and annihilation operators:

$$\langle \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^- \rangle = P_{\nu\mu} ; \quad (23)$$

and

$$\langle \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^+ \hat{\varphi}_\rho^- \hat{\varphi}_\kappa^- \rangle = \Gamma_{\kappa\rho\mu\nu} , \quad (24)$$

calculated for the actual wave function. (Note that  $\Gamma_{\kappa\rho\mu\nu} = \Gamma_{\rho\kappa\nu\mu} = -\Gamma_{\rho\kappa\mu\nu}$  etc.) As it is known, in the case of *single determinant* (SD) wave functions the second order density matrix can be expressed through the first order one, so one has

$$\langle \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^+ \hat{\varphi}_\rho^- \hat{\varphi}_\kappa^- \rangle_{SD} = P_{\kappa\mu} P_{\rho\nu} - P_{\kappa\nu} P_{\rho\mu} . \quad (25)$$

*Using “mixed” set of operators*

In this version, first presented in [1], we collect the matrices  $\mathbf{S}^{-1}$  necessary to form operators  $\hat{\varphi}_\mu^-$ , but let the other matrices  $\mathbf{S}^{-1}$  to appear explicitly. (This increases the number of summation indices to be explicitly written out.) Thus we obtain an expression of  $\hat{H}$  that contains individual terms that are not Hermitian—although the overall  $\hat{H}$ , of course, is:

$$\hat{H} = \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} + \sum_{\mu,\nu,\rho} S_{\rho\mu}^{-1} h_{\mu\nu} \hat{\chi}_\rho^+ \hat{\varphi}_\nu^- + \frac{1}{2} \sum_{\mu,\nu,\rho,\tau,\lambda,\sigma} S_{\lambda\mu}^{-1} S_{\sigma\nu}^{-1} [\mu\nu|\rho\tau] \hat{\chi}_\lambda^+ \hat{\chi}_\sigma^+ \hat{\varphi}_\tau^- \hat{\varphi}_\rho^- \quad (26)$$

The advantage of this form is that it permits to work only with quantities related to the original, nonorthogonal basis orbitals; we recall in that respect that operators  $\hat{\varphi}_\mu^-$  can be considered as the “true” annihilation operators, in light of the anticommutation rule (17)—they *act* (to right) in the non-orthogonal framework exactly in the manner as usual annihilation operators do in the orthogonal case. This approach has been utilized when CHA has been applied to the BSSE problem of intermolecular interactions [1,3–4].

As for a Hermitian Hamiltonian  $\hat{H}$  one obviously has  $\hat{H} \equiv \frac{1}{2}(\hat{H} + \hat{H}^\dagger)$ , one can symmetrize each term of (26), and get:

$$\begin{aligned} \hat{H} &= \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} + \frac{1}{2} \sum_{\mu,\nu,\rho} \left( S_{\rho\mu}^{-1} h_{\mu\nu} \hat{\chi}_\rho^+ \hat{\varphi}_\nu^- + h_{\nu\mu} S_{\mu\rho}^{-1} \hat{\varphi}_\nu^+ \hat{\chi}_\rho^- \right) \\ &+ \frac{1}{4} \sum_{\mu,\nu,\rho,\tau,\lambda,\sigma} \left( S_{\lambda\mu}^{-1} S_{\sigma\nu}^{-1} [\mu\nu|\rho\tau] \hat{\chi}_\lambda^+ \hat{\chi}_\sigma^+ \hat{\varphi}_\tau^- \hat{\varphi}_\rho^- + [\rho\tau|\mu\nu] S_{\mu\lambda}^{-1} S_{\nu\sigma}^{-1} \hat{\varphi}_\rho^+ \hat{\varphi}_\tau^+ \hat{\chi}_\sigma^- \hat{\chi}_\lambda^- \right) \end{aligned} \quad (27)$$

This possibility was not considered previously. To save space, we shall not develop it in any detail either here, only note that the respective formulae of this type can be obtained from those discussed in the forthcoming sections by substituting for every creation operator  $\hat{\varphi}_\mu^+$  its explicit expansion

$$\hat{\varphi}_\rho^+ = \sum_{\mu} S_{\mu\rho}^{-1} \hat{\chi}_\mu^+ . \quad (28)$$

and, if necessary, symmetrize like it was done for Eq. (27).

#### 4. The “chemical” Hamiltonian

The different forms of the “chemical Hamiltonian” are obtained if one introduces into formulae (21), (26) and (27) the integral approximations discussed previously.

When introducing the projective integral approximations into these equations, we shall group the terms according to the centers involved. The one-electron matrix elements  $h_{\mu\nu}$  do not contain any three-center integrals if

$\mu, \nu \in A$ , *i.e.*, both basis orbitals  $\chi_\mu$  and  $\chi_\nu$  are centered on the same atom  $A$ . In this case no approximation is needed. If, however  $\mu \in A, \nu \in B$  ( $A \neq B$ ), then  $h_{\mu\nu}$  will contain both two-center integrals and three-center ones—and the latter should be approximated according to Eq. (8). For treating the genuine two-center contributions in this case, it is worth to introduce the one-electron Hamiltonian  $\hat{h}^{AB}$  corresponding to the diatomic fragment  $AB$ :

$$\hat{h}^{AB} = -\frac{1}{2}\Delta - \frac{Z_A}{r_A} - \frac{Z_B}{r_B}. \quad (29)$$

The two-electron integrals need be grouped not only according to the number of centers involved, but also depending on whether the two orbitals in the “ket” part of the integral in (21) are centered on the same or on different atoms.

Performing the grouping of the terms, one obtains the approximation to the Hamiltonian (21) as

$$\begin{aligned} \hat{H} \implies & \sum_A \sum_{\mu, \nu \in A} h_{\mu\nu} \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^- \\ & + \sum_{\substack{A, B \\ A \neq B}} \sum_{\substack{\mu \in A \\ \nu \in B}} \left[ h_{\mu\nu}^{AB} - \frac{1}{2} \sum_{\substack{C \\ C \neq A, B}} \left( \sum_{\rho \in BC} A_{\mu\rho}^{BC} \langle \rho | \frac{Z_C}{r_C} | \nu \rangle \right. \right. \\ & \left. \left. + \sum_{\rho \in AC} \langle \mu | \frac{Z_C}{r_C} | \rho \rangle A_{\rho\nu}^{AC\dagger} \right) \right] \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^- \\ & + \frac{1}{2} \sum_A \sum_{\mu, \nu, \kappa, \rho \in A} [\mu\nu | \kappa\rho] \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^+ \hat{\varphi}_\rho^- \hat{\varphi}_\kappa^- \\ & + \frac{1}{4} \sum_{\substack{A, B \\ A \neq B}} \left[ \sum_{\kappa, \rho \in A} \sum_{\substack{\mu, \nu \in AB \\ (\mu \notin A) \vee (\nu \notin A)}} \left( [\mu\nu | \kappa\rho] \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^+ \hat{\varphi}_\rho^- \hat{\varphi}_\kappa^- + [\rho\kappa | \nu\mu] \hat{\varphi}_\kappa^+ \hat{\varphi}_\rho^+ \hat{\varphi}_\nu^- \hat{\varphi}_\mu^- \right) \right. \\ & + \sum_{\substack{\kappa \in A \\ \rho \in B}} \sum_{\mu, \nu \in AB} \left( [\mu\nu | \kappa\rho] \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^+ \hat{\varphi}_\rho^- \hat{\varphi}_\kappa^- + [\rho\kappa | \nu\mu] \hat{\varphi}_\kappa^+ \hat{\varphi}_\rho^+ \hat{\varphi}_\nu^- \hat{\varphi}_\mu^- \right) \\ & + \sum_{\kappa, \rho, \tau, \eta \in A} \sum_{\mu \in B} \sum_{\substack{\nu \\ (\nu \notin ab)}} \left( A_{\mu\tau}^A A_{\nu\eta}^A [\tau\eta | \kappa\rho] \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^+ \hat{\varphi}_\rho^- \hat{\varphi}_\kappa^- \right. \\ & \left. + [\rho\kappa | \eta\tau] A_{\eta\nu}^{A\dagger} A_{\tau\mu}^{A\dagger} \hat{\varphi}_\kappa^+ \hat{\varphi}_\rho^+ \hat{\varphi}_\nu^- \hat{\varphi}_\mu^- \right) \\ & + \sum_{\substack{\kappa \in A \\ \rho \in B}} \sum_{\tau, \eta \in AB} \sum_{\substack{\mu, \nu \\ (\mu \notin AB) \vee (\nu \notin AB)}} \left( A_{\mu\tau}^{AB} A_{\nu\eta}^{AB} [\tau\eta | \kappa\rho] \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^+ \hat{\varphi}_\rho^- \hat{\varphi}_\kappa^- \right) \end{aligned} \quad (30)$$

$$+ [\rho\kappa|\eta\tau]A_{\eta\nu}^{AB\dagger}A_{\tau\mu}^{AB\dagger}\hat{\varphi}_\kappa^+\hat{\varphi}_\rho^+\hat{\varphi}_\nu^-\hat{\varphi}_\mu^- \Big]$$

This is a Hermitian Hamiltonian that does not contain explicitly three- and four-center integrals any more. It requires some further regrouping in order to present it as a sum of terms that can be assigned to the individual atoms and pairs of atoms. For that reason we introduce the atomic one-electron Hamiltonian  $\hat{h}^A$

$$\hat{h}^A = -\frac{1}{2}\Delta - \frac{Z_A}{r_A} . \quad (31)$$

and perform projections of all relevant quantities to atomic subspaces in order to separate out effective atomic Hamiltonians. However, the error of projecting two-center quantities on the one-center ones is not neglected but is assigned to the diatomic terms of the Hamiltonian. In this manner we get

$$\hat{H} \implies \sum_A \hat{H}_A + \sum_{A<B} \hat{H}_{AB} , \quad (32)$$

where

$$\begin{aligned} \hat{H}_A = & \frac{1}{2} \sum_{\nu,\tau \in A} \sum_{\mu} \left( A_{\mu\tau}^A h_{\tau\nu}^A \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^- + h_{\nu\tau}^A A_{\tau\mu}^{A\dagger} \hat{\varphi}_\nu^+ \hat{\varphi}_\mu^- \right) \\ & + \frac{1}{4} \sum_{\eta,\kappa,\tau,\rho \in A} \sum_{\mu,\nu} \left( A_{\mu\tau}^A A_{\nu\eta}^A [\tau\eta|\kappa\rho] \hat{\varphi}_\mu^+ \hat{\varphi}_\nu^+ \hat{\varphi}_\rho^- \hat{\varphi}_\kappa^- + [\kappa\rho|\tau\eta] A_{\tau\mu}^{A\dagger} A_{\eta\nu}^{A\dagger} \hat{\varphi}_\kappa^+ \hat{\varphi}_\rho^+ \hat{\varphi}_\nu^- \hat{\varphi}_\mu^- \right) \end{aligned} \quad (33)$$

and

$$\begin{aligned}
\hat{H}_{AB} = & \frac{Z_A Z_B}{R_{AB}} - \frac{1}{2} \sum_{\tau \in AB} \sum_{\nu} \left[ \sum_{\mu \in A} \left( A_{\nu\tau}^{AB} \langle \tau | \frac{Z_B}{r_B} | \mu \rangle \hat{\varphi}_{\nu}^+ \hat{\varphi}_{\mu}^- + \langle \mu | \frac{Z_B}{r_B} | \tau \rangle A_{\tau\nu}^{AB\dagger} \hat{\varphi}_{\mu}^+ \hat{\varphi}_{\nu}^- \right) \right. \\
& \left. + \sum_{\mu \in B} \left( A_{\nu\tau}^{AB} \langle \tau | \frac{Z_A}{r_A} | \mu \rangle \hat{\varphi}_{\nu}^+ \hat{\varphi}_{\mu}^- + \langle \mu | \frac{Z_A}{r_A} | \tau \rangle A_{\tau\nu}^{AB\dagger} \hat{\varphi}_{\mu}^+ \hat{\varphi}_{\nu}^- \right) \right] \\
& + \frac{1}{2} \sum_{\substack{\kappa \in A \\ \rho \in B}} \sum_{\eta, \tau \in AB} \sum_{\mu, \nu} \left( A_{\mu\tau}^{AB} A_{\nu\eta}^{AB} [\tau\eta | \kappa\rho] \hat{\varphi}_{\mu}^+ \hat{\varphi}_{\nu}^+ \hat{\varphi}_{\rho}^- \hat{\varphi}_{\kappa}^- \right. \\
& \left. + [\kappa\rho | \tau\eta] A_{\tau\mu}^{AB\dagger} A_{\eta\nu}^{AB\dagger} \hat{\varphi}_{\kappa}^+ \hat{\varphi}_{\rho}^+ \hat{\varphi}_{\nu}^- \hat{\varphi}_{\mu}^- \right) \\
& + \frac{1}{2} \sum_{\substack{\nu \in A \\ \mu \in B}} \left[ \left( h_{\mu\nu}^A - \sum_{\tau \in A} A_{\mu\tau}^A h_{\tau\nu}^A + h_{\mu\nu}^B - \sum_{\tau \in B} h_{\mu\tau}^B A_{\tau\nu}^{B\dagger} \right) \hat{\varphi}_{\mu}^+ \hat{\varphi}_{\nu}^- \right. \\
& \left. + \left( h_{\nu\mu}^A - \sum_{\tau \in A} h_{\nu\tau}^A A_{\tau\mu}^{A\dagger} + h_{\nu\mu}^B - \sum_{\tau \in B} A_{\nu\tau}^B h_{\tau\mu}^B \right) \hat{\varphi}_{\nu}^+ \hat{\varphi}_{\mu}^- \right] \\
& + \frac{1}{2} \left\{ \sum_{\kappa, \rho \in A} \sum_{\substack{\mu, \nu \in AB \\ (\mu \notin A) \vee (\nu \notin A)}} \left[ \left( [\mu\nu | \kappa\rho] - \sum_{\eta, \tau \in A} A_{\mu\tau}^A A_{\nu\eta}^A [\tau\eta | \kappa\rho] \right) \hat{\varphi}_{\mu}^+ \hat{\varphi}_{\nu}^+ \hat{\varphi}_{\rho}^- \hat{\varphi}_{\kappa}^- \right. \right. \\
& \left. \left. + \left( [\kappa\rho | \mu\nu] - \sum_{\eta, \tau \in A} [\kappa\rho | \tau\eta] A_{\tau\mu}^{A\dagger} A_{\eta\nu}^{A\dagger} \right) \hat{\varphi}_{\kappa}^+ \hat{\varphi}_{\rho}^+ \hat{\varphi}_{\nu}^- \hat{\varphi}_{\mu}^- \right] \right. \\
& \left. + \sum_{\kappa, \rho \in B} \sum_{\substack{\mu, \nu \in AB \\ (\mu \notin B) \vee (\nu \notin B)}} \left[ \left( [\mu\nu | \kappa\rho] - \sum_{\eta, \tau \in B} A_{\mu\tau}^B A_{\nu\eta}^B [\tau\eta | \kappa\rho] \right) \hat{\varphi}_{\mu}^+ \hat{\varphi}_{\nu}^+ \hat{\varphi}_{\rho}^- \hat{\varphi}_{\kappa}^- \right. \right. \\
& \left. \left. + \left( [\kappa\rho | \mu\nu] - \sum_{\eta, \tau \in B} [\kappa\rho | \tau\eta] A_{\tau\mu}^{B\dagger} A_{\eta\nu}^{B\dagger} \right) \hat{\varphi}_{\kappa}^+ \hat{\varphi}_{\rho}^+ \hat{\varphi}_{\nu}^- \hat{\varphi}_{\mu}^- \right] \right\}
\end{aligned} \tag{34}$$

In this presentation the monoatomic terms of the Hamiltonian contain only one-center integrals, the diatomic terms contain one- and two-center ones. While the first few terms in Eq. (34) describe direct diatomic interactions (electron-nuclear and electron-electron), most of the terms contain differences between a two-center integral related to *intraatomic* interactions and its approximation by one-center integrals and projection-related matrices  $\mathbf{A}^X$ , like the term

$$h_{\mu\nu}^A - \sum_{\tau \in A} A_{\mu\tau}^A h_{\tau\nu}^A. \tag{35}$$

These terms account for the effects of the basis extension from the atomic description to the diatomic fragments. Their role should diminish as the basis set increases, and in Ref. 1 terms of this type were assigned to the finite basis correction ones. Here they are conserved as to provide that the diatomics (diatomic fragments) are treated without any approximations.

Contrary to the integrals, a part of the creation and annihilation operators, run over the whole basis, so there occur operator strings involving three and four centers. When the energy is calculated as the expectation value of the Hamiltonian, the expectation values of the operator strings give the density matrix elements according to Eq.s (23)–(25). Combined with the elements of the matrices  $\mathbf{A}^X$ , in the single determinant case they lead to the *projected density matrices* [9]  $\mathbf{B}^X$  and  $\mathbf{C}^{\sigma X}$ ,  $\sigma = \alpha$  or  $\beta$ :

$$B_{\mu\nu}^X = \sum_{\gamma} D_{\mu\gamma} A_{\gamma\nu}^X ; \quad C_{\mu\nu}^{\sigma X} = \sum_{\gamma} P_{\mu\gamma}^{\sigma} A_{\gamma\nu}^X ; \quad (\nu \in X) , \quad (36)$$

which implicitly account for the three- and four-center effects—without the need to deal with them explicitly. In Eq. (36)

$$\mathbf{D} = \mathbf{P}^{\alpha} + \mathbf{P}^{\beta} , \quad (37)$$

is the usual spinless density matrix, while  $\mathbf{P}^{\sigma}$  is the density matrix for spin  $\sigma$  ( $\sigma = \alpha$  or  $\beta$ ). The expectation values of the operators  $\hat{H}_A$  and  $\hat{H}_{AB}$  are equal to the energy components  $\hat{E}_A$  and  $\hat{E}_{AB}$ , respectively, quoted in [9]; we shall not display them here explicitly. (We note, however, that a further decomposition of these energy components into terms of different physical origin has also been accomplished in [18].)

We shall mention that using the “mixed” second quantized formalism of Ref. 1, already mentioned, it is possible to present the “chemical” Hamiltonian (32)–(34) in a form in which each term of the Hamiltonian contains only creation and annihilation operators assigned to the corresponding atom or pair of atoms. To save place, we shall illustrate that only by considering the first term of Eq. (33)—all the other terms can be treated analogously. The first term in question is

$$\sum_{\nu, \tau \in A} \sum_{\mu} A_{\mu\tau}^A h_{\tau\nu}^A \hat{\varphi}_{\mu}^+ \hat{\varphi}_{\nu}^- . \quad (38)$$

We substitute the explicit expansions  $\hat{\varphi}_{\mu}^+ = \sum_{\rho} S_{\rho\mu}^{-1} \hat{\chi}_{\rho}^+$ , and  $A_{\mu\tau}^A = \sum_{\lambda \in A} S_{\mu\lambda} S_{(A)\lambda\tau}^{-1}$ , and get

$$\begin{aligned} \sum_{\nu, \tau \in A} \sum_{\mu} A_{\mu\tau}^A h_{\tau\nu}^A \hat{\varphi}_{\mu}^+ \hat{\varphi}_{\nu}^- &= \sum_{\lambda, \nu, \tau \in A} \sum_{\mu, \rho} S_{\mu\lambda} S_{(A)\lambda\tau}^{-1} h_{\tau\nu}^A S_{\rho\mu}^{-1} \hat{\chi}_{\rho}^+ \hat{\varphi}_{\nu}^- \\ &= \sum_{\lambda, \nu, \tau \in A} \sum_{\rho} \delta_{\rho\lambda} S_{(A)\lambda\tau}^{-1} h_{\tau\nu}^A \hat{\chi}_{\rho}^+ \hat{\varphi}_{\nu}^- = \sum_{\lambda, \nu, \tau \in A} S_{(A)\lambda\tau}^{-1} h_{\tau\nu}^A \hat{\chi}_{\lambda}^+ \hat{\varphi}_{\nu}^- . \end{aligned} \quad (39)$$

When calculating expectation values, the three- and four-center effects will again be accounted for through the “projected density matrices” Eq. (36),

owing to the fact that for the expectation values of the “mixed” pairs of creation and annihilation operators one has (in the single determinant case) [1,6]

$$\langle \hat{\chi}_\mu^+ \hat{\varphi}_\nu^- \rangle = (\mathbf{PS})_{\nu\mu} = \sum_\tau P_{\nu\tau} S_{\tau\mu} , \quad (40)$$

and

$$\langle \hat{\chi}_\mu^+ \hat{\chi}_\nu^+ \hat{\varphi}_\rho^- \hat{\varphi}_\kappa^- \rangle = (\mathbf{PS})_{\kappa\mu} (\mathbf{PS})_{\rho\nu} - (\mathbf{PS})_{\kappa\nu} (\mathbf{PS})_{\rho\mu} . \quad (41)$$

The overlap matrix elements appearing in these expressions, combined with the elements of matrices  $\mathbf{S}_{(X)}^{-1}$  in the terms like (39) give elements of matrices  $\mathbf{A}^X$ , occurring in the definitions (36).

Equation (33) contains also the adjoint of the term considered in Eq. (38). After the transformations analogous to those in Eq. (39), it will contain the subscripts of the matrices interchanged (complex conjugation) and the operator string  $\hat{\chi}_\lambda^+ \hat{\varphi}_\nu^-$  replaced by  $\hat{\varphi}_\nu^+ \hat{\chi}_\lambda^-$ ; its expectation value will be the complex conjugate of that for the term (38).

Based on these consideration, it is easy to see that the atomic Hamiltonians Eq. (33) can be obtained by Hermitizing the non-Hermitian atomic Hamiltonians  $\hat{H}'_A$  defined in Ref. 1:

$$\hat{H}_A = \frac{1}{2} (\hat{H}'_A + \hat{H}'_A^\dagger) . \quad (42)$$

As a consequence of this Hermitization, the antisymmetrized products of the full CI atomic solutions is not an eigenfunction of the sum of atomic operators  $\hat{H}_A$ , as was the case for the sum of non-Hermitian operators  $\hat{H}'_A$ . However, considering  $\hat{H}'_A$  acting to right and  $\hat{H}'_A^\dagger$  acting to left, one can easily see that the *expectation value* of that operator sum calculated with the antisymmetrized product of the atomic full CI solutions will be equal to the sum of atomic full CI energies.

The possibility to write down an (even if approximate) Hermitian Hamiltonian representing the sum of mono- and diatomic terms, has a significant conceptual importance, in particular because the expectation values of these terms of the Hamiltonian reproduce the one- and two-center energy components in the CECA analysis [9]. We hope that this way of writing the Hamiltonian will permit to accomplish some *a priori* approaches to molecular structure problems, and not only *a posteriori* ones like the energy decomposition. In the next section we shall consider the application of our approach at the SCF level of theory; it is not utilizing explicitly the detailed form (32)–(34) of the Hamiltonian.

## 5. SCF equations

The fact that the projective integral approximations discussed in Section 2 lead to the approximate Hermitian Hamiltonian (30), opens a quite straightforward way to introduce the respective approximate SCF equations. As the Hamiltonian in the second quantized framework is defined by the *integrals* over the basis orbitals, one should simply introduce the same integral approximations in the SCF equations as were used for the Hamiltonian.

Admitting unrestricted Hartee-Fock (UHF) case, the Hartree-Fock-Roothaan (HFR) equations are

$$\mathbf{F}^\sigma \mathbf{c}_i^\sigma = \varepsilon_i^\sigma \mathbf{S} \mathbf{c}_i^\sigma \quad (43)$$

where  $\mathbf{c}_i^\sigma$  is the vector of the LCAO coefficients of the  $i$ -th molecular orbital of spin  $\sigma$  ( $\sigma = \alpha$  or  $\beta$ ),  $\varepsilon_i^\sigma$  is its orbital energy, and the matrix elements of the Fockian are given in terms of the *integrals over the spatial orbitals* by

$$F_{\mu\nu}^\sigma = h_{\mu\nu} + \sum_{\rho,\tau} \left( D_{\tau\rho} [\mu\rho|\nu\tau] - P_{\tau\rho}^\sigma [\mu\rho|\tau\nu] \right) . \quad (44)$$

When introducing here the projective integral approximations, one should treat separately the cases, when the subscripts  $\mu$  and  $\nu$  of  $F_{\mu\nu}^\sigma$  correspond the same atom ( $\mu, \nu \in A$ ) and when they refer to different atoms ( $\mu \in A, \nu \in B; A \neq B$ ). By performing somewhat lengthy derivations outlined in the Appendix, and turning to the convention (11|22) for the two-electron integrals, usually preferred in the programming work, we get for the one-center Fock-matrix elements:

$$\begin{aligned} F_{\mu\nu}^\sigma \Big|_{\mu,\nu \in A} &\implies h_{\mu\nu} + \sum_{\rho,\tau \in A} \left[ D_{\rho\tau} (\mu\nu|\rho\tau) - P_{\rho\tau}^\sigma (\mu\rho|\nu\tau) \right] \\ &+ \sum_{\rho \in A} \sum_{\substack{B \\ B \neq A}} \sum_{\tau \in B} \left\{ D_{\rho\tau} (\mu\nu|\rho\tau) - \frac{1}{2} P_{\rho\tau}^\sigma [(\mu\rho|\nu\tau) + (\mu\tau|\nu\rho)] \right\} \\ &+ \sum_{\substack{B \\ B \neq A}} \sum_{\tau \in B} \sum_{\eta \in AB} \left\{ B_{\tau\eta}^{AB} (\mu\nu|\eta\tau) - \frac{1}{2} C_{\tau\eta}^{\sigma AB} [(\mu\tau|\eta\nu) + (\mu\eta|\nu\tau)] \right\} . \end{aligned} \quad (45)$$

In the case of two-center Fock-matrix elements, it is also possible to add and subtract terms as to get an expression with the “projected density matrices”  $\mathbf{B}^{AB}$  and  $\mathbf{C}^{\sigma AB}$ ; however that expression would contain a number of correction terms with sums containing one-center to two-center corrections, like the difference  $[\mu\rho|\nu\tau] - \sum_{\eta,\lambda \in B} A_{\mu\eta}^B A_{\rho\lambda}^B [\eta\lambda|\nu\tau]$ , essentially similar to those occurring in Eq (34). For that reason we separate out only the terms containing only one- and two-center integrals, and conserve explicitly the projective



expansion of the three- and four-center ones:

$$\begin{aligned}
F_{\mu\nu}^\sigma \Big|_{\substack{\mu \in A, \nu \in B \\ A \neq B}} &\implies h_{\mu\nu}^{AB} - \frac{1}{2} \sum_{\substack{C \\ C \neq A, B}} \left[ \sum_{\tau \in BC} A_{\mu\tau}^{BC} \langle \tau | \frac{Z_C}{r_C} | \nu \rangle + \sum_{\tau \in AC} A_{\nu\tau}^{AC} \langle \mu | \frac{Z_C}{r_C} | \tau \rangle \right] \\
&+ \sum_{\rho, \tau \in AB} \left[ D_{\rho\tau}(\mu\nu|\rho\tau) - P_{\rho\tau}^\sigma(\mu\rho|\nu\tau) \right] \\
&+ \frac{1}{2} \sum_{\substack{C, D \\ \{C, D\} \neq \{A, B\}}} \sum_{\rho \in C} \sum_{\tau \in D} \left[ \left( D_{\rho\tau} \sum_{\eta, \lambda \in BD} A_{\mu\eta}^{BD} A_{\rho\lambda}^{BD} \right. \right. \\
&\qquad\qquad\qquad \left. \left. - P_{\tau\rho}^\sigma \sum_{\eta, \lambda \in BD} A_{\mu\lambda}^{BD} A_{\rho\eta}^{BD} \right) (\eta\nu|\lambda\tau) \right. \\
&\left. + \left( D_{\rho\tau} \sum_{\eta, \lambda \in AC} A_{\nu\eta}^{AC} A_{\tau\lambda}^{AC} - P_{\tau\rho}^\sigma \sum_{\eta, \lambda \in AC} A_{\nu\lambda}^{AC} A_{\tau\eta}^{AC} \right) (\mu\eta|\rho\lambda) \right] \quad (46)
\end{aligned}$$

Here the notation  $\{C, D\} \neq \{A, B\}$  is used to indicate that at least one of the centers  $C, D$  is different from both  $A$  and  $B$ . When three-center integrals are expanded, it happens that  $D = B$  or  $C = A$ ; then obviously one should assume  $\mathbf{A}^{AA} \equiv \mathbf{A}^A$  and  $\mathbf{A}^{BB} \equiv \mathbf{A}^B$ .

An interesting property of these equations is that the respective SCF energy—the expectation value of the Hamiltonian (30)—will be an exact sum of the one- and two-center CECA energy components. The SCF energy may be calculated by using the standard formula

$$E = \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} + \frac{1}{2} \left\{ Tr \left[ \mathbf{P}^\alpha (\mathbf{h}^{eff} + \mathbf{F}^\alpha) \right] + Tr \left[ \mathbf{P}^\beta (\mathbf{h}^{eff} + \mathbf{F}^\beta) \right] \right\} \quad (47)$$

Here the effective core matrix  $\mathbf{h}^{eff}$  is defined by the one-electron components of the Fock-matrix elements (45), (46).

The conceptual approach behind these equations is quite similar to that we used [3,4] with success in the theory of intermolecular interactions in order to get wave functions which are free of the so called “basis set superposition error”. However, in contrast to that case, the present SCF equations are Hermitian and, as a consequence, may be directly used also to calculate the energy.

The actual programming of these equations may require introduction of different intermediate matrices; the effectiveness of the whole procedure may depend decisively on what quantities may be stored in the computer’s memory. However, we think that the exclusion of the explicit appearance of the

three- and four-center integrals will worth of these complications. A promising special applications of these equations may be their use as a special intermediate layer in the ONIOM-type approaches, between the parts used with full *ab initio* and those treated at the semiempirical level.

## 6. Conclusions

An attempt is made to develop a new scheme of non-empirical SCF-LCAO-MO calculations, which may represent an alternative for both the “orthodox” *ab initio* scheme and the semiempirical theories. (It may also be a useful intermediate layer in the ONIOM-type approaches.) For that reason it is suggested to treat all the one- and two-center integrals in a strict *ab initio* manner and to use approximate projective expansions for the three- and four-center ones—the same as were used in the CECA energy decomposition scheme [9]. These projective integral expansions permit to express the leading “physical” components of the three- and four-center integrals through one- center and two-center integrals and the overlap ones. These expansions are utilized to rewrite the second quantized Born-Oppenheimer LCAO Hamiltonian in an approximate form not containing any three- and four-center integrals, and to write down a Hermitian version of the “Chemical Hamiltonian” [1], containing only mono- and diatomic terms. Incorporating these projective integral approximations in the HFR equations, one obtains some modified SCF equations. The calculations will require only one- and two-center integrals and some quantities calculated by using the overlap matrix. Nevertheless, for large basis sets this method should converge to the usual Hartree-Fock limit. The approach is in the spirit of the CHA-SCF equations [3, 4] used with success to exclude basis set superposition error in the theory of intermolecular interactions, but here the Fockian is Hermitian, and can also directly be applied to calculate energy.

## Appendix. Derivation of Eq. (45)

When considering the integral approximations, we should stick to the [12|12] convention for the integrals permitting to distinguish the terms originating from the “bra”-s and “ket”-s, respectively; in the final formulae we have turned to the (11|22) convention more convenient in programming.

Systematizing the terms according to the centers of the orbitals involved, for the one-center matrix elements of matrix  $\mathbf{F}^\sigma$  one has

$$\begin{aligned}
F_{\mu\nu}^\sigma \Big|_{\mu,\nu \in A} &= h_{\mu\nu} + \sum_{\rho,\tau \in A} \left( D_{\tau\rho}[\mu\rho|\nu\tau] - P_{\tau\rho}^\sigma[\mu\rho|\tau\nu] \right) \\
&+ \sum_{\substack{B \\ B \neq A}} \sum_{\rho \in B} \sum_{\tau \in A} \left( D_{\tau\rho}[\mu\rho|\nu\tau] - P_{\tau\rho}^\sigma[\mu\rho|\tau\nu] \right) \\
&+ \sum_{\substack{B \\ B \neq A}} \sum_{\tau \in B} \sum_{\rho \in A} \left( D_{\tau\rho}[\mu\rho|\nu\tau] - P_{\tau\rho}^\sigma[\mu\rho|\tau\nu] \right) \\
&+ \sum_{\substack{B,C \\ B,C \neq A}} \sum_{\rho \in B} \sum_{\tau \in C} \left( D_{\tau\rho}[\mu\rho|\nu\tau] - P_{\tau\rho}^\sigma[\mu\rho|\tau\nu] \right)
\end{aligned} \tag{48}$$

Only the last sum of Eq. (48) contain three- or four-center integrals that need to be approximated, therefore we shall consider its terms in detail. At first, we substitute the approximations (6) in the first term of that sum:

$$\begin{aligned}
\sum_{\substack{B,C \\ B,C \neq A}} \sum_{\rho \in B} \sum_{\tau \in C} D_{\tau\rho}[\mu\rho|\nu\tau] &\implies \sum_{\substack{B,C \\ B,C \neq A}} \sum_{\rho \in B} \sum_{\tau \in C} D_{\tau\rho} \frac{1}{2} \left( \sum_{\lambda,\eta \in AC} A_{\mu\lambda}^{AC} A_{\rho\eta}^{AC} [\lambda\eta|\nu\tau] \right. \\
&\left. + \sum_{\lambda,\eta \in AB} A_{\lambda\nu}^{AB\dagger} A_{\eta\tau}^{AB\dagger} [\mu\rho|\lambda\eta] \right)
\end{aligned} \tag{49}$$

Both subscripts of the coefficient  $A_{\mu\lambda}^{AC}$  in the first term are belonging to the diatomic fragment  $AC$ ; as noted above, the intra-fragment blocks of the matrices  $\mathbf{A}$  are unit-matrices, therefore this coefficient reduces to the Kronecker delta  $\delta_{\mu\lambda}$ . Similarly, in the second term  $A_{\lambda\nu}^{AB\dagger} = \delta_{\lambda\nu}$ . Utilizing this we get:

$$\begin{aligned}
\sum_{\substack{B,C \\ B,C \neq A}} \sum_{\rho \in B} \sum_{\tau \in C} D_{\tau\rho}[\mu\rho|\nu\tau] &\implies \sum_{\substack{B,C \\ B,C \neq A}} \sum_{\rho \in B} \sum_{\tau \in C} D_{\tau\rho} \frac{1}{2} \left( \sum_{\eta \in AC} A_{\rho\eta}^{AC} [\mu\eta|\nu\tau] \right. \\
&\left. + \sum_{\eta \in AB} A_{\eta\tau}^{AB\dagger} [\mu\rho|\nu\eta] \right) .
\end{aligned} \tag{50}$$

In the followings we shall assume that we use real basis orbitals and orbital coefficients—as it is usually the case in the practice. Then  $D_{\tau\rho} = D_{\rho\tau}$ ,  $A_{\eta\tau}^{AB\dagger} = A_{\tau\eta}^{AB}$ ,  $[\mu\rho|\lambda\eta] = [\lambda\eta|\mu\rho]$ , and interchanging some summation indices we can conclude that the two sums are equal. Thus we have in the real case

$$\sum_{\substack{B,C \\ B,C \neq A}} \sum_{\rho \in B} \sum_{\tau \in C} D_{\tau\rho} [\mu\rho|\nu\tau] \implies \sum_{\substack{B,C \\ B,C \neq A}} \sum_{\rho \in B} \sum_{\tau \in C} D_{\tau\rho} \sum_{\eta \in AC} A_{\rho\eta}^{AC} [\mu\eta|\nu\tau]. \quad (51)$$

The summation over  $\rho \in B$ ;  $B \neq A$  in the right-hand side of Eq. (51) means that  $\rho$  runs over all the orbital indices, except those assigned to atom  $A$ ; we may add and subtract the sum for the case  $\rho \in A$ :

$$\begin{aligned} \sum_{\substack{B,C \\ B,C \neq A}} \sum_{\rho \in B} \sum_{\tau \in C} D_{\tau\rho} [\mu\rho|\nu\tau] &\implies \sum_{\substack{C \\ C \neq A}} \sum_{\rho} \sum_{\tau \in C} D_{\tau\rho} \sum_{\eta \in AC} A_{\rho\eta}^{AC} [\mu\eta|\nu\tau] \\ &- \sum_{\substack{C \\ C \neq A}} \sum_{\rho \in A} \sum_{\tau \in C} D_{\tau\rho} \sum_{\eta \in AC} A_{\rho\eta}^{AC} [\mu\eta|\nu\tau]. \end{aligned} \quad (52)$$

In the first term on the right-hand side we can sum over  $\rho$  to get the “projected density matrix element”  $B_{\tau\eta}^{AC}$ , while in the second term the coefficient  $A_{\rho\eta}^{AC}$  again reduces to the Kronecker delta  $\delta_{\rho\eta}$ . Thus we get, changing the summation index  $C$  to  $B$  in the right-hand side:

$$\begin{aligned} \sum_{\substack{B,C \\ B,C \neq A}} \sum_{\rho \in B} \sum_{\tau \in C} D_{\tau\rho} [\mu\rho|\nu\tau] &\implies \sum_{\substack{B \\ B \neq A}} \sum_{\tau \in B} \sum_{\eta \in AB} B_{\tau\eta}^{AB} [\mu\eta|\nu\tau] \\ &- \sum_{\substack{B \\ B \neq A}} \sum_{\rho \in A} \sum_{\tau \in B} D_{\tau\rho} [\mu\rho|\nu\tau]. \end{aligned} \quad (53)$$

The second sum just cancels the respective term in the third line of Eq. (48).

The second (exchange) term in the fourth line of Eq. (48) transforms analogously. However, in that case the two terms are not equal, as were in Eq. (50), and there is no full canceling of the second term in the third line of Eq. (48); instead the *half* of the respective terms in both second and third lines is canceled.

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