# A CNDO/INDO Molecular Orbital Formalism for the Elements H to Br. Theory

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A CNDO and INDO formalism is presented that can be used for any atom combination up to bromine under inclusion of the first transition metal series. The semiempirical parameters were chosen to reproduce results of *ab initio* calculations on metalorganic compounds. The calculational results are invariant to rotations of the coordinate system but not to a general transformation into other basis functions. The one-center Coulomb-expressions were selected in order to include intraatomic correlation contributions. Within the CNDO model this could be achieved by the scaled monopole term $F_0$, while in the INDO framework the one-center Coulomb integrals are given as a sum of the monopole-contribution $F_0$ and higher multipole contributions expressed as a linear combination of Slater–Condon parameters. The invariance problem in the case of local rotations within the INDO approximation was solved by considering the combination of one-center Coulomb and exchange integrals as a function of $l$ but independent of $m$. The two-center electron-electron interaction terms were calculated via the Dewar–Sabelli, Ohno–Klopman relation. Penetration effects were treated according to Fischer and Kollmar. For the resonance integral $H_{\mu\nu}^{AB}$ parameters are used which carry information related to the directed nature of the chemical bond by using optimized Klondyke functions. The core-core repulsion is constructed as a superposition of a soft potential function, describing polarization effects of the atomic cores, and a hard repulsion function, avoiding the collapse of the atomic cores with decreasing distance.

**Key words:** Semiempirical LCAO-methods – CNDO- and INDO-approximation – Transition metal compounds – theory and parametrization.

## 1. Introduction

To understand the electronic structure and chemistry of organometallic compounds two calculational strategies are currently advocated: qualitative type

of calculations based on the Wolfsberg–Helmholtz effective Hamiltonian on one side, and *ab initio* calculations on small species on the other. The first approach has been used by R. Hoffmann and coworkers [1] within the framework of the Extended Hückel (EH) method. With this method nearly all systems of interest can be treated provided one focuses on qualitative features only. Typical examples for *ab initio* calculations that reach double zeta quality are: $MnO_4^-$ [2], bis($\pi$-allyl)nickel [3], ferrocene [4], $Cr(CO)_5$ [5] $HCo(CO)_4$ [6], $CuCl_4^{2-}$ [7] $NiCl_4$ [7]. Unfortunately, the prohibitive computational expense prevents the applicability of this approach to most organometallic compounds of general interest.

A path avoiding the shortcomings of the EH procedure and the inherent computational difficulties of an *ab inito* approach seems to be offered by semiempirical LCAO methods, trying to mimic the results of a complete *ab initio* approach with an effective approximate Hamiltonian containing various adjustable parameters. The theoretical aspects of such a $1:1$ correspondence between an *ab initio* approach and semiempirical models have been discussed by several authors [8].

In the following we report on a MO model based on the Neglect of Differential Overlap (NDO) approximation for all atoms up to bromine including the first transition metal series. In the proposed semiempirical approach it is possible to include intraatomic and interatomic electron correlation within the Hartree–Fock (HF) scheme and thus in principle to go beyond an *ab initio* HF calculation. In order to carry out fast calculations we have chosen the two simplest NDO approximations, the CNDO (Complete Neglect of Differential Overlap) [9] and INDO (Intermediate Neglect of Differential Overlap) [10] procedure.

In recent years several attempts to extend the CNDO and INDO approximation to transition metals have appeared [11–13]. The first systematic transfer of Pople's CNDO/2 approximation [9] to the complete $3d$ series from Sc to Cu was performed by Clack, Hush and Yandle [14] followed by an extension to the INDO model [15]. Both formalisms took over the shortcomings of the early NDO parametrization schemes [9, 10], e.g. the tendency to place $\sigma$ orbitals at too high energies [16]. This fact limits very much the CNDO/INDO results for those interested in electronic absorption spectra or photoelectron spectra. Among the many other semiempirical NDO versions [17–20] the most recent ones by Freund and Hohlneicher [21] and Bacon and Zerner [22] should be mentioned. Freund and Hohlneicher make use of parameters of the Pople CNDO/2 version in case of atoms of the first row, while Zerner and coworkers include in their INDO version all one-center integrals including hybrid terms for the $3d$ atomic orbitals [22]. Our main goal is to develop a unique model which can be used to interpret photoelectron spectra of transition metal compounds and which is applicable to the following atoms:

(a) the second period from Li to F, for which CNDO/2 and INDO originally was developed [9, 10]
(b) the third period from Na to Cl, in analogy to the Santry–Segal extension of the CNDO/2 formalism to a *sp*, *spd* and *sp'd'* version [23]
(c) the elements Ga to Br that have been parametrized by Hase and Schweig in a CNDO/2 modification [24].

For the elements Ga to Br only a CNDO model could be designed as the necessary experimental Slater–Condon parameters are not available for these atoms. For the same reason the elements of the third period can be treated with a $sp'$ basis (CNDO and INDO) but within a $sp'd'$ basis only a CNDO approximation is possible. Due to the enormous number of interatomic combinations it is not possible to determine the semiempirical parameters by means of a least square procedure with respect to experimental observables (geometries, heats of formation, dipole moments, ionization potentials). The parameters were adjusted by comparison with the results of *ab initio* calculations and experimental equilibrium geometries of organic molecules and transition metal compounds. In case of transition metal complexes we were anyhow limited to such a procedure as most of the necessary experimental data (heats of formation, dipole moments) are not known. As reference data we have chosen the results of *ab initio* calculations on about 100 molecules not containing a $3d$ atom [25–27]. The reference systems of the first transition metal series are collected in Table 1. In this table also the *ab initio* basis before and after contraction (in every case Gaussian functions were used as atomic basis) is listed which allows an estimate of the *ab initio* quality we used as comparison. The semiempirical parameters of those $3d$ transition metals not contained in Table 1 were determined by linear interpolation across the complete series.

## 2. Basis Equations

Starting point of our approximation is the LCAO-formalism within the Hartree–Fock model. The energies of the canonical Hartree–Fock orbitals are obtained by diagonalization of the Fock-matrix [28].

$$\mathbb{F} \cdot \mathbb{C} = \mathbb{S} \cdot \mathbb{C} \cdot \mathbb{E}. \tag{1}$$

In the matrix-representation (1) $\mathbb{F}$ symbolizes the Fock-operator, $\mathbb{S}$ the overlap-matrix, $\mathbb{C}$ the LCAO-eigenvectors and $\mathbb{E}$ the orbital energies. In the case of Löwdin orthogonalized atomic orbitals (OAO) $\mathbb{E}$ is calculated via (2) where $^\lambda\mathbb{F}$ and $^\lambda\mathbb{C}$ are related to $\mathbb{F}$ and $\mathbb{C}$ through (3) and (4).

$$^\lambda\mathbb{F} \cdot {}^\lambda\mathbb{C} = {}^\lambda\mathbb{C} \cdot {}^\lambda\mathbb{E} \tag{2}$$

$$^\lambda\mathbb{C} = \mathbb{S}^{1/2} \cdot \mathbb{C} \tag{3}$$

$$^\lambda\mathbb{F} = \mathbb{S}^{-1/2} \cdot \mathbb{F} \cdot \mathbb{S}^{-1/2}. \tag{4}$$

If the well known NDO-approximations (5) and (6) are used within the Hartree–Fock framework the approximate correspondence (7) exists.

$$\langle \mu\nu|\lambda\sigma\rangle = \langle \mu\mu|\lambda\lambda\rangle\delta_{\mu\nu}\delta_{\lambda\sigma} \tag{5}$$

$$\mathbb{S}_{\mu\nu} = \langle \mu|\nu\rangle = \delta_{\mu\nu} \tag{6}$$

$$^{\text{NDO}}\mathbb{F} \approx {}^\lambda\mathbb{F} \tag{7}$$

$\mu$, $\nu$, $\lambda$ and $\sigma$ represent AO-basis-functions. In the present work we are focused to (2) as framework of our CNDO/INDO-model as the NDO-approximation simulates a basis of orthogonal atomic orbitals [29].

**Table 1.** Selected *ab initio* calculations on transition metal compounds used as reference systems for the parametrization

| Compound | GTO before contraction $s/p/d$ | | GTO after contraction $s/p/d$ | | Reference |
|---|---|---|---|---|---|
| $MnO_4^-$ | Mn | 24/15/5 | Mn | 4/3/1 | a |
| | O | 12/5 | O | 2/1 | |
| $MnO_4^-/CrO_4^{2-}$ | Mn(Cr) | 12/9/6 | Mn(Cr) | 4/3/2 | b |
| | O | 6/3 | O | 2/1 | |
| $MnO_4^-$ | Mn | 16/13/6 | Mn | 14/10/5 | [2] |
| | O | 10/6 | 0 | 7/3 | |
| $MnO_4^-/CrO_4^{2-}/VO_4^{3-}$ | Mn(Cr, V) | 12/9/6 | Mn(Cr, V) | 4/3/2 | [48a] |
| | O | 6/3 | O | 6/3 | |
| $MnO_4^-$ | Mn | 15/11/5 | Mn | 4/3/2 | c |
| | O | 8/5 | '> | 2/2 | |
| $MnO_4^-$ | Mn | 11/7/5 | Mn | 4/3/2 | d |
| | Mn | 12/8/6 | Mn | 5/4/3 | |
| | O | 8/4 | O | 3/2 | |
| | O | 8/5 | O | 3/2 | |
| $CuCl_4^{2-}$ | Cu | 10/6/3 | Cu | 5/3/2 | e |
| | Cl | 8/4 | Cl | 3/3 | |
| $CuCl_4^{2-}$ | Cu | 12/8/5 | Cu | 5/4/2 | f |
| | Cl | 10/6 | Cl | 3/3 | |
| $CuCl_4^{2-}/NiCl_4^{2-}$ | Cu(Ni) | 14/9/5 | Cu(Ni) | 9/5/3 | g |
| | Cl | 12/9 | Cl | 7/5 | |
| $Ni(CO)_4/Cr(CO)_6$ | Ni(Cr) | 12/9/6 | Ni(Cr) | 4/3/2 | h |
| | C(O) | 6/3 | C(O) | 2/1 | |
| $Ni(CO)_4/Ni(CN)_4^{2-}$ | Ni | 12/8/5 | Ni | 5/4/2 | i |
| | C | 8/4 | C | 2/1 | |
| | N(O) | 8/4 | N(O) | 2/1 | |
| $Ni(CO)_4$ | pseudopot. | | pseudopot. | | j |
| $Cr(CO)_5$ | Cr | 12/8/5 | Cr | 4/3/3 | [5] |
| | C(O) | 6/3 | C(O) | 2/1 | |
| $Ni(CN)_4^{2-}$ | Ni | 12/8/5 | Ni | 5/4/2 | k |
| | C | 8/4 | C | 3/2 | |
| | N | 8/4 | C | 2/1 | |
| $FeF_3$ | Fe | 14/9/5 | Fe | 9/5/2 | l |
| | F | 9/5 | F | 4/2 | |
| $NiF_6^{4-}$ | Ni | 15/11/5 | Ni | 5/3/2 | m |
| | F | 8/5 | F | 2/2 | |
| $Fe(C_5H_5)_2$ | Fe | 12/7/5 | Fe | 4/3/2 | n |
| | C | 8/4 | C | 2/1 | |
| | H | 3 | H | 1 | |

**Table 1.** Continued

| Compound | GTO before contraction $s/p/d$ | | GTO after contraction $s/p/d$ | | References |
|---|---|---|---|---|---|
| $Fe(C_5H_5)_2$ | Fe | 12/6/4 | Fe | 8/4/3 | [4] |
| | C | 7/3 | C | 4/2 | |
| | H | 4/1 | H | 2/1 | |
| $Ni(C_3H_5)_2$ | Ni | 10/6/3 | Ni | 5/4/2 | o |
| | C | 6/3 | C | 2/1 | |
| | H | 3 | H | 1 | |
| $Ni(C_3H_5)_2$ | Ni | 11/7/5 | Ni | 4/3/2 | [3] |
| | C | 8/4 | C | 3/2 | |
| | H | 4 | H | 2 | |
| $HCo(CO)_4/Co(CO)_4^-$ | Co | 12/7/4 | Co | 4/3/2 | [6] |
| | C(O) | 7/3 | C(O) | 3/2 | |
| | H | 4 | H | 2 | |

GTO = Gauss-Type-Orbital
pseudopot. = pseudopotential-approximation

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Within NDO-based Hartree–Fock equations there are different possibilities to satisfy parts of invariance criteria [28, 9, 30]. We make use of an algorithm where the approximations are invariant under transformations of the local axes but not under a transformation into a hybrid basis. This criterion is the foundation of the MCZDO-formalism of Brown and Roby [31].

With this degree of freedom the following matrix-elements for the Fock-operator are obtained in the CNDO- and INDO-formalism in the case of a closed shell and a UHF open shell problem [32]:

CNDO closed shell

$$F_{\mu\mu} = H_{\mu\mu} + \sum_\lambda P_{\lambda\lambda}(\mu\mu|\lambda\lambda) - \tfrac{1}{2}P_{\mu\mu}(\mu\mu|\mu\mu) \tag{8}$$

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}(\mu\mu|\nu\nu). \tag{9}$$

CNDO open shell

$$F^{\alpha}_{\mu\mu} = H_{\mu\mu} + \left(\sum_{\lambda \in A} P_{\lambda\lambda} - P^{\alpha}_{\lambda\lambda}\right)(\mu\mu|\lambda\lambda) + \sum_{\lambda \in B}^{B \neq A} P_{\lambda\lambda}(\mu\mu|\lambda\lambda) \tag{10}$$

$$F^{\alpha}_{\mu\nu} = H_{\mu\nu} - P^{\alpha}_{\mu\nu}(\mu\mu|\nu\nu). \tag{11}$$

INDO closed shell

$$F^{AA}_{\mu\mu} = H_{\mu\mu} + \sum_{\lambda \in A} P_{\lambda\lambda}[(\mu\mu|\lambda\lambda) - \tfrac{1}{2}(\mu\lambda|\mu\lambda)] + \sum_{\sigma \in B}^{B \neq A} P_{\sigma\sigma}(\mu\mu|\sigma\sigma) \tag{12}$$

$$F^{AA}_{\mu\nu} = H_{\mu\nu} - \tfrac{3}{2}P_{\mu\nu}(\mu\nu|\mu\nu) - \tfrac{1}{2}P_{\mu\nu}(\mu\mu|\nu\nu) \tag{13}$$

$$F^{AB}_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}(\mu\mu|\nu\nu). \tag{14}$$

INDO open shell

$$F^{AA\alpha}_{\mu\mu} = H_{\mu\mu} + \sum_{\lambda \in A} [P_{\lambda\lambda}(\mu\mu|\lambda\lambda) - P^{\alpha}_{\lambda\lambda}(\mu\lambda|\mu\lambda)] + \sum_{\sigma \in B}^{B \neq A} P_{\sigma\sigma}(\mu\mu|\sigma\sigma) \tag{15}$$

$$F^{AA\alpha}_{\mu\nu} = (2P_{\mu\nu} - P^{\alpha}_{\mu\nu})(\mu\nu|\mu\nu) - P^{\alpha}_{\mu\nu}(\mu\mu|\nu\nu) \tag{16}$$

$$F^{AB\alpha}_{\mu\nu} = H_{\mu\nu} - P^{\alpha}_{\mu\nu}(\mu\mu|\nu\nu). \tag{17}$$

The symbols in Eqs. (8)–(17) correspond to the standard labels defined in the literature [9, 10]. $F_{\mu\mu}$ stands for a diagonal-element of the Fock-operator while $F_{\mu\nu}$, $F^{AA}_{\mu\nu}$ and $F^{AB}_{\mu\nu}$ symbolize off-diagonal elements. In the INDO-model one has to differ between $F^{AA}_{\mu\nu}$ where both atomic basis functions are centered at atom $A$ and $F^{AB}_{\mu\nu}$ where $\mu$ is placed at $A$ and $\nu$ at $B$. The open shell equations are given for $\alpha$-spin orbitals and a corresponding set also holds for $\beta$-spin orbitals [32]. $H_{\mu\nu}$ and $H_{\mu\mu}$ define the elements of the core-Hamiltonian

$$H_{\mu\nu} = \langle\mu|H^{\text{core}}|\nu\rangle \tag{18}$$

The electron-electron interaction-integrals are generally defined in (19).

$$(\mu\nu|\lambda\sigma) = \langle\mu(1)\nu(1)|\frac{1}{r_{12}}|\lambda(2)\sigma(2)\rangle. \tag{19}$$

In the case of the INDO equations (12)–(17) the one-center exchange integrals $(\mu\nu|\mu\nu)$ ($\mu \in A$, $\nu \in A$) are taken into account leading to the EMZDO (Exchange Modified Zero Differential Overlap) model of Dixon [10], the well known INDO-version of Pople [10] and the Many-Center-ZDO-extension of Brown and Roby [31]. The elements of the bond-order matrix, $P_{\mu\nu}$, are defined in the usual way [9, 10].

The expressions for the total energies $E_{\text{tot}}$ for closed and open shell systems are given in (20) and (21); here $E^{\text{core}}_{AB}$ stands for the repulsion of the atomic cores $A$ and $B$.

Closed shell system

$$E_{\text{tot}} = \tfrac{1}{2} \cdot \sum_{\mu} \sum_{\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) + \sum_{A<B} \sum E_{AB}^{\text{core}}. \tag{20}$$

Open shell system

$$E_{\text{tot}} = \tfrac{1}{2} \cdot \sum_{\mu} \sum_{\nu} [P_{\mu\nu}^{\alpha}(H_{\mu\nu} + F_{\mu\nu}^{\alpha}) + P_{\mu\nu}^{\beta} \quad (H_{\mu\nu} + F_{\mu\nu}^{\beta})] + \sum_{A<B} \sum E_{AB}^{\text{core}}. \tag{21}$$

In the UHF-formalism for open shell systems the Hartree–Fock determinant for $\alpha$- and $\beta$-spin orbitals is an eigenfunction of the operator $S_z$ ($z$ component of the total spin $S$) but not an eigenfunction of $S^2$. There are contributions of higher spin states in the HF groundstate determinant. By means of spin-projection it is possible to create HF-solutions that are approximate eigenfunctions of $S^2$. In most semiempirical MO-versions, on the other hand, it has been demonstrated that the approximate annihilation of a single spin-component [33] did not improve the computational results significantly while also the lowering of the total energy was negligible [22, 34]. Often calculated spin-densities before annihilation were in better agreement with experimental findings than after simple annihilation. Therefore in the present study no use of spin-projection is made in the open shell calculations.

For the computation of the elements of the Fock-matrix the following terms must be determined either theoretically or by semiempirical estimation techniques: one-center Coulomb-integrals, one-center exchange-integrals (INDO), two-center Coulomb-intergrals, diagonal-elements of the core-Hamiltonian $H_{\mu\mu}$, the corresponding nondiagonal contributions $H_{\mu\nu}$ and a repulsion potential $E_{AB}^{\text{core}}$ between the cores of the atoms $A$ and $B$. Additionally an AO-basis must be defined. A detailed description of the necessay parametrization scheme is given in the following section.

## 3 Parametrization

In the present CNDO/INDO-formalism only the valence electrons are treated explicitly, all other electrons belong to the atomic cores. The valence AO's for the various atoms are defined below:

H: $1s$
Li–F: $2s$, $2p$
Na–Cl: $3s$, $3p$, $(3d)$
K–Zn: $4s$, $4p$, $3d$
Ga–Br: $4s$, $4p$

For the determination of the zeta exponents a set of single-zeta Slater-type orbitals is used. Although this single-zeta limitation is not particularly adequate when going beyond the elements of the third period, for reasons of computational simplicity we adhered to this basis set as there are several efficient techniques to

compensate for the failures and shortcomings of a single-zeta basis within a semiempirical LCAO-version. All exponents were determined by Burns' rules [35] which have been derived by matching the corresponding wavefunctions to accurate atomic HF-functions instead of minimizing the total energy (of the atoms) as a function of the zeta-parameters. Thus Burns' exponents should be a useful basis for the calculation of expectation values in the bonding region.

Within the CNDO/INDO-formalism the electron–electron interaction-integrals can be devided into two classes, the one-center integrals (Coulomb ($J_{\mu\nu}$) and exchange ($K_{\mu\nu}$) integrals) and two-center contributions (of Coulomb-type only). Due to different approximations within the one-center terms in the case of the CNDO- and INDO-formalism the corresponding integrals must be treated differently in the two NDO-procedures. To describe electron–electron interaction for CNDO and for INDO we have extended a procedure of Fischer–Hjalmars [36] as we combine theoretically calculated and spectroscopically observed increments for the determination of the one-center Coulomb-integrals.

The monopole-term of the Laplace–Neumann-expansion, $F_0$, is calculated analytically:

$$F_0 = (\mu\mu|\nu\nu)_0 = \langle s_\mu(1)s_\mu(1)|\frac{1}{r_{12}}|s_\nu(2)s_\nu(2)\rangle. \tag{22}$$

$s_\mu(1)$ and $s_\nu(2)$, respectively, symbolize AO's of $s$-symmetry which give rise to the monopole-contribution. To take into account intraatomic correlation the analytically calculated $F_0$-value is multiplied by a scaling factor $f$ reducing the absolute value of $F_0$:

$$F_0^{exp} = F_0 \cdot f. \tag{23}$$

For the determination of $f$ we made use of atom spectroscopic data [37], the theoretical results of Brown and Roby [31, 38] (who analyzed scaling procedures in detail) and by comparison with the integral-evaluation via the Saturno-operator where the electron motion is completely correlated [39]:

$$\frac{1}{r_{12}} \rightarrow \frac{1}{r_1 + r_2}. \tag{24}$$

The scaling factors were determined in a way that the calculated monopole terms of the Laplace–Neumann-expansion agreed both with $F_0^{exp}$ values derived from the experimental data of Ref. 37 by subtracting the associated higher multipole contributions and with Coulomb-integrals calculated for some sample atoms via the $1/(r_1 + r_2)$ operator.

The scale-factors together with the single-zeta values are collected in Table 2.

Due to the invariance condition with respect to a local rotation of the atomic coordinate system the CNDO Coulomb-integrals are completely determined by the scaled monopole-expression (25):

$$J_{\mu\nu}^{CNDO} = (\mu\mu|\nu\nu)^{CNDO} \approx F_0 \cdot f. \tag{25}$$

**Table 2.** Burns exponents and scaling factors

| Atom | $\zeta_s$ | $\zeta_p$ | $\zeta_d$ | $f_s$ | $f_p$ | $f_d$ |
|------|-----------|-----------|-----------|-------|-------|-------|
| H  | 1.300[a]   |         |         | 0.741 |        |       |
| Li | 0.600      | 0.500   |         | 0.848 | 0.934  |       |
| Be | 0.900      | 0.750   |         | 0.814 | 0.888  |       |
| B  | 1.1225     | 1.000   |         | 0.780 | 0.842  |       |
| C  | 1.500      | 1.325   |         | 0.746 | 0.796  |       |
| N  | 1.79825[b] | 1.56875[a] |      | 0.712 | 0.750  |       |
| O  | 2.200      | 1.975   |         | 0.678 | 0.704  |       |
| F  | 2.525      | 2.300   |         | 0.644 | 0.658  |       |
| Na | 0.900      | 0.533   | 0.330   | 0.670 | 0.870  | 1.00  |
| Mg | 1.100      | 0.700   | 0.417   | 0.670 | 0.870  | 1.00  |
| Al | 1.317      | 0.867   | 0.500   | 0.670 | 0.870  | 1.00  |
| Si | 1.533      | 1.083   | 0.667   | 0.670 | 0.870  | 1.00  |
| P  | 1.750      | 1.300   | 0.833   | 0.670 | 0.870  | 1.00  |
| S  | 1.967      | 1.517   | 1.000   | 0.670 | 0.870  | 1.00  |
| Cl | 2.183      | 1.733   | 1.167   | 0.670 | 0.870  | 1.00  |
| K  | 0.700      | 0.450   | 1.500   | 0.786 | 1.000  | 0.609 |
| Ca | 0.825      | 0.525   | 1.783   | 0.786 | 1.000  | 0.607 |
| Sc | 0.950      | 0.600   | 2.067   | 0.786 | 1.000  | 0.605 |
| Ti | 1.075      | 0.675   | 2.283   | 0.786 | 1.000  | 0.603 |
| V  | 1.200      | 0.750   | 2.500   | 0.786 | 1.000  | 0.601 |
| Cr | 1.325      | 0.825   | 2.650   | 0.786 | 1.000  | 0.599 |
| Mn | 1.450      | 0.900   | 2.933   | 0.786 | 1.000  | 0.597 |
| Fe | 1.575      | 0.975   | 3.150   | 0.786 | 1.000  | 0.595 |
| Co | 1.700      | 1.050   | 3.367   | 0.786 | 1.000  | 0.593 |
| Ni | 1.825      | 1.125   | 3.583   | 0.786 | 1.000  | 0.591 |
| Cu | 1.950      | 1.200   | 3.733   | 0.786 | 1.000  | 0.589 |
| Zn | 2.075      | 1.272   | 4.067   | 0.786 | 1.000  | 0.587 |
| Ga | 2.238      | 1.400   |         | 0.4553 | 0.7153 |      |
| Ge | 2.400      | 1.563   |         | 0.4553 | 0.7153 |      |
| As | 2.563      | 1.725   |         | 0.4553 | 0.7153 |      |
| Se | 2.726      | 1.888   |         | 0.4553 | 0.7153 |      |
| Br | 2.889      | 2.050   |         | 0.4553 | 0.7153 |      |

[a] The H-exponent is taken in contrast to Burns rules [35] as 1.300, a standard-value in most semiempirical LCAO-versions.
[b] In the case of N the $\zeta$ values have been optimized by means of MO calculations on various compounds with nitrogen.

Within the INDO-framework higher multipole components have to be added to $F_0$ in the Laplace–Neumann-expansion. In the case of an $s$, $p$, $d$ basis the following Slater–Condon-parameters [40] for the one-center Coulomb- and exchange-integrals are observed:

$$F_2^{pp}, F_2^{dd}, F_4^{dd}, G_1^{sp}, G_2^{sd}, G_1^{pd}, G_3^{pd}.$$

Thus a one-center Coulomb-integral in the INDO-model is given by the scaled monopole-term $F_0 \cdot f$ and a particular combination of Slater–Condon-parameters. All necessary values ($F_2^{pp}$, $F_2^{dd}$, $F_4^{dd}$, $G_1^{sp}$, $G_2^{sd}$, $G_1^{pd}$ and $G_3^{pd}$) are known from atom spectroscopic data and are collected in Tables 3 and 4.

**Table 3.** Slater–Condon-parameter for the INDO-formalism; $F$-intergrals $(cm^{-1})$

| Atom | $F_2^{pp}$ | | $F_2^{dd}$ | $F_4^{dd}$ |
|------|-----------|---|-----------|-----------|
| H | | | | |
| Li | 426 [a] | | | |
| Be | 857 [60] | | | |
| B | 1123 [60] | | | |
| C | 1455 [60] | | | |
| N | 2084 [60] | | | |
| O | 2227 [60] | | | |
| F | 2774 [61] | | | |
| Na | 196 [a] | | | |
| Mg | 1056 [60] | | | |
| Al | 517 [60] | | | |
| Si | 730 [60] | | | |
| P | 951 [60] | | | |
| S | 1464 [60] | | | |
| Cl | 2056 [60] | | | |
| K | 46 [a] | | 199 [c] | 5.0 [c] |
| Ca | 93 [60] | | 400 [63] | 10.0 [63] |
| Sc | 330 [c] | | 745 [b] | 53.5 [b] |
| Ti | 350 [62] | | 875 [62] | 63.0 [62] |
| V | 370 [62] | | 1005 [62] | 72.5 [62] |
| Cr | 390 [62] | | 1135 [62] | 82.0 [62] |
| Mn | 410 [62] | | 1265 [62] | 91.5 [62] |
| Fe | 430 [62] | | 1395 [62] | 101.0 [62] |
| Co | 450 [62] | | 1525 [62] | 110.5 [62] |
| Ni | 470 [62] | | 1655 [62] | 120.0 [62] |
| Cu | 490 [62] | | 1785 [62] | 129.5 [62] |
| Zn | 510 [b] | | 1915 [b] | 139.0 [b] |

[a] Extrapolated from the values cited under [60].
[b] Extrapolated from the values cited under [62].
[c] Extrapolated from the values cited under [63].

The $F_0$-contributions together with the higher multipole components ($F$- and $G$-integrals) have to be combined to rotationally invariant one-center integrals. For an $s$, $p$ and $d$ atomic orbital basis this is discussed in the literature [41]. Invariance with respect to local rotations can be maintained if the set of one-center Coulomb-integrals $J_{\mu\mu}$, $J_{\mu\nu}$ and the exchange term $K_{\mu\nu}$ ($\mu$ and $\nu$ correspond to the same azimutal quantum number $l$) are interrelated by means of Eq. (26):

$$J_{\mu\mu} = J_{\mu\nu} + 2K_{\mu\nu}. \tag{26}$$

With this condition the integral pattern in Scheme 1 is observed for the INDO-formalism. In the upper right the one-center Coulomb-integrals are collected (including the diagonal), the corresponding exchange terms are given in the lower left. The index $T$ in the various fragments means that the parameter has been calculated theoretically (with the already described scaling procedure) while $SP$

**Table 4.** Slater–Condon-parameter for the INDO-formalism, $G$-integrals (cm$^{-1}$)

| Atom | $G_1^{sp}$ | | $G_2^{sd}$ | | $G_1^{pd}$ | | $G_3^{pd}$ | |
|------|-----------|---|-----------|---|-----------|---|-----------|---|
| H | | | | | | | | |
| Li | 6735 | [61] | | | | | | |
| Be | 10292 | [60] | | | | | | |
| B | 14522 | [60] | | | | | | |
| C | 18545 | [60] | | | | | | |
| N | 24085 | [60] | | | | | | |
| O | 31766 | [60] | | | | | | |
| F | 38963 | [61] | | | | | | |
| Na | 4188 | a | | | | | | |
| Mg | 6658 | b | | | | | | |
| Al | 9031 | [60] | | | | | | |
| Si | 12938 | [60] | | | | | | |
| P | 2817 | [60] | | | | | | |
| S | 8269 | [60] | | | | | | |
| Cl | 10142 | a | | | | | | |
| K | 2745 | a | 488 | a | 238 | a | 5.0 | a |
| Ca | 4195 | [60] | 746 | [60] | 364 | [60] | 8.0 | [60] |
| Sc | 2250 | c | 1957 | c | 420 | c | 15.7 | c |
| Ti | 2400 | c | 2000 | [62] | 450 | [62] | 16.8 | [62] |
| V | 2550 | c | 2100 | [62] | 480 | [62] | 17.9 | [62] |
| Cr | 2700 | c | 2100 | [62] | 510 | [62] | 19.1 | [62] |
| Mn | 2850 | c | 1900 | [62] | 540 | [62] | 20.2 | [62] |
| Fe | 3000 | c | 1800 | [62] | 570 | [62] | 21.3 | [62] |
| Co | 3150 | c | 2100 | [62] | 600 | [62] | 22.4 | [62] |
| Ni | 3300 | c | 2000 | [62] | 630 | [62] | 23.5 | [62] |
| Cu | 3450 | c | 2300 | [62] | 660 | [62] | 24.6 | [62] |
| Zn | 3600 | [62] | 2118 | c | 690 | [62] | 25.7 | c |

a Extrapolated from the values cited under [60].
b Value of reference [60] multiplied by $10^{-1}$.
c Extrapolated from the values cited under [62].

symbolizes a spectroscopically observed increment. Inspection of Scheme 1 clearly displays that within an atomic $s$, $p$ basis four different Coulomb-integrals and two exchange-integrals are necessary to describe electron–electron interaction of a particular atom. Inclusion of $d$-orbitals raises the number of different integrals to eight Coulomb-terms and five exchange-parameters. In contrast to Pople's INDO-version all increments are treated in a consistent manner. The spectroscopically observed increments include intraatomic correlation. Due to the scaling of $F_0$ also the monopole-term contains this correlation effect. In Pople's treatment a purely theoretical $F_0$-value (without consideration of correlation) is combined with experimental $F$- and $G$-parameters which include electron correlation. We now have to define the scaling factors of the corresponding $F_0$-integrals: $F_0^{sp}$, $F_0^{sd}$, $F_0^{pd}$. $F_0^{sp}$ is scaled with the $s$-parameter in the first complete period, in the second and third the $p$-factor is used. The integrals with $d$-contribution $F_0^{sd}$ and $F_0^{pd}$ are scaled by the corresponding $d$-parameters. In

**Scheme 1.** One-center Coulomb- and exchange-integrals within the INDO-formalism

| $J_{\mu\nu}$ $K_{\mu\nu}$ | s | p | p' | d | d' |
|---|---|---|---|---|---|
| s | $F_0^{ss}$  <br> T | $F_0^{sp}$  <br> T | $F_0^{sp}$  <br> T | $F_0^{sd}$  <br> T | $F_0^{sd}$  <br> T |
| p | $G_1^{sp}$  <br> SP | $F_0^{pp}+4F_2^{pp}$  <br> T $\quad$ SP | $F_0^{pp}-2F_2^{pp}$  <br> T $\quad$ SP | $F_0^{pd}$  <br> T | $F_0^{pd}$  <br> T |
| p' | $G_1^{sp}$  <br> SP | $3F_2^{pp}$  <br> SP | $F_0^{pp}+4F_2^{pp}$  <br> T $\quad$ SP | $F_0^{pd}$  <br> T | $F_0^{pd}$  <br> T |
| d | $G_2^{sd}$  <br> SP | $2G_1^{pd}+21G_3^{pd}$  <br> SP $\quad$ SP | $2G_1^{pd}+21G_3^{pd}$  <br> SP $\quad$ SP | $F_0^{dd}+4F_2^{dd}+36F_4^{dd}$  <br> T $\quad$ SP $\quad$ SP | $F_0^{dd}-F_2^{dd}-9F_4^{dd}$  <br> T $\quad$ SP $\quad$ SP |
| d' | $G_2^{sd}$  <br> SP | $2G_1^{pd}+21G_3^{pd}$  <br> SP $\quad$ SP | $2G_1^{pd}+21G_3^{pd}$  <br> SP $\quad$ SP | $2.5F_2^{dd}+22.5F_4^{dd}$  <br> SP $\quad$ SP | $F_0^{dd}+4F_2^{dd}+36F_0^{dd}$  <br> T $\quad$ SP $\quad$ SP |

Scheme 2 we have listed the CNDO Coulomb-integrals in the one-center limit. The nondiagonal elements between AO's of the same $l$-value ($p|p'$ and $d|d'$) arise from the CNDO invariance criterion due to the neglect of the one-center exchange-terms, the nondiagonal-elements of the form $J_{sp}$, $J_{sd}$ and $J_{pd}$ are the result of the one-center limit ($R_{AB}=0$) of the corresponding two-center expressions. In the case of a $s, p$ basis three different Coulomb-integrals are necessary to describe the local electron interaction while the inclusion of $d$-orbitals causes six different integrals.

**Scheme 2.** One-center Coulomb-integrals within the CNDO-formalism

| $J_{\mu\nu}$ | s | p | p' | d | d' |
|---|---|---|---|---|---|
| s | $F_0^{ss}$ | $\dfrac{F_0^{ss}+F_0^{pp}}{2}$ | $\dfrac{F_0^{ss}+F_0^{pp}}{2}$ | $\dfrac{F_0^{ss}+F_0^{dd}}{2}$ | $\dfrac{F_0^{ss}+F_0^{dd}}{2}$ |
| p | | $F_0^{pp}$ | $F_0^{pp}$ | $\dfrac{F_0^{pp}+F_0^{dd}}{2}$ | $\dfrac{F_0^{pp}+F_0^{dd}}{2}$ |
| p' | | | $F_0^{pp}$ | $\dfrac{F_0^{pp}+F_0^{dd}}{2}$ | $\dfrac{F_0^{pp}+F_0^{dd}}{2}$ |
| d | | | | $F_0^{dd}$ | $F_0^{dd}$ |
| d' | | | | | $F_0^{dd}$ |

As the one-center two-electron integrals already contain intraatomic correlation corrections, the corresponding two-center Coulomb-terms must be calculated in a fashion where interatomic correlation effects are also included. Thus, we have to focus our attention to semiempirical formulas that are well known in theoretical organic chemistry. The two most important approaches that meet these demands are the Mataga–Nishimoto (MN)-approximation (27) [42] and the Dewar-Sabelli. Ohno–Klopman (DSOK) relation (29) [43] [44]:

MN

$$\gamma_{\mu\nu}^{AB} = (\mu^A\mu^A|\nu^B\nu^B) = \frac{e^2}{R_{AB}+a_{\mu\nu}^{AB}} \tag{27}$$

$$a_{\mu\nu}^{AB} = \frac{2e^2}{(J_{\mu\mu}^{AA}+J_{\nu\nu}^{BB})} \tag{28}$$

DSOK

$$\gamma_{\mu\nu}^{AB} = (\mu^A\mu^A|\nu^B\nu^B) = \frac{e^2}{\sqrt{R_{AB}^2+(e^2/4)(1/J_{\mu\mu}^{AA}+1/J_{\nu\nu}^{BB})^2}} \tag{29}$$

Detailed investigations have shown that correlation effects are overestimated in the case of the MN-relation if the one-center integrals already have been scaled down [45]. Therefore we used the DSOK-relation in our CNDO/INDO-formalism.

The diagonal elements $H_{\mu\mu}$ can be partitioned into two different terms.

$$H_{\mu\mu}^{AA} = U_{\mu\mu}^A + \sum_{B\neq A} (\mu^A|V_B|\mu^A) \tag{30}$$

$U_{\mu\mu}^A$ is a local atomic quantity, the energy of a valence electron in the $\mu$th AO in the potential-field of the core $A$. The summation (second term) describes the electron-core-interaction between the various cores $B$ and an electron in AO$\mu$ centered at $A$.

Within Pople's CNDO/INDO-procedure $U_{\mu\mu}$ is calculated via semiempirical formulae from approximative Coulomb- and exchange-integrals and atomic data (ionization potentials and electron affinities) [9], [10]. The disadvantage of such a procedure is evident as all shortcomings with respect to the representation of the one-center $F$- and $G$-integrals are transferred to the corresponding values of $U_{\mu\mu}$ which are the dominant terms determining the basis-energy of the AO's. As all CNDO/INDO extensions to the transition metal series are based on the original Pople versions this drawback is clearly part of the existing semiempirical MO-versions within the $3d$-class.

Therefore we used $U_{ss}$, $U_{pp}$ and $U_{dd}$ parameters that were determined from spectroscopic data as had been done by Sichel and Whitehead [46] within the CNDO approximation and in Dewar's MINDO-versions [47a]. In Table 5 the experimental values for $U_{ss}$, $U_{pp}$ and $U_{dd}$ are collected. As the cited parameters

**Table 5.** Core-integrals $U_{ss}$, $U_{pp}$ and $U_{dd}$ for the CNDO- and INDO-formalism (in eV)

| Atom | $U_{ss}^{CNDO}$ | $U_{pp}^{CNDO}$ | $U_{dd}^{CNDO}$ | Reference | $U_{ss}^{INDO}$ | $U_{pp}^{INDO}$ | $U_{dd}^{INDO}$ |
|---|---|---|---|---|---|---|---|
| H | −13.595 | | | [46] | −12.575 | | |
| Li | −4.999 | −3.673 | | [46] | −4.905 | −3.603 | |
| Be | −15.543 | −12.280 | | [46] | −15.123 | −11.948 | |
| B | −30.371 | −24.702 | | [46] | −29.308 | −23.837 | |
| C | −50.686 | −41.530 | | [46] | −48.507 | −39.744 | |
| N | −70.093 | −57.848 | | [46] | −66.518 | −54.898 | |
| O | −101.306 | −84.284 | | [46] | −95.329 | −79.311 | |
| F | −129.544 | −108.933 | | [46] | −120.865 | −101.634 | |
| Na | −4.502 | −3.247 | −1.216 | [46] | −4.254 | −3.068 | |
| Mg | −13.083 | −9.603 | −3.664 | [46] | −12.298 | −9.027 | |
| Al | −22.828 | −18.592 | −6.974 | [46] | −21.344 | −17.384 | |
| Si | −36.494 | −30.375 | −12.442 | [46] | −33.939 | −28.249 | |
| P | −56.230 | −42.310 | −20.302 | [64] | −52.013 | −39.137 | |
| S | −66.796 | −58.008 | −29.470 | [46] | −61.452 | −53.367 | |
| Cl | −86.774 | −75.681 | −20.704 | [46] | −79.398 | −69.248 | |
| K | −3.170 | −3.115 | −3.080 | [46] | −2.378 | −1.869 | −3.032 |
| Ca | −9.842 | −7.696 | −7.270 | [46] | −7.382 | −4.618 | −7.159 |
| Sc | −20.900 | −16.340 | −23.620 | a | −15.675 | −9.804 | −23.270 |
| Ti | −30.200 | −23.920 | −36.900 | [37b] | −22.650 | −14.352 | −36.369 |
| V | −40.020 | −31.930 | −51.370 | [37b] | −30.015 | −19.158 | −50.651 |
| Cr | −50.360 | −40.370 | −67.030 | [37b] | −37.770 | −24.222 | −66.118 |
| Mn | −61.220 | −49.240 | −83.880 | [37b] | −45.915 | −29.544 | −82.773 |
| Fe | −72.600 | −58.540 | −101.920 | [37b] | −54.450 | −35.124 | −100.615 |
| Co | −84.500 | −68.270 | −121.150 | [37b] | −63.375 | −40.962 | −119.648 |
| Ni | −96.920 | −78.430 | −141.570 | [37b] | −72.690 | −47.058 | −139.871 |
| Cu | −109.860 | −89.020 | −163.180 | [37b] | −81.645 | −53.412 | −161.287 |
| Zn | −123.300 | −100.000 | −186.000 | a | −92.475 | −60.000 | −183.917 |
| Ga | −25.032 | −19.807 | | [46] | | | |
| Ge | −35.844 | −29.973 | | [46] | | | |
| As | −50.151 | −44.485 | | [46] | | | |
| Se | −66.005 | −57.927 | | [46] | | | |
| Br | −76.413 | −65.412 | | [46] | | | |

a Extrapolated from the values of [37b].

were coordinated to our CNDO-scheme the INDO-values then had to be extracted in a way characterized in (31):

$$U_{\mu\mu}^{INDO} = U_{\mu\mu}^{CNDO} + f(F_2^{pp}, F_2^{dd}, F_4^{dd}, G_1^{sp}, G_2^{sd}, G_1^{pd}, G_3^{pd}). \qquad (31)$$

The $3d$ elements in the third period have been estimated by relation (32) where $U_{ss}$ and $U_{pp}$ are the $U$-values of the $3s$ and $3p$ electrons while $I_s$, $I_p$ and $I_d$ symbolize the valence-state ionization potentials:

$$U_{dd} = \left( \frac{U_{ss} + U_{pp}}{I_s + I_p} \right) I_d. \qquad (32)$$

Various detailed investigations concerning the $3d$ and $4s$, $4p$ participation, respectively, in the series Na to Cl and Sc to Zn revealed [14] [15] [23] [48] that the virtual atomic orbitals have unrealistically high populations. In the first transition metal series the calculated populations for the $4s/4p$ functions often reach values of 2.00 $e$ [48]. A detailed analysis of these anomalies in the population of complex compounds can be found in the work of Hoffman et al. [49].

In trying to mimic the electron population resulting from very sophisticated *ab initio* procedures in the frame of a semiempirical allvalence electron treatment, one has to introduce a screening potential for the corresponding core integrals ($U_{4s4s}$, $U_{4p4p}$ and $U_{3d3d}$ in third period):

$$U_{\mu\mu}^{\text{eff}} = (1 - K_{SC})U_{\mu\mu}. \tag{33}$$

In this expression $K_{SC}$ is a screening constant to reduce the population of the $\mu$th AO. The following parameters meet the requirement discussed above:

|       |          | $K_{\text{SC}}$ | $U_{\mu\mu}^{\text{eff}}$ |
|-------|----------|-----------------|---------------------------|
| $3d$  | Na to Cl | 0.20            | $0.80\ U_{dd}$            |
| $4s$  | Sc to Zn | 0.20            | $0.80\ U_{ss}$            |
| $4p$  | Sc to Zn | 0.25            | $0.75\ U_{pp}$            |

According to Pariser and Parr [50] the core-operator $V_B$ can be decomposed into two parts as follows:

$$V_B = Z_B \cdot V_B(1) = V_B^0 - \sum_{\lambda \in B} n_\lambda [J_\lambda(1) - \tfrac{1}{2}K_\lambda(1)]. \tag{34}$$

In this equation $Z_B$ stands for the core-charge of center $B$, $V_B^0(1)$ symbolizes the operator of the interaction of an electron at $A$ and the neutral atom $B$. This latter operator gives rise to the so-called penetration integrals. The expressions $J_\lambda(1)$ and $K_\lambda(1)$ symbolize the Coulomb and exchange operators while $n_\lambda$ means the occupation number of atomic orbital $\lambda$ in the neutral atom. In current semi-empirical procedures (CNDO/2, INDO and various MINDO programs) the penetration integral is neglected completely and thus the core-electron integral reduces to:

$$V_B^{AA} = \bar{\gamma}_{AB} = V_A^{BB} \tag{35}$$

In (35) $\bar{\gamma}_{AB}$ symbolizes the mean value of a two-center Coulomb integral depending only on the type of the atoms $(A, B)$ but not on the involved atomic basis functions. Our approximation to $\bar{\gamma}_{AB}$ symbolically can be written as $\bar{\gamma}_{A(\mu)B}$ as the $\mu'$th AO on $A$ is explicitly taken into account while the core-contribution from $B$ is given by a selected reference orbital.

We decided to take into account penetration effects at least partially since for the higher elements (beyond the second period) the neglected penetration terms

reach up to 5 eV [38]. As a basis for our approach we have used the approximation of Fischer and Kollmar [51]:

$$Z_B V_B^{AA} = Z_B \left[ \alpha \cdot \bar{\gamma}_{AB} + f^1 (1-\alpha) \left( R_{AB}^2 + \frac{1}{\xi^2} \right)^{-1/2} \right] \qquad (36)$$

$$f^1 = \left[ \frac{f_A + f_B}{2} \right]^{2/3} .$$

$f_A$ and $f_B$ represent the atomic scaling factors of Table 2 associated to the atomic orbitals which are defined below (Eq. (38) and (39) respectively).

In expression (36) $\alpha$ is the parameter that determines the degree of penetration. For $\alpha = 1$, one simulates the CNDO/2 or MINDO parametrizations where penetration effects are completely neglected. In the case of $\alpha = 0$ the total amount of penetration is considered. We assume that $\alpha$ depends on the nature of the atomic orbital under consideration; diffuse atomic orbitals have to show larger penetration effects than strongly localized ones. Therefore the following function was used for the determination of $\alpha$.

$$\alpha = \left[ \frac{\zeta_A}{\zeta_H \cdot n_A} \right] \qquad (37)$$

$\zeta_A$ is the zeta-exponent of the atomic orbital localized at center $A$, $n_A$ is the corresponding principal quantum number and $\zeta_H$ is the Burns-exponent of hydrogen. Thus the penetration of the $1s$ orbital of H is zero while all other atoms show definitie graduation from the H limit. Below we have collected some $\alpha$-parameters for the second and third period:

| atom | $\alpha_s$ | $\alpha_p$ |
|------|--------|--------|
| Be | 0.7670 | 0.7329 |
| C | 0.8787 | 0.8449 |
| N | 0.9119 | 0.8813 |
| O | 0.9591 | 0.9336 |
| F | 0.9927 | 0.9698 |
| Mg | 0.7288 | 0.6509 |
| S | 0.8427 | 0.7895 |
| Cl | 0.8650 | 0.8165 |

This summary clearly demonstrates that an electron in a $p$-orbital shows a more pronounced penetration-effect in comparison with the associated $s$-atomic orbital and that $\alpha$ decreases within a period. Within the $3d$ transition metal series $\alpha$ is set to 1.00 for the $3d$-atomic orbitals, which are more localized at the atomic centers than the diffuse $4s$ and $4p$ functions.

$f^1$ is a caling-parameter for the $(R_{AB}^2 + (1/\zeta^2))$-contribution to $Z_B V_B^{AA}$ which is necessary in our approximation scheme as also the $\bar{\gamma}_{AB}$-term in (36) is scaled via the one-center integrals. The $\bar{\gamma}_{AB}$-integrals for atomic orbital $\mu$ at atom $A$ and the core $B$ are defined below:

$$\bar{\gamma}_{AB} = (\mu^A \mu^A | s^B s^B) \quad B \notin Sc - Zn \tag{38}$$

$$\bar{\gamma}_{AB} = (\mu^A \mu^A | d^B d^B) \quad B \in Sc - Zn \tag{39}$$

Equation (39) corresponds to the MNDO expression of Dewar and Thiel [47], while in the case of the transition metal series a $3d$ AO is the reference function at the core $B$. Numerous computational test calculations demonstrated that the results of the semiempirical approach are improved in the case of hetero-bonds $X-Y$ where most of the current semiempirical versions (CNDO, INDO, MINDO) create too strong charge separations. In the case of (36) the electropositive element of the $X-Y$ bond is stabilized with respect to the negative partner due to a more pronounced penetration.

Of crucial importance in any semiempirical MO procedure is the definition of the nondiagonal elements of the core-Hamiltonian. Within the ZDO approximation the following expression is observed:

$$H_{\mu\nu}^{AB} = (\mu^A | -\tfrac{1}{2}\nabla^2 - V_A - V_B | \nu^B) - \sum_{C \neq AB} (\mu^A | V_C | \nu^B)$$

$$= (\mu^A | -\tfrac{1}{2}\nabla^2 - V_A - V_B | \nu^B). \tag{40}$$

As all other parameters of the semiempirical Hamiltonian are not direction dependent due to the various invariance criteria $H_{\mu\nu}^{AB}$ is the only increment that takes into account the directed nature of the chemical bond. Thus the resonance integral $H_{\mu\nu}^{AB}$ has been the subject of various theoretical investigations [52], [53] to analyze the physical origin that is part of $H_{\mu\nu}^{AB}$.

The physical, quantumchemical information of the resonance integral shows that $H_{\mu\nu}^{AB}$ is proportional to an interference density $\bar{p}_{\mu\nu}^{AB}$ which is a measure of the charge transferred into the bonding region due to bond formation. In contrast to the well known approximations of most semiempirical MO parametrizations the relation (41) between $H_{\mu\nu}^{AB} (\bar{p}_{\mu\nu}^{AB})$ and the overlap integral $S_{\mu\nu}^{AB}$ holds:

$$H_{\mu\nu}^{AB} \propto \bar{p}_{\mu\nu}^{AB} \propto S_{\mu\nu}^{AB} (1 - |S_{\mu\nu}^{AB}|). \tag{41}$$

Thus the interference desnity is proportional to an overlap-function of the type $S_{\mu\nu}^{AB} (1 - |S_{\mu\nu}^{AB}|)$. With decreasing $R_{AB}$ $(R_{AB} \to 0)$ the interference density goes to zero. This means that $H_{\mu\nu}^{AB}$ runs through a maximum at a definite value of $R_{AB}$ while in current semiempirical methods $H_{\mu\nu}^{AB}$ reaches its maximum at $R_{AB} = 0$ as a result of the proportionality $H_{\mu\nu}^{AB} \propto S_{\mu\nu}^{AB}$. In the case of $H_2^+$ Ruedenberg and coworkers [52] separated the various energy components that contribute to the interference density. The predominant contribution is the kinetic energy $T_I$ while the potential energy $V_I$ is negligible. The resonance integral $H_{\mu\nu}^{AB}$ therefore is

influenced primarily by the $-\frac{1}{2}\nabla^2$-operator. Phenomenologically the results of Ruedenberg and Kutzelnigg were confirmed by Nicholson in a large series of model calculations (e.g. $H_2$, HLi, HB, HN, HF, $B_2$, CO, $N_2$, $F_2$) [16].

It can be shown that under the NDO- or ZDO-approximation the $H_{\mu\nu}^{AB}$-integral is coined more by kinetic factors than in a full overlap basis [54]. As the NDO-model is equivalent to a simulation of an orthogonal basis (7) Cook has investigated $H_{\mu\nu}^{AB}$ in the Löwdin-basis. Here all potential energy contributions have been vanished and $H_{\mu\nu}^{AB}$ is given by (42):

$$^\lambda H_{\mu\nu}^{AB} \approx {}^\lambda TK_{\mu\nu} \approx \frac{1}{(1-S_{\mu\nu}^2)}\left[ TK_{\mu\nu} - \frac{S_{\mu\nu}}{2}(TK_{\mu\mu} + TK_{\nu\nu})\right].$$                  (42)

$TK_{\mu\nu}$ symbolizes the kinetic energy operator for the AO's $\mu$ and $\nu$. It should be clear that $H_{\mu\nu}^{AB}$ must be determined in a way that on one hand the asymptotic behaviour at least in the region of characteristical bond lengths is reproduced by the selected formula. On the other hand we have to modulate $H_{\mu\nu}^{AB}$ in such a way that differences in the bonding type ($\sigma\sigma$, $\pi\pi$, $\delta\delta$) are reproduced in the splitting pattern of the semiempirical eigenvalues. Thus we have used the following factorization of the resonance integral:

$$H_{\mu\nu}^{AB} = A_{\mu\nu}^{AB} \cdot I_{\mu\nu}^{AB} \cdot M_{\mu\nu}^{AB}.$$                  (43)

Here $A_{\mu\nu}^{AB}$ is a function of atomic parameters of the AO's $\mu$ and $\nu$, $I_{\mu\nu}^{AB}$ is an interference function within the definition of Ruedenberg and Kutzelnigg while $M_{\mu\nu}^{AB}$ is a variable flexible function necessary to mimic the results of timeconsuming *ab initio* calculations with the semiempirical Hamiltonian.

$A_{\mu\nu}^{AB}$ is a weighted mean value of the valence-state ionization potentials $I_\mu^A$ and $I_\nu^B$ given by (44):

$$A_{\mu\nu}^{AB} = \tfrac{1}{2}[(1+\Delta)I_\mu^A + (1-\Delta)I_\nu^B]$$                  (44)

$$\Delta = \frac{I_\mu^A - I_\mu^B}{I_\mu^A + I_\mu^B}.$$

The valence-state ionization energies are collected in Table 6.

For the interference function the expression (45) was used:

$$I_{\mu\nu}^{AB} = (\text{tanhyp}_{\mu\nu}^{AB})^2 \cdot (1-S_{\mu\nu}^2)S_{\mu\nu}$$                  (45)

$$\text{tanhyp}_{\mu\nu}^{AB} = 1 - 0.20\left(\frac{e^{2f''}-1}{e^{2f''}+1}\right)$$                  (46)

$$f'' = c_1(R_{AB} - C_2)$$                  (47)

The factor $(1-S_{\mu\nu}^2)S_{\mu\nu}$ in Eq. (45) is close to the approximate relation (41) connecting $H_{\mu\nu}^{AB}$, the interference density $\bar{p}_{\mu\nu}^{AB}$ and the overlap integral $S_{\mu\nu}^{AB}$. Test

**Table 6.** Valence-state ionization potentials (in eV)

| Atom | $I_s$ | $I_p$ | $I_p$ | Reference |
|------|-------|-------|-------|-----------|
| H  | 13.06 |       |       | [61] |
| Li |  5.39 |  3.54 |       | [61] |
| Be |  9.32 |  5.96 |       | [61] |
| B  | 14.05 |  8.30 |       | [61] |
| C  | 19.44 | 10.67 |       | [61] |
| N  | 25.88 | 13.19 |       | [61] |
| O  | 32.38 | 15.85 |       | [61] |
| F  | 40.42 | 18.66 |       | [61] |
| Na |  5.14 |  3.04 |  1.52 | [65] |
| Mg |  7.64 |  4.52 |  1.74 | [65] |
| Al | 11.32 |  5.97 |  1.96 | [65] |
| Si | 15.15 |  7.62 |  2.04 | [65] |
| P  | 19.37 | 10.84 |  2.86 | [65] |
| S  | 20.52 | 10.78 |  3.06 | [65] |
| Cl | 25.29 | 13.99 |  3.59 | [65] |
| K  |  4.44 |  2.83 |  1.77 | [66] |
| Ca |  6.11 |  3.96 |  3.54 | [66] |
| Sc |  5.70 |  3.22 |  4.71 | [67] |
| Ti |  6.07 |  3.35 |  5.58 | [67] |
| V  |  6.32 |  3.47 |  6.32 | [67] |
| Cr |  6.57 |  3.47 |  7.19 | [67] |
| Mn |  6.82 |  3.59 |  7.93 | [67] |
| Fe |  7.06 |  3.72 |  8.67 | [67] |
| Co |  7.31 |  3.84 |  9.42 | [67] |
| Ni |  7.56 |  3.84 | 10.04 | [67] |
| Cu |  7.68 |  3.97 | 10.66 | [67] |
| Zn |  7.81 |  4.09 | 11.17 | [67] |
| Ga | 12.64 |  5.95 |       | [66] |
| Ge | 15.61 |  7.56 |       | [66] |
| As | 17.60 |  9.05 |       | [66] |
| Se | 20.82 | 10.78 |       | [66] |
| Br | 24.04 | 12.52 |       | [66] |

calculations within the selected approximation scheme favoured the empirical relation (45) with the $(1 - S_{\mu\nu}^2)$ modulation instead of the theoretical $(1 - |S_{\mu\nu}|)$ proportionality.

The constant values $c_1$ and $c_2$ for the various bonding interactions are collected below; $c_1$ and $c_2$ were chosen to modify the $I_{\mu\nu}^{AB}$ term in the region of characteristic bond lengths smoothly, avoiding extreme interference contributions in the limit $R_{AB} \to 0$ and $R_{AB} \to \infty$. The $I_{\mu\nu}^{AB}$-functions not listed in the following scheme are negligible and $I_{\mu\nu}^{AB}$ is set to 1.00. A similar behaviour has been found in the MINDO/2 derivative SPINDO/1 (**S**pectroscopic **P**otentials adjusted-INDO)

[55] where $H_{\mu\nu}^{AB}$ has been modulated to reproduce the PE-spectra of hydro-carbons.

|  | $c_1$ | $c_2$ |
|---|---|---|
| $\langle 2p\sigma \mid 2p\sigma \rangle$ | 1.350 | 1.250 |
| $\langle 2p\sigma \mid 3p\sigma \rangle$ | 1.700 | 1.250 |
| $\langle 3p\sigma \mid 3p\sigma \rangle$ | 1.700 | 1.250 |
| $\langle 2p\pi \mid 2p\pi \rangle$ | 1.325 | 1.600 |
| $\langle 2p\pi \mid 3p\pi \rangle$ | 1.60 | 1.60 |
| $\langle 3p\pi \mid 3p\pi \rangle$ | 1.60 | 1.60 |

**Scheme 3.**

$$(\text{tanhyp}_{\mu\nu}^{AB})^2 = 1 \quad \text{for all other AO combinations}$$
$$= 0.50 \quad \text{if } \mu \text{ or } \nu \in 4s \text{ Sc}-\text{Zn}$$
$$= 0.75 \quad \text{if } \mu \text{ or } \nu \in 4p \text{ Sc}-\text{Zn}$$
$$= 1.50 \quad \text{if } \mu \text{ or } \nu \in 3d \text{ Sc}-\text{Zn}$$

To reproduce the orbital sequence of *ab initio* calculations with its various direction dependent integrals within an NDO-framework with spherical averages for most parameters of the Hamilton-operator we have chosen the empirical relation (48). $R_{AB}$ is the distance between centers $A$ and $B$, $\text{SYM}_{\mu\nu}$ is a measure of nonpolarized AO's with spherical behaviour while $\text{POL}_{\mu\nu}$ characterizes the deformation and polarization of the AO's into the bonding region via the $T_{\mu\nu}$ expressions:

$$M_{\mu\nu}^{AB} = \left[ \frac{R_{AB}^2 + \text{SYM}_{\mu\nu}^2}{R_{AB}^2 + \text{POL}_{\mu\nu}^2} \right]^{3/2} \tag{48}$$

$$\text{SYM}_{\mu\nu} = \frac{1}{2}\left[ \frac{1}{J_{\mu\mu}} + \frac{1}{J_{\nu\nu}} \right] \tag{49}$$

$$\text{POL}_{\mu\nu} = \frac{1}{2}\left[ \frac{T_{\mu\nu}}{J_{\mu\mu}} + \frac{T_{\nu\mu}}{J_{\nu\nu}} \right]. \tag{50}$$

In the nominator and demnominator of (48) the second terms dominate with decreasing $R_{AB}$ and thus $M_{\mu\nu}^{AB}$ is a strongly direction dependent function in the bonding region. With increasing distance between $A$ and $B$ $M_{\mu\nu}^{AB}$ asymptotically reaches the value 1.00; significant modulation effects are found between bonded centers and between 1, 3 neighbours (a similar $H_{\mu\nu}^{AB}$ expression has been derived by Coffey and Jug [56] based on the commutator-equation of the core-Hamiltonian and the dipole-operator). For the functions $T_{\mu\nu}$ Klondyke-parameters [57] were used, originally developed by Dewar and Klopman [58] to polarize spherical averages of two-center Coulomb-integrals. The Klondyke-parameters $T_{\mu\nu}$ were optimized by comparison with the results of *ab initio* calculations and are collected in Scheme 4:

**Scheme 4.**

| $\mu$ | $\nu$ | $T_{\mu\nu}$ | |
|---|---|---|---|
| $1s$ | $ns, np\sigma, 3d\sigma$ | $\frac{1}{2}[1 + \exp(-R'_{AB})]$ | |
| $ns, n \neq 1$ | $ns, np\sigma, 3d\sigma$ | $(\frac{1}{4}[3 + \exp(-R'_{AB})])^{-1}$ | |
| $np\sigma, 3d\sigma$ | $ns$ | $1$ | |
| $np\sigma$ | $np\sigma, 3d\sigma$ | $[\exp(-R'_{AB})]^{1.65}$ | |
| $3d\sigma$ | $np\sigma, 3d\sigma$ | $[\exp(-R'_{AB})]^c$ | $c = 1.5$ (Sc–Zn) $c = 1.0$ (Na–Cl) |
| $np\pi$ | $np\pi, 3d\pi$ | $(\frac{1}{3}[2 + \exp(-R'_{AB})])^{-1}$ | |
| $3d\pi$ | $np\pi, 3d\pi$ | $(\frac{1}{2}(1 + \exp(-R'_{AB})))^c$ | $c = 1.5$ (Sc–Zn) $c = 1.0$ (Na–Cl) |
| $3d\delta$ | $3d\delta$ | $(\frac{1}{2}[1 + \exp(-R'_{AB})])^c$ | $c = 1.5$ (Sc–Zn) $c = 1.0$ (Na–Cl) |

$$R'_{AB} = \frac{R_{AB}}{T'_{\mu\nu}} \tag{51}$$

$$T'_{\mu\nu} = \frac{1}{J_{\mu\mu}} + \frac{1}{J_{\nu\nu}}. \tag{52}$$

With this flexible set of increments $(A^{AB}_{\mu\nu}, I^{AB}_{\mu\nu}, M^{AB}_{\mu\nu})$ the resonance integral $H^{Ab}_{\mu\nu}$ is completely determined. $H^{AB}_{\mu\nu}$ is at first calculated in the diatomic coordinate systems $(A, B)$ and the rotated via the transformation-matrices $O_{\mu\alpha}$ and $O_{\mu\beta}$ into the molecular system:

$$H^{AB}_{\alpha\beta} = \sum_{\mu}\sum_{\nu} O_{\mu\alpha} O_{\mu\beta} H^{AB}_{\mu\nu}. \tag{53}$$

The chosen approximation for the $H^{AB}_{\mu\nu}$ integral follows up to different objects. On one side the approximation has to prevent inevitable computational short-comings arising in the theoretical framework of a single-zeta allvalence NDO-Hamiltonian. On the other side we tried to use parameters based on reliable quantumchemical, physical models and arguments (e.g. the construction of the electron–electron interaction-integrals, the consideration of penetration effects, the crucial importance of the interference density upon bond formation). These models of physical significance hindered an excessive modulation of different parameters of the approximate Hamiltonian. The connecting link between desired accuracy (*ab initio* caculations and experimental results), constrains due to the NDO inherent approximations and the use of meaning-rich model assumptions was achieved by a highly flexible design in $I^{AB}_{\mu\nu}$ and $M^{AB}_{\mu\nu}$ to adjust the computational results. Hence the use of a definite $H^{AB}_{\mu\nu}$ parametrization always has to take into account the success of the method. Test calculations on an early stage of the development of the CNDO/INDO procedure with well known standard approximations for $H^{AB}_{\mu\nu}$ ($H^{AB}_{\mu\nu} \propto S^{AB}_{\mu\nu}$) guided to computational

results far from the desired *ab initio* quality. Specially the splitting pattern of the one-electron functions (e.g. energy separation between $\sigma$, $\pi$ and $\delta$ type orbitals, energy gap between metal $3d$ and fragment orbitals of the organic ligands) was predicted with dramatical errors. Inspection of the CNDO-formalism of Freund and Hohlneicher [21] as well as the INDO approach of Bacon and Zerner [22] obviously shows that the same difficulties due to the ZDO allvalence limitation of the molecular Hamiltonian were encountered. In the work of Freund and Hohlneicher the loss of directional bonding interactions were partially compensated by means of very diffuse $3d$ zeta-exponents [21], optimized by only a few test calculations. The resulting $3d$ single-zeta-exponents are as diffuse as the long-range $3d$ exponent of a double-zeta basis of Slater-type orbitals, an approximation not taking into account the decay of $3d$ AO's in a physical proper way.

Such an approach clearly leads to an imbalanced AO-basis. Bacon and Zerner [22] on the other hand used a distance-dependent $3d$ exponent leading to a discontinuous function, a serious drawback if the optimization of molecular geometries is desired, and different constants in $H_{\mu\nu}^{AB}$ depending on the type of bonding.

The comparison of our $H_{\mu\nu}^{AB}$ approximation with the work of Freund/Hohlneicher and Bacon/Zerner respectively indicates the inherent model-dependent difficulties to find approximate formulae and parameters in transition metal compounds that allow economic and satisfactorical MO calculations of theroretical properties of general interest.

Now all electronic parameters of the semiempirical CNDO/INDO Hamiltonian are defined and only the definition of the core-core-repulsion in the formulae (20) and (21) for the total energy are left. To take into account polarization effects of the atomic cores we have approximated $E_{AB}^{\text{core}}$ by a soft potential function making use of the charge clouds of the valence electrons. To this soft function a hard potential is superimposed as the repulsion of the smeared charge clouds is too weak at small interatomic distances; in the case of a geometry-optimization the atomic cores would collapse. Our empirical core-core-potential (54) corresponds to the MNDO function of Dewar and Thiel [47b]:

$$E_{AB}^{\text{core}} = Z_A Z_B (\mu^A \mu^A | \nu^B \nu^B) + f_{\text{rep}}(R_{AB}). \tag{54}$$

$Z_A$ and $Z_B$ represent the core-charges of the centers $A$ and $B$ while $(\mu^A \mu^A | \nu^B \nu^B)$ is a two-center Coulomb-integral of valence electrons $\mu$ and $\nu$ at $A$ and $B$. The proper $\gamma$-integrals are defined in (55)–(58) for various atom combinations:

$(\mu^A \mu^A | \nu^B \nu^B)$

| | | |
|---|---|---|
| $(s^A s^A | s^B s^B)$ | $A \notin$ and $B \notin$ (Sc–Zn) | (55) |
| $(d^A d^A | s^B s^B)$ | $A \in$ but $B \notin$ (Sc–Zn) | (56) |
| $(s^A s^A | d^B d^B)$ | $A \notin$ but $B \in$ (Sc(Zn) | (57) |
| $(d^A d^A | d^B d^B)$ | $A \in$ and $B \in$ (Sc–Zn) | (58) |

$$f_{\text{rep}}(R_{AB}) = Z_A Z_B (\mu^A \mu^A | \nu^B \nu^B)[\exp(-\alpha_A \times R_{AB}) + \exp(-\alpha_B \times R_{AB})] \tag{59}$$

**Table 7.** $\alpha$-parameter and $f_{\text{eff}}$-values for $3d$ elements

| Atom | $\alpha$ | Atom | $\alpha$ | $f_{\text{eff}}$ |
|------|----------|------|----------|------------------|
| H | $\infty$ | K | $\infty$ | |
| Li | 0.9600 | Ca | 1.3200 | |
| Be | 1.1700 | Sc | 1.3436 | |
| B | 1.9644 | Ti | 1.4840 | 0.9875 |
| C | 2.2320 | V | 1.4750 | |
| N | 2.8772 | Cr | 1.9345 | |
| O | 2.9370 | Mn | 2.3757 | |
| | | Fe | 2.2050 | 0.9050 |
| F | 3.3330 | Co | 2.3569 | 0.9000 |
| Na | 0.5760 | Ni | 2.5214 | 0.9250 |
| Mg | 0.9075 | Cu | 2.7624 | 0.9125 |
| Al | 1.1853 | Zn | 2.4809 | |
| Si | 1.3490 | Ga | 1.0631 | |
| P | 1.5225 | Ge | 1.1400 | |
| S | 1.7703 | As | 1.1534 | |
| Cl | 2.0520 | Se | 1.4993 | |
| | | Br | 2.0861 | |

The $\alpha_A$ and $\alpha_B$ parameters in (59) were optimized by test calculations on the complete series of homonuclear diatomic molecules where $\alpha_A$ and $\alpha_B$ were varied to reproduce the experimental equilibrium distance. The optimized values are collected in Table 7. In the case of weakly bound metalorganic compounds the $Z_A Z_B (\mu^A \mu^A | \nu^B \nu^B)$-term in (54) and (59) had to be modified by a scale-factor $f_{\text{eff}}$ (60) to reproduce the equilibrium geometries of these species:

$$E_{AB}^{\text{core}} = f_{\text{eff}} Z_A Z_B (\mu^A \mu^A | \nu^B \nu^B) + f_{\text{rep}} R_{AB}. \tag{60}$$

The $f_{\text{eff}}$-values of selected transition-elements are also collected in Table 7. For the geometry-optimizations a Fletcher-Powell-algorithm [59] has been used.

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