

# On the Application of the Intermediate Neglect of Differential Overlap Method to Inorganic Complexes

T. ZIEGLER

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada

A new semiquantitative SCF LCAO MO calculation scheme has been applied to:  $\text{Ni}(\text{CO})_4$ ,  $\text{Ni}(\text{CN})_4^{2-}$ ,  $\text{Cr}(\text{CO})_6$ , and  $\text{Fe}(\text{C}_5\text{H}_5)_2$ . Comparison is made to current *ab initio* calculations.<sup>1-3</sup>

## 1. INTRODUCTION

The advent of *ab initio* calculations on inorganic complexes<sup>4-5</sup> has since been followed up by calculations with more extended basis sets<sup>6</sup> leading to a recent Hartree-Fock limit calculation.<sup>7</sup>

The great advantage of such examinations compared with semiempirical and semiquantitative theories is of course an elimination of all empirical parameters such as atomic ionization energies and scaling factors, which are often introduced in a somewhat arbitrary way, in order to fit the electronic spectrum.

The disadvantage of *ab initio* calculations is the great number of integrals, especially when any arbitrariness in the choice of atomic orbitals (minimal basis set) has to be avoided by the use of a rather flexible set of functions (extended basis set).

The possible manner in which to reduce the number of integrals by a suitable set of numerical approximations, and then calculating the remaining exact, has been discussed by Dahl and Ballhausen<sup>8</sup> inside the CNDO (complete neglect of differential overlap) scheme. Due to the lack of photoelectron spectra and *ab initio* calculations, they could only check their approximation scheme rather crudely by comparison between electronic spectra and transition energies determined from ground state calculations.

Now a much more safe test can be made by direct comparison with *ab initio* calculations. The present work suggests an INDO (intermediate neglect of differential overlap<sup>9</sup>) scheme, which is discussed in connection with *ab initio* calculations and photoelectron spectra.

## 2. DESCRIPTION OF METHOD

*2a. Core and valence orbitals.* Consider an inorganic complex for which the ground state is a totally symmetric singlet state. In the Hartree-Fock model we represent it by a single Slater determinant:

$$\mathcal{E} = |\mu^+_1 \mu^-_{-1} \dots \mu^+_i \mu^-_{-i} \dots \mu^+_q \mu^-_{-q}| \quad (1)$$

where  $\mu_i$  depends only on the three space coordinates. The + and - refer to alpha and beta spin functions in the usual way. The molecular orbitals (MO's)  $\mu_i$  are divided into core orbitals, denoted  $\psi^{\text{core}}$ , and valence orbitals, denoted  $\psi$ .

The core orbitals include the ligand *1s* orbitals and the *1s*, *2s*, and *2p* orbitals of the central metal ion; these orbitals are all assumed to be the same as in the free ions.

The valence MO's are constructed as linear combinations of atomic orbitals, LCAO's:

$$\psi_i = \sum_{r=1}^m A_{ri} \chi_r \quad (2)$$

assuming *m* atomic orbitals (AO's), denoted  $\chi_r$  or just *r*, *s*, *t*,...

The problem is now to determine  $A_{ri}$  of eqn. (2) together with the molecular orbital energy, denoted  $\epsilon_i$ , by the aid of Roothaan's method.<sup>9</sup>

2b. *Roothaan's method.* The core orbitals, as defined in Section 2a, come close to being orthogonal to each other, and also the "strong orthogonality condition":

$$\int \psi_i^{\text{core}}(1) \varphi_j(1) d\tau_1 = 0 \quad (3)$$

for all pairs  $(\psi_j, \psi_i^{\text{core}})$  is reasonably fulfilled. It is then expedient to introduce the one electron core operator:

$$H^{\text{core}}(1) = T(1) + \sum_g V_g(1) \quad (4a)$$

$$V_g(1) = -\frac{Z_g e^2}{r_{1g}} + \sum_{j \text{ on } g} [2J_j^{\text{core}}(1) - K_j^{\text{core}}(1)] \quad (4b)$$

where  $g$  numbers the various nuclei, with charges  $Z_g e$ .  $T(1)$  is the kinetic energy operator, and  $J_j^{\text{core}}(1)$  and  $K_j^{\text{core}}(1)$  are the usual Coulomb and exchange operators:

$$J_j^{\text{core}}(1) \psi_i(1) = \int \psi_j^{\text{core}}(2) \psi_j^{\text{core}}(2) \frac{e^2}{r_{12}} d\tau_2 \times \psi_i(1) \quad (5a)$$

$$K_j^{\text{core}}(1) \psi_j(1) = \int \psi_j^{\text{core}}(2) \psi_i(2) \frac{e^2}{r_{12}} d\tau_2 \times \psi_j^{\text{core}}(1) \quad (5b)$$

Application of Roothaan's method then leads to the following set of equations:<sup>9</sup>

$$\sum_{s=1}^m \{ (r|H^{\text{core}}(1)|s) + \sum_{t,u} P'_{tu} \{ [rs|tu] - \frac{1}{2}ru|ts] \} \} A_{si} = \epsilon_i \sum_{s=1}^m (\delta_{rs} + S_{rs}) A_{si} \quad (6)$$

with  $r=1, 2, \dots, m$ , and:

$$(r|H^{\text{core}}(1)|s) = \int \chi_r(1) H^{\text{core}}(1) \chi_s(1) d\tau_1 \quad (7a)$$

$$[rs|tu] = \iint \chi_r(1) \chi_s(1) \frac{e^2}{r_{12}} \chi_t(2) \chi_u(2) d\tau_1 d\tau_2 \quad (7b)$$

$$P'_{tu} = 2 \sum_j^n A_{tj} A_{uj} \quad (7c)$$

$$S_{rs} = \int (\chi_s(1) \chi_r(1) - \delta_{rs}) d\tau_1. \quad (7d)$$

Here  $n$  is the number of occupied MO's and  $\delta_{rs}$  the well known Kronecker symbol.

2c. *Symmetrical orthogonalization.* As suggested in an article by Löwdin,<sup>10</sup> the AO's  $\chi_r$  are replaced by a set of orbitals  $\lambda_r$ :

$$\lambda_r = \chi_r - \sum_{v \neq r} \frac{1}{2} S_{rv} \chi_v \quad (8)$$

orthonormal to first order in  $S_{rv}$ . In the  $\lambda$ -basis the Roothaan equations have the form:

$$\sum_s^m \left\{ (\lambda_r | H^{\text{core}}(1) | \lambda_s) + \sum_{t,u} P_{tu} \{ [\lambda_r \lambda_s | \lambda_t \lambda_u] - \frac{1}{2} [\lambda_r \lambda_u | \lambda_t \lambda_s] \} \right\} C_{si} = \epsilon_i C_{ri} \quad (9)$$

with

$$\psi = \sum_{r=1}^n C_{ri} \lambda_r \quad (10)$$

and

$$P_{tu} = \sum_j^n C_{tj} C_{uj} \quad (11)$$

2d. *Integral approximations.* A number of semiquantitative features are now introduced to facilitate the evaluation of integrals in eqn. (9).

In the case of a two center charge distribution we have adopted either the general Löwdin approximation:<sup>11</sup>

$$\chi_r(1) \chi_s(1) \simeq \alpha \tilde{\chi}_r(1) \tilde{\chi}_s(1) + \beta \tilde{\chi}_s(1) \tilde{\chi}_s(1) \quad (12)$$

$$\alpha + \beta = S_{rs} \quad (13)$$

or the special Mulliken approximation:<sup>12</sup>

$$\chi_r(1) \chi_s(1) \simeq \frac{1}{2} S_{rs} (\tilde{\chi}_r(1) \tilde{\chi}_r(1) + \tilde{\chi}_s(1) \tilde{\chi}_s(1)) \quad (14)$$

In order to keep the approximations rotationally invariant, all one center charge distributions to the right in (12) and (14) have been replaced by their spherical averages, indicated by a  $[\sim]$ . Table I gives a detailed description of the approximations. Here column one and two show the integrals and number of centers, whereas column three contains expressions for the charge distributions  $\lambda_r \lambda_s$  in terms of  $\chi_r$  and  $\chi_s$ .

Additionally we have adopted the point charge approximation:

$$V_g(1) \simeq -Z_g^{(\text{ef})} / r_{1g} \quad (15)$$

when more than one center is involved. Here  $Z_g^{(\text{ef})}$  denotes the number of valence electrons from center  $g$ .

2e. *Relation to other methods.* The method described in the previous sections can be considered as the INDO counterpart to the CNDO scheme suggested by Dahl and Ballhausen.<sup>8</sup> As a deviation, however, we have chosen only to retain terms to first order in the overlap.

Table 1. Integral approximations.

Integral	Orbitals	$\lambda_r \lambda_s$
$(\lambda_r   T   \lambda_s)$	[r,s] arbitrary	$\chi_r \chi_s - S_{rs}(\chi_r \chi_r - \chi_s \chi_s)/2$ [exact to first order in $S_{rs}$ ]
$(\lambda_r   V_a   \lambda_s)$	[r,s] on the same a	$\chi_r \chi_s$ [exact to first order in $S_{rs}$ ]
	[r,s] on the same center b, different from a	$\widetilde{\chi}_r \widetilde{\chi}_r \delta_{rs}$ [including a spherical average exact to first order in $S_{rs}$ ]
	[r,s] on two centers (a,b)	$\chi_r \chi_s - S_{rs}(\widetilde{\chi}_r \widetilde{\chi}_r + \widetilde{\chi}_s \widetilde{\chi}_s)/2$ [including a spherical average exact to first order in $S_{rs}$ ]
	[r,s] on two centers (b,c)	$(\alpha - S_{rs}/2)\widetilde{\chi}_r \widetilde{\chi}_r + (\beta - S_{rs}/2)\widetilde{\chi}_s \widetilde{\chi}_s$ [with the Löwdin-approximation exact to first order in $S_{rs}$ ]
$(\lambda_r \lambda_s   \lambda_t \lambda_u)$	[r,s] and [t,u] all on the same center	$\chi_r \chi_s, \chi_t \chi_u$ [exact to first order in $S_{rs}$ ]
	[r,s] and [t,u] on more than one center	$\widetilde{\chi}_r \widetilde{\chi}_r \cdot \delta_{rs}, \widetilde{\chi}_t \widetilde{\chi}_t \cdot \delta_{tu}$ [with the Mulliken-approximation exact to first order in $S_{rs}$ ]

Table 2. STO basis B1 and B2.

	1s	2s	3s	4s	2p	3p	4p	3d	3d
Ni [B1]	27.4	10.6	4.9	1.5	11.5	4.6	1.2	4.2	2.6
	1s	2s	3s	3s	2p	3p	3p	3d	3d
Ni [B2]	27.4	10.6	4.9	2.8	11.5	4.6	2.7	4.2	2.6
Fe [B2]	25.4	9.3	4.6	2.7	11.1	4.3	2.5	3.7	2.2
Cr [B2]	23.4	8.5	4.1	2.5	10.0	3.8	2.3	3.3	2.0
C	5.7	1.6	—	—	1.6	—	—	—	—
O	7.7	2.2	—	—	2.2	—	—	—	—
H	1.2	—	—	—	—	—	—	—	—

### 3. RESULTS AND DISCUSSIONS

3a. Radial functions. Two STO (Slater Type Orbitals) basis sets have been used (see Table 2). In the first [B1] 1s, 2s, and 2p on the metal and 1s on the ligands were taken as core with 3s, 3p, 3d, 4s, 4p from the central atom and 2s, 2p on the ligands in the valence shell. The exponents for B1 were taken from Clementi *et al.*,<sup>13</sup> but in order to simulate the basis of Demuynck *et al.*<sup>3</sup> a 3d polarization component was added.

In B2 polarization functions were added to 3s, 3p on the metal, whereas the 4s, 4p orbitals were omitted. Each STO component was Schmidt orthogonalized to the inner shells.

The geometries of Ni(CO)<sub>4</sub>, Ni(CN)<sub>4</sub><sup>2-</sup> and Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> were taken as in Ref. 2 and that of Cr(CO)<sub>6</sub> from Ref. 14.

3b. Comparison with ab initio calculations. In Table 3 we have the eigenvalues and atomic composition from a B1 INDO calculation on Ni(CN)<sub>4</sub><sup>2-</sup>, together with the calculated eigen-

Table 3. INDO Calculation on Ni(CN)<sub>4</sub><sup>2-</sup> using [B1].

Orbital energies (a.u.)			Symmetry	Atomic composition (%)						
				Ni orbital		C orbital		N orbital		
				3d	4s	4p	2s	2p	2s	2p
.0157 <sup>a</sup>	-.185 <sup>b</sup>	.033 <sup>c</sup>	9a <sub>1g</sub>	94.0	5.2		.3	1.0	0.2	0.2
-.0013	-.267	-.013	2e <sub>g</sub>	83.2				1.6		15.2
-.0609	-.335	-.026	2b <sub>2g</sub>	72.9				3.7		23.4
-.1277	-.123	-.116	1a <sub>2g</sub>					34.3		65.7
-.1319	-.136		1b <sub>2u</sub>					46.0		54.0
-.1445	-.121	-.113	8e <sub>u</sub>			0.7	0.1	19.7	0.1	79.4
-.1617	-.132		1e <sub>g</sub>	13.8				46.0		40.2
-.2141	-.160		3a <sub>2u</sub>			17.6		46.9		35.5
-.2392	-.156		1b <sub>2g</sub>	22.9				44.4		32.7
-.2670	-.182		5b <sub>1g</sub>	13.0			10.4	36.3	23.9	36.4
-.3562	-.195		7e <sub>u</sub>			1.7	6.1	5.98	45.4	40.8
-.3578	-.231		8a <sub>1g</sub>	1.7	0.1		5.8	4.9	49.0	38.5
-.4540	-.263		4b <sub>1g</sub>	7.			50.0	6.4	23.3	13.3
-.8702			6e <sub>u</sub>				20.7	37.6	4.3	0.4
-.9898			7a <sub>1g</sub>		36.0		43.4	16.0	0.9	3.7
-1.2578			3b <sub>1g</sub>				18.8	22.8	43.7	14.7
-1.2655			6a <sub>1g</sub>		2.2		10.3	31.0	42.4	14.1
-1.2858			5e <sub>u</sub>			3.9	27.3	13.3	41.1	14.4

<sup>a</sup> This work. <sup>b</sup> Ref. 2. <sup>c</sup> Calculated ionization potentials from Ref. 2.

Table 4. INDO on Ni(CO)<sub>4</sub> using [B1].

Orbital energies (a.u.)				Symmetry	Atomic composition (%)						
					Ni orbital			C orbital		O orbital	
					3d	4s	4p	2s	2p	2s	2p
.2024 <sup>a</sup>				11t <sub>2</sub>	3.3		36.3	35.0	4.1	2.9	18.2
-.1891				9a <sub>1</sub>		34.3		40.8	.3	1.3	23.3
.0125				10t <sub>2</sub>	11.2			56.4			21.2
.0442				3e	10.8			60.1			29.1
-.0102				2t <sub>1</sub>				63.6			36.4
-.3847	-.35 <sup>b</sup>	-.395 <sup>c</sup>	-.3234 <sup>d</sup>	9t <sub>2</sub>	64.4		7.1	.5	6.3		21.7
-.4371	-.39	-.471	-.3564	2e	80.1			1.6			18.3
-.6384	-.43	-.653		1t <sub>1</sub>				29.4			70.6
-.6642	-.45	-.644	-.5439	8t <sub>2</sub>	5.8		.3	.8	31.7	.1	61.3
-.6713	-.46	-.665		1e	6.4			31.5			62.1
-.8571	-.50	-.662		7t <sub>2</sub>	.1		2.4	7.1	9.1	31.1	48.2
-.8648	-.53	-.693	-.6688	8a <sub>1</sub>		1.2		9.3	6.1	35.6	47.8
-1.2315	-.56	-.793		6t <sub>2</sub>	1.0		32.6	35.4	24.5	1.5	5.0
-1.3983	-.58	-.809		7a <sub>1</sub>		42.3		39.4	12.7	1.5	4.1
-1.9184	-.95	-1.530		5t <sub>2</sub> , 6a <sub>1</sub>				14.5	20.0	55.2	10.6

<sup>a</sup> This work. <sup>b</sup> Eigenvalues extrapolated from Fig. 5 in Ref. 3. <sup>c</sup> Eigenvalues from Ref. 2. <sup>d</sup> Photoelectron spectrum as assigned by Ref. 2.

values and ionization potentials from Demuyneck *et al.*<sup>3</sup> The agreement is good for the highest 4 levels, between our eigenvalues and the calculated ionization potentials in Ref. 2.

Koopmans' theorem is thus reasonably well fulfilled in our case. This is in contrast to the claim by Demuyneck *et al.*, that this theorem is invalid for Ni(CN)<sub>4</sub><sup>2-</sup>. A possible explanation of

Table 5. INDO calculation on Ni(CO)<sub>4</sub> using [B2].

Orbital energies (a.u.)		Symmetry	Atomic composition (%)						
			Ni 3d	Ni 3p	3s	C orbital		O orbital	
						2s	2p	2s	2p
-.2335	-.3234 <sup>a</sup>	9t <sub>2</sub>	62.4			5.7	8.0	1.0	22.9
-.2977	-.3564	2e	74.9				3.7		21.4
-.5526	-.5439	1t <sub>1</sub>					30.6		69.4
-.5694	-	8t <sub>2</sub>	1.5				34.6		63.8
-.5742	-	1e	4.4				33.9		61.7
-.6090	-	8a <sub>1</sub>			12.3	31.4	27.0	4.9	24.4
-.7032	-.6688	7t <sub>2</sub>	10.1	2.6		12.5	24.9	16.0	33.9
-.8198	-	7a <sub>1</sub>			1.5	36.0	1.2	29.2	32.1
-.8436	-	6t <sub>2</sub>	3.7	1.0		51.9	2.6	20.1	20.7
-1.8205	-	6a <sub>1</sub>				14.4	21.1	54.1	10.4
-1.8344	-	5t <sub>2</sub>				13.9	22.0	53.8	10.3

<sup>a</sup> Photoelectron spectrum (Ref. 2).Table 6. INDO calculation on Fe(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> using [B2].

Orbital energies (a.u.)				Symmetry	Atomic composition (%)					
					Fe orbital		C orbital		H orbital	
				3d	3s	3p	2s	2p	1s	
-.3491	-.530 <sup>b</sup>	-.3050 <sup>c</sup>	-.2499 <sup>a</sup>	3e <sub>2g</sub>	70.0				28.8	1.2
-.4165	-.429	-.4079	-.2646	4e <sub>1u</sub>	71.2				27.9	.9
-.4360	-.609	-.3711	-.3234	4a <sub>1g</sub>	86.4				11.5	2.1
-.4972	-.437	-.4116	-.3417	4e <sub>1g</sub>	12.4				84.6	3.0
-.6242	-.589	-.5567	-	3a <sub>2u</sub>			9.3		89.8	.9
-.6621	-.585	-	-	3e <sub>2u</sub>				1.2	79.4	19.4
-.6782	-	-	-	4a <sub>1g</sub>	7.5	10.4			80.5	1.6
-.6819	-	-	-	3e <sub>1g</sub>				9.3	62.3	28.4
-.6892	-.594	-	-	2e <sub>2g</sub>				7.8	60.4	31.8
-.6901	-	-	-	3e <sub>1g</sub>	5.1			1.9	58.0	35.0
-.8304	-	-	-	2a <sub>2u</sub>			1.5	14.4	48.0	36.1
-.8584	-	-	-	3a <sub>1g</sub>	4.2	.5		14.4	44.6	36.3
-.9836	-	-	-	2e <sub>1g</sub>				26.9	54.7	18.4
-.9957	-	-	-	1e <sub>2g</sub>				2.2	25.0	54.5
-1.2396	-	-	-	2e <sub>1u</sub>				2.0	62.4	28.1
-1.2737	-	-	-	1e <sub>1g</sub>	2.9			64.4	27.8	4.9
-1.6413	-	-	-	2a <sub>2u</sub>	11.6			57.6	29.9	.9
-1.6631	-	-	-	2a <sub>1g</sub>	2.4	8.5		57.9	39.8	.5
-2.9892	-	-	-	1e <sub>1u</sub>			100			
-3.1376	-	-	-	1a <sub>2u</sub>			100			
-4.5993	-	-	-	1a <sub>1g</sub>	100					

<sup>a</sup> Photoelectron spectrum (Ref. 2). <sup>b</sup> Orbital energies from Ref. 1. <sup>c</sup> Calculated ionization potentials from Ref. 1.

the improved agreement with experimental ionization potentials may lie in our use of a Slater orbital as a 3d polarization function, where Demuyneck *et al.* use a single Gaussian orbital.

For the two non-bonding  $\pi$ -orbitals (1a<sub>2g</sub>, 1b<sub>2u</sub>), the four bonding  $\pi$ -orbitals (8e<sub>u</sub>, 1e<sub>g</sub>, 3a<sub>2u</sub>, 1b<sub>2g</sub>) and the remaining  $\sigma$ -orbitals, no comparison can be made, as Demuyneck *et al.* have not directly calculated the ionization po-

Table 7. INDO calculation on Ni(CN)<sub>4</sub><sup>2-</sup> using [B2].

Orbital energies (a.u.)	Symmetry	Atomic composition						
		3s	Ni orbital 3p	3d	C orbital 2s 2p		N orbital 2s 2p	
.1532	9a <sub>1g</sub>	1.7		85.8	5.8	2.7	.4	3.6
.1073	2e <sub>g</sub>			89.0		.3		10.7
.0429	2b <sub>2g</sub>			77.0		3.3		19.7
-.0406	1b <sub>2u</sub>					41.0		59.0
-.0556	8e <sub>u</sub>		0.5		5.8	41.2	0.8	52.7
-.0671	1a <sub>2g</sub>					48.3		51.7
-.0873	3a <sub>2u</sub>					48.3		51.7
-.0880	1e <sub>g</sub>			7.6		48.3		44.1
-.1441	1b <sub>2g</sub>			18.1		50.1		31.8
-.1707	7e <sub>u</sub>		4.5		15.7	31.6	16.3	31.6
-.1903	8a <sub>1g</sub>	5.7		10.2	10.0	22.1	21.2	30.8
-.2042	5b <sub>1g</sub>			7.4	10.3	25.0	25.6	31.7
-.3459	6e <sub>u</sub>		2.3		46.1	4.5	15.1	32.0
-.3599	7a <sub>1g</sub>	4.5		3.2	46.9	4.5	26.3	14.6
-.3620	4b <sub>1g</sub>			5.9	52.4	6.4	21.5	13.8
-1.1788	6a <sub>1g</sub>				23.1	21.2	41.0	14.7
-1.1860	5e <sub>u</sub>				21.4	21.6	42.2	14.9
-1.1948	3b <sub>1g</sub>				18.6	23.1	41.0	17.3

Table 8. INDO calculation on Cr(CO)<sub>6</sub> using [B2].

Orbital energies (a.u.)	Symmetry	Atomic composition (%)						
		3d	Cr Orbital 4s	4p	C Orbital 2s 2p		O Orbital 2s 2p	
-.2684	-.3087 <sup>a</sup>	2t <sub>2g</sub>	63.3			12.7		24.0
-.5660	-.4895	1t <sub>1g</sub>				31.1		68.9
-.5747	-.5189	5t <sub>1u</sub>			.7	4.0	.1	67.7
-.5842	-.5325	1t <sub>2u</sub>				37.3		62.7
-.6268	-.5586	1t <sub>2g</sub>	3.6			41.9		54.5
-.6928	-.5733	4t <sub>1u</sub>		9.4	16.0	28.1	5.2	43.0
-.7281	-.6424	4a <sub>1g</sub>		12.3	8.1	24.0	17.3	38.3
-.7799	-.6872	3e <sub>g</sub>	5.1			15.1	30.1	49.7
-.8591	-.7092	3t <sub>1u</sub>			2.2	43.6	1.2	23.9
-.8887		3a <sub>1g</sub>		8.8	54.0	3.8	17.3	16.1
-.9570		2e <sub>1g</sub>	18.0		60.3	11.6	3.0	7.1
-1.8573		2a <sub>1g</sub>			17.3	19.4	54.0	9.3
-1.8650		2t <sub>1u</sub>		1.7	11.6	18.0	54.3	14.4
-1.8826		1e <sub>1g</sub>			12.3	17.1	53.2	17.4

<sup>a</sup> Photoelectron spectrum (Ref. 14).

tentials for all of those orbitals as their basis seems to require.

In Table 4 we compare eigenvalues from an INDO calculation on Ni(CO)<sub>4</sub> with those of Ref. 2 and a recent X $\alpha$  calculation by Johnson *et al.*<sup>3</sup> Our ordering of the occupied levels is in agreement with that of Ref. 3, and differ only for closely spaced orbitals from the ordering in

Ref. 2. In addition, the magnitude of the eigenvalues is the same for INDO and *ab initio*. However, as the eigenvalues of Ref. 3 are defined differently they cannot be brought directly into this comparison.

As for the lower lying levels there is a qualitative as well as a quantitative difference between the INDO and the *ab initio* calculation, in as

much as our calculations give a significant  $4s$  and  $4p$  population. We will discuss this point in the next section.

*3c. Limitations of the method.* Consider the overlap charge distribution between two orbitals on the centres (a,b):

$$Q_{a,b} = \chi_a(1)\chi_b(1) \quad (16)$$

In case the gravity point of  $Q_{a,b}$  is placed close to one of the centres (a,b), say a, then the Mulliken approximation is quite inadequate for the hybrid type integral:

$$\int \chi_b(1)\chi_a(1)\chi_a(2)\chi_a(2) \frac{1}{r_{12}} d\tau_1 d\tau_2$$

and it would be unbalanced to calculate the analogous one electron nucleus split integral:

$$\int \chi_b(1)\chi_a(1) \frac{1}{r_a} d\tau_1$$

exactly as suggested in Section 2.

Investigations show that errors will enter into the Fock-matrix element between  $\chi_a$  and  $\chi_b$ , increasing it numerically up to 200 %.

In calculations on inorganic complexes this situation is important if  $4s$  and  $4p$  atomic orbitals are used, as the charge distribution of those orbitals usually has a maximum close to the ligand nucleus. The results in Section 3b are representative for a vast number of INDO calculations using  $4s$  and  $4p$  atomic orbitals. Due to the overestimation of the Fock-matrix elements between  $2s_L$  and  $4s_M$ , and between  $2s_L$  and  $4p_M$  the calculations usually predicted considerably  $4s$  and  $4p$  populations.

Fortunately, it is only calculations relying on spectroscopic data that has to use  $4s$  and  $4p$  atomic orbitals for the sake of consistency.

In methods where all matrix elements are calculated over the basis set it is hard to see how  $4s$  and  $4p$  atomic orbitals with group overlaps up to 0.7 can add much new to the basis. For the calculations in the next section we have therefore replaced the  $4s$  and  $4p$  by more contracted  $3s$  and  $3p$  polarization functions [B2].

A number of calculations on small molecules show that the method estimates too small bond distances. In the case of CO our INDO method calculated an equilibrium bond distance of 0.83 Å compared to the experimental of 1.13 Å.

This trend can be accounted for by the spherical average used in Section 2. Such an approximation does not treat the repulsion be-

tween two orbitals pointing towards each other correctly.

In the CNDO/2 scheme<sup>9</sup> this deficiency is corrected by replacing:

$$\int \chi_a(1)\chi_a(1) \frac{1}{r_b} \text{ with } \int \chi_a(1)\chi_a(1)\chi_b(2)\chi_b(2) \frac{1}{r_{12}} d\tau_1 d\tau_2,$$

and this possibility might be investigated in a later work.

*3d. Use of the basis [B2].* The nature of the bonding in Ni(CO)<sub>4</sub> has been a matter of dispute between an *ab initio* calculation by Demuynek *et al.*<sup>3</sup> and an X $\alpha$  scattered-wave calculation by Johnson *et al.*<sup>3</sup>

Whereas Johnson *et al.* do not find any significant metal to ligand  $\pi$ -back bonding, Demuynek calculates an increase in the  $2p\pi_C$  population when going from CO to the Ni(CO)<sub>4</sub>. This trend is taken as an indication of  $\pi$ -back bonding. In our calculations on Ni(CO)<sub>4</sub>, Ni(CN)<sub>4</sub><sup>2-</sup>, and Cr(CO)<sub>6</sub>, Tables 9, 11, and 12, a similar increase in the  $2p\pi_C$  was found, greatest in the case of Cr(CO)<sub>6</sub> and smallest in Ni(CN)<sub>4</sub><sup>2-</sup>. As for the ordering of the levels, the reader is referred to Tables 5, 7, and 8.

We will close this section by presenting a calculation on Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>. Although it is a different system, the situation is the same as for our previous comparison with the *ab initio* calculation on Ni(CN)<sub>4</sub><sup>2-</sup>. Our assignment, Table 6, only agrees with that of Ref. 2 after Demuynek *et al.* have performed calculations on the ionization potentials.

In Table 10 we give the population analysis of Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> compared to C<sub>5</sub>H<sub>5</sub><sup>-</sup>. The trend is the same as in the *ab initio* calculation: an increase in the population on  $1s_H$  and a decrease in the population of  $2p\pi_C$ , when going from Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> to C<sub>5</sub>H<sub>5</sub><sup>-</sup>.

Table 9. Gross atomic and orbital populations from an INDO calculation on Ni(CO)<sub>4</sub> using [B2].

	Ni(CO) <sub>4</sub>			CO	
	Ni	C	O	C	O
3s/2s	0.18	1.74	1.79	1.85	1.79
3p $\pi$ /2p $\sigma$	0.08	1.04	1.33	1.02	1.33
3p $\nu$ /2p $\pi$	0.08	0.77	1.41	0.57	1.42
3p $\nu$ /2p $\pi$	0.08	0.77	1.41	0.57	1.42
3d <sub>12</sub>		1.62			
3d <sub>e</sub>		1.58			

Table 10. Gross atomic and orbital populations from an INDO calculation on  $\text{Fe}(\text{C}_5\text{H}_5)_2$  using [B2].

	Fe	C	H
<i>S</i>	6.30	3.19(3.15) <sup>a</sup>	.86(.98)
<i>p<sub>x</sub> + p<sub>y</sub></i>	8.24	1.96(1.92)	
<i>p<sub>z</sub></i>	4.25	1.17(1.19)	
<i>d<sub>xz</sub>, d<sub>yz</sub></i>	.43		
<i>d<sub>xy</sub>, d<sub>x<sup>2</sup>-y<sup>2</sup></sub></i>	1.45		
<i>d<sub>z<sup>2</sup></sub></i>	2.03		

Table 11. Gross atomic and orbital populations from an INDO calculation on  $\text{Cr}(\text{CO})_6$ .

	Cr	$\text{Cr}(\text{CO})_6$		CO	
		C	O	C	O
<i>3s/2s</i>	0.29	1.60	1.79	1.85	1.79
<i>3p<sub>x</sub>/2p<sub>σ</sub></i>	0.20	1.04	1.46	1.02	1.33
<i>3p<sub>y</sub>/2p<sub>π</sub></i>	0.20	0.82	1.22	0.57	1.42
<i>3p<sub>z</sub>/2p<sub>π</sub></i>	0.20	0.82	1.22	0.57	1.42
<i>3d<sub>t<sub>2g</sub></sub></i>	4.01	—	—	—	—
<i>3d<sub>e</sub></i>	0.92	—	—	—	—

Table 12. Gross atomic and orbital populations from an INDO calculation on  $\text{Ni}(\text{CN})_4^{2-}$  using [B2].

	Ni	$\text{Ni}(\text{CN})_4^{2-}$		$\text{CN}^-$	
		C	N	C	N
<i>3s/2s</i>	0.13	1.7	1.81	1.85	1.81
<i>3p<sub>x</sub>/2p<sub>σ</sub></i>	0.1	1.09	1.19	1.09	1.24
<i>3p<sub>y</sub>/2p<sub>π</sub></i>	0.1	0.95	1.07	0.86	1.13
<i>3p<sub>z</sub>/2p<sub>π</sub></i>	0.0	0.96	1.06	0.86	1.13
<i>3d<sub>xy</sub></i>	1.92				
<i>3d<sub>xz</sub>, 3d<sub>yz</sub></i>	1.93				
<i>3d<sub>z<sup>2</sup></sub></i>	2.0				
<i>3d<sub>x<sup>2</sup>-y<sup>2</sup></sub></i>	0.28				

#### 4. CONCLUSION

A new semiquantitative SCF LCAO MO calculation scheme has been applied to  $\text{Ni}(\text{CO})_4$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{C}_5\text{H}_5)_2$ , and  $\text{Ni}(\text{CN})_4^{2-}$ . Comparison to recent *ab initio* calculations seems promising, and calculations on tetrahedral tetrahalid complexes<sup>15</sup> and tetrahedral oxo complexes<sup>16</sup> are now in preparation.

*Acknowledgement.* A large part of the work described in this paper was carried out at the Department of Physical Chemistry, University of Copenhagen, and the author would like to thank Dr. J. P. Dahl for valuable discussions.

A general program (ODIN) based on our method has been developed by J. A. Geer and D. R. Truax of the Department of Chemistry, University of Calgary.

#### REFERENCES

- Coutiere, M. M., Demuynck, J. and Veillard, A. *Theor. Chim. Acta* 27 (1972) 281.
- Demuynck, J. and Veillard, A. *Theor. Chim. Acta* 28 (1973) 241.
- Johnson, K. H. and Walgren, U. *Int. J. Quantum Chem.* 6S (1971) 250.
- Demuynck, J. and Veillard, A. *Chem. Phys. Lett.* 6 (1970) 204.
- Hilliers, I. H. and Saunders, V. R. *Chem. Commun.* (1969) 1275.
- Hilliers, I. H. and Saunders, V. R. *Chem. Phys. Lett.* 9 (1971) 219.
- Johansen, H. *Chem. Phys. Lett.* 17 (1972) 569.
- Dahl, J. P. and Ballhausen, C. J. *Advan. Quantum Chem.* 4 (1968) 170.
- Pople, J. A., Santry, D. P. and Segal, G. A. *J. Chem. Phys.* 43 (1965) S129.
- Löwdin, P. O. *Phil. Mag. Suppl.* Vol. 5 (1956) No. 17.
- Löwdin, P. O. *J. Chem. Phys.* 21 (1953) 374.
- Mulliken, R. S. *J. Chim. Phys. Physicochim. Biol.* 46 (1949) 675.
- Clementi, E. and Raimolmi, D. L. *J. Chem. Phys.* 38 (1968) 2686.
- Caulton, K. G. and Fenske, R. F. *Inorg. Chem.* 7 (1968) 1273.
- Geer, J. A., Truax, D. R. and Ziegler, T. *To be published.*
- Ziegler, T. *To be published.*

Received July 2, 1973.