SIMULATED SEMIEMPIRICAL MOLECULAR ORBITAL CALCULATIONS I.

*Transferability of Fock matrix elements**

By

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(Received October 25, 1979)

Converged Fock matrix elements over Slater-type atomic orbitals and hybridized orbitals obtained in semiempirical (EHT, CNDO, INDO and MINDO) quantum chemical calculations have been compared in case of alkanes, olefins, O-containing polar molecules and various closed-shell and open-shell molecules and molecular fragments. Good agreements between parallel Fock matrix elements in different molecules foreshadow their transferability from one molecule to another. Successful transference has been proved for alkanes. The aim of this series of studies is to establish the principles, rules, possibilities and limitations of transferability. The findings by semiempirical procedures will very likely be applicable in general by more rigorous approximations and may find their use in the approximate calculations of very large organic and inorganic (such as transition metal complex) systems by reasonable computing times.

The principle of transference is of great significance in chemistry; everywhere and everytime this principle is functioning and is exploited for the advantages which are arising from its use. This is happening whenever a given chemical bond is regarded to be essentially the same independently of the nature of the molecule in which it appears and of its location in the molecule. The additivities of bond moments and covalent bond radii, the use of characteristic bond frequencies in the *i.r.* spectroscopy and the concept of chromophoric groups in the visible-*u.v.* spectroscopy are all examples of the manifestations of this principle. The "chemical sense" or the "chemist's intuition" is quite often based upon the implicit transference of chemical bonds or characteristic chemical features.

All this make it quite comprehensible why the theoretical chemist has long been kept employed by the question of transferability and is searching partly for suitable "building blocks" which consistently carry the essential chemical properties and informations transferable from one molcule to another without any fundamental change and partly for the electronic structural reasons, evidences and explanations of transferability.

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* Parts of this work were presented at the Quantum Chemistry Seminar held in Visegrád, Nov. 8—10, 1978 and at the Conference on Structure of Matter and Molecules held in Mátrafüred, Oct. 8—10, 1979.

It seems to be obvious to find the ultimate "building blocks" in the wave functions of the molecule by presuming the similarities in the wave functions of similar molecules or similar parts of molecules. According to some quantum chemical sense one could expect that localized MO orbitals will be transferable with greater success than fully delocalized orbitals which extend over the whole molecule so being more strongly affected by structural changes even though the molecules or molecular fragments to be compared are more or less similar to one another.

A number of quite recent studies [1—7] has really shown that the transference of localized orbitals can in numerous cases be carried out with success especially if the transfer takes place between similar environments. DEPLUS and others [8] proved the transferability of Fock matrix elements over localized orbitals on an orthogonal basis, however transference through localization of non-orthogonal orbitals may be of particular interest [9].

In the MO theory, *"ab initio"* quantum chemical calculations have given very useful results for relatively small molecules. Nevertheless, such calculations for larger molecules are prohibitively lengthy and expensive owing mainly to the large number of two-electron repulsion integrals which have to be evaluated. Calculations on very large organic molecules and transition metal coordination compounds are rather time-consuming and money-wasting even by semiempirical methods. The SCF—LCAO—MO scheme, in none of its approximation levels utilizes the fundamental fact that the physical and chemical properties of a molecular fragment or functional group are almost entirely independent of the particular molecule in which such molecular pieces occur, therefore, each molecule is treated as a new case even though several molecules have identical or similar common parts. However, this very fact suggests the possibility of developing procedures in which results of accurate calculations on smaller molecules could be used in the approximate calculation of larger molecules containing the same molecular fragments or functional groups. Thus, in spite of the expectations by mere speculations, transferable features of molecules can truly be revealed even when using completely delocalized canonical orbitals obtained in MO calculations. The process of expanding the molecular orbitals in terms of atomic orbitals and optimizing the linear combinations of atomic orbitals through the iterative solution of the Hartree—Fock—Roothaan eigenvalue equation brings to light the transferable properties of molecules. Transference in MO theory was first used in the work of ORLOFF and FITTS [10] who approximated the Hamiltonian diagonal matrix elements in the Hückel MO calculation of large molecules by appropriate matrix elements obtained from *ab initio* calculations on smaller molecules. This concept was extended to σ-electrons and off-diagonal matrix elements in the nonempirical molecular orbital (NEMO) procedure [11] and transference of molecular orbitals themselves was applied in the "Molecules in Molecules" (MIM) approach [12]. The "Simulated Ab Initio Molecular Orbital" (SAMO) method [13—22] utilizes the transferability of *ab initio* Fock matrix elements of small molecules in the construction of Fock matrices of large molecules. The SAMO method has been successfully applied to aliphatic hydrocarbons [14], polymers, polyethylene and polyene [15], a large biologically active (carcinogenic) substance [16], organic radicals using a spin unrestricted open-shell formalism [17], saturated cyclic hydrocarbons [18], aromatic molecules [19], polar molecules such as alcohols, amines, aldehydes and acids [20], large poly-

nuclear aromatic hydrocarbons [21] and open-shell radicals, ionized and excited states using a spin restricted Hartree—Fock scheme [22].

The SAMO method seems to have the widest applicability among the transference methods therefore we decided to perform semiempirical (EHT, CNDO, INDO, MINDO, etc.) calculations following the SAMO suggestions. Thus, when assemblying the Fock matrix of a large (target) molecule, the converged Fock matrix elements of small (pattern) molecules containing the same fragments or functional groups as the large molecule are transferred from direct semiempirical calculations. Both diagonal and off-diagonal matrix elements can be transferred from semiempirical calculations. The synthetic Fock matrix of the target molecule thus constructed can be used in two different ways: either to generate the molecular orbitals and orbital energies for the target molecule by a single non-iterative solution of the eigenvalue problem or to use it as a starting Fock matrix in the SCF iteration procedure. In the first case approximate results less accurate than those of the pattern molecules can be obtained for the large target molecule in computer times which are only the fractions of those for the direct calculations. In the second case a solution of comparable accuracy to the direct semiempirical calculations can be achieved but still for less expense, regarding the decrease in the number of iteration cycles owing to better convergence.

The aim of our simulated semiempirical MO calculations is to establish, at a lower cost than the original SAMO version of transference does, the principles, rules, possibilities and limitations concerning the transferability of Fock matrix elements and perhaps to find other transferable properties (*e.g.* density matrix blocks, etc.) overlooked so far. Another purpose of this series of our studies is to attempt finding evidences for the transferability among transition metal complexes. It can easily be realized that the reason why works on transference methods keep away from this subject so that practically no reference on successful transference can as yet be found in this field is to be looked for mainly in financial motives: the expense of repeating *ab initio* calculations at a range of different geometries would be enormous even for relatively small transition metal complexes or fragments of such containing the metal with its many orbitals and electrons.

The first paper of this series is mainly dealing with results obtained by CNDO/2 calculations [23] since this method — using its CLACK's version [24] — can easily be extended to studying coordination compounds of transition elements. Our preliminary investigations, however, have justified the transference of Fock matrix elements obtained in EHT, INDO and MINDO calculations as well. Next papers will give wider account on uses of such results. It is hoped that most of the conclusions on transference properties drawn by semiempirical methods will also be applicable by more rigorous (*e.g.* various level *ab initio*) calculations.

The Fock matrix elements are critically dependent on molecular configuration, the choice of the coordinate system, the orientation of the molecule relative to an external coordinate system, geometry factors, bonding data (internal coordinates: bond distances and angles), conformation of the molecule, presence or absence of net charges on the molecule as a whole, multiplicity of the ground state of the molecule, and the nature and location of neighbouring atoms or groups. Individually or collectively these factors may drastically affect the magnitude of matrix elements.

To test for similarities the parallel matrix elements in different molecules and molecular fragments, complete semiempirical (EHT, CNDO/2, INDO and MINDO/1) calculations were performed for a number of molecules and molecular fragments using standardized geometries and unhybridized and standard hybridized bases.

In Table I typical Fock matrix elements over Slater-type AO-s calculated by CNDO/2 for ethane in two different orientations are presented. In orientation 1

Table I

Typical Fock matrix elements over AO-s calculated by CNDO/2 for ethane in 2 different orientations

Interacting* orbitals	Orientation** 1	Orientation** 2
$C_s - C_s$	−0.5203	−0.5203
$C_s - C_{p_x}$	0.0062	0.0000
$C_s - C_{p_y}$	0.0062	0.0036
$C_s - C_{p_z}$	0.0062	0.0101
$C_s - C'_s$	−0.3048	−0.3048
$C_s - C'_{p_x}$	0.2064	0.0000
$C_{p_x} - C'_{p_x}$	0.0065	−0.1767
$C_{p_x} - C'_{p_y}$	0.1832	0.0000
$C_{p_y} - C'_{p_y}$	0.0065	−0.1157
$C_{p_y} - C'_{p_z}$	0.1832	0.1726
$C_{p_z} - C'_{p_z}$	0.0065	0.3119

* C − C denotes intragroup elements and C − C′ neighbouring group elements.
** The values of Fock matrix elements are in hartrees.

one of the C-atoms of the ethane molecule is located in the origin of the coordinate system and the C—C bond is directed towards direction (1, 1, 1). In orientation 2 one of the H-atoms is placed in the origin the neighbouring C-atom being in the y-axis and the C—C bond in the yz-plane. From the data of Table I it is evident that most of the correspondent matrix elements are differring from one another thus upsetting the possibility of their uses in transference procedures. To avoid such difficulties the transferability can in general be ensured in two alternative ways: *i*) by maintaining the same relative orientations for both the pattern molecules and the target molecule; in this case even matrix elements over AO-s can be transferred, and *ii*) by employing ideally hybridized bases; in this case matrix elements over hybridized atomic orbitals (HAO-s) can be transferred. The use of HAO-s facilitates the accurate comparisons between the corresponding Fock matrix elements because the HAO-s are determined by the internal reference framework of the molecule whereas unhybridized AO-s are defined by reference to the external coordinate system.

In Table II Fock matrix elements over AO-s calculated by CNDO/2 method for aliphatic hydrocarbons oriented identically and in Table III matrix elements over HAO-s calculated by CNDO/2 method for the same first four members in

the homologous series of alkanes oriented differently are compared. The numbering of hybrid orbitals and the H 1s orbitals is displayed on Fig. 1. As one can see, in case of hybrid orbitals no matter whatever orientation is in effect, the corresponding matrix elements can always be parallelled.

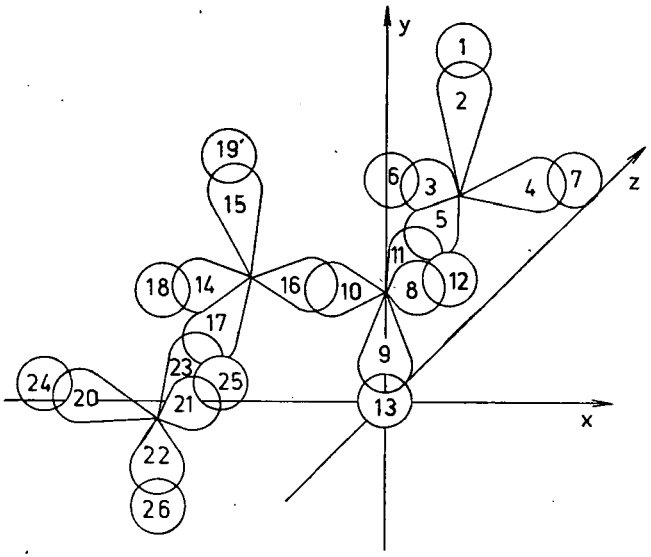

Fig. 1. Numbering of hybrid atomic orbitals in alkanes

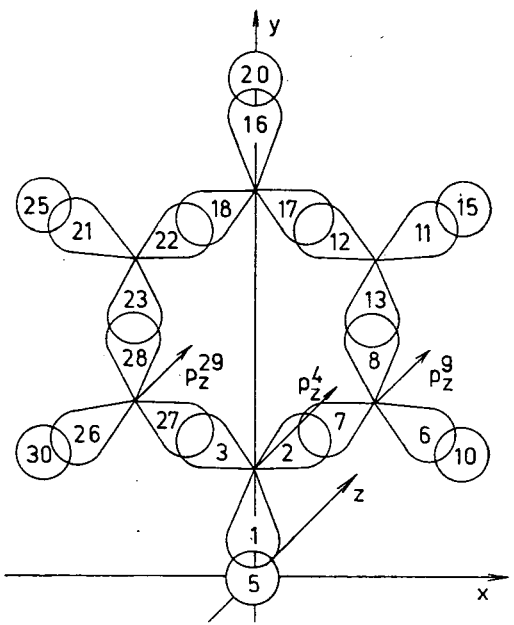

Fig. 2. Numbering of hybrid atomic orbitals in olefins

Table II

Typical parallel Fock matrix elements over AO-s calculated by CNDO/2 for alkanes (in hartrees)

Interacting* orbitals	Methane	Ethane	Propane	Butane
		Methyl intragroup		
C_s —C_s	−0.5271	−0.5203	−0.5232	−0.5226
C_{p_x}—C_{p_x}	−0.1958	−0.1959	−0.1982	−0.1972
C_s —C_{p_y}	0.0000	0.0036	0.0040	0.0038
H_i —H_i	−0.2580	−0.2628	−0.2631	−0.2630
H_i —H_j	−0.0573	−0.0557	−0.0553	−0.0553
C_s —H	−0.3907	−0.3890	−0.3882	−0.3879
C_{p_z}—H	0.2625	0.2164	0.2162	0.2160
		Methylene intragroup**		
C_s —C_s	—	(−0.5203)	−0.5159	−0.5189
C_{p_x}—C_{p_x}	—	(−0.1959)	−0.1976	−0.2001
C_s —C_{p_y}	—	(0.0036)	0.0055	0.0053
H_i —H_i	—	(−0.2628)	−0.2595	−0.2603
H_i —H_j	—	(−0.0557)	−0.0545	−0.0547
C_s —H	—	(−0.3890)	−0.3871	−0.3874
C_{p_z}—H	—	(−0.2164)	−0.2157	−0.2158
		First neighbour groups		
C_s —C'_s	—	−0.3048	−0.3042	−0.3039
C_{p_x}—C'_{p_x}	—	−0.1767	−0.1760	−0.1760
C_{p_y}—C'_{p_y}	—	−0.1157	−0.1125	−0.1126
C_{p_z}—C'_{p_z}	—	0.3119	0.3108	0.3112
H —H′	—	−0.0160	−0.0160	−0.0160
C_s —H′	—	−0.0650	−0.0645	−0.0644
C_{p_z}—H′	—	−0.0723	−0.0716	−0.0714
		Second neighbour groups		
C_s —C''_s	—	—	−0.0568	−0.0569
C_{p_x}—C''_{p_x}	—	—	−0.0211	−0.0212
C_{p_y}—C''_{p_y}	—	—	−0.0594	−0.0592
C_{p_z}—C''_{p_z}	—	—	0.0183	0.0167
H —H″	—	—	−0.0100	−0.0100
C_s —H″	—	—	−0.0219	−0.0219
C_{p_z}—H″	—	—	−0.0077	−0.0077

* Atomic orbitals with prime and double prime denote those on first and second neighbour group atoms, with respect to the group whose atoms bear on no prime.

** For sake of comparisons ethane methyl intragroup values are displayed in brackets.

Other than CNDO/2 semiempirical calculations exhibit similar possibilities concerning transferences of matrix elements. When comparing the results of CNDO/2, EHT, INDO and MINDO/1 calculations for alkanes in Table II and Table IV, it can be seen that perhaps the best transferabilities can be expected from

MINDO/1 and the worst from EHT calculations. Table V and Table VI show comparisons of parallel matrix elements for olefins using AO-s and HAO-s as bases. The numbering of hybrid orbitals, the H 1s and C $2p_z$ orbitals is as in Fig. 2. A number of typical equivalent Fock matrix elements over AO-s in CNDO/2 calculations for some polar carbon compounds containing a carbonyl group listed in Table VII show transferabilities comparable to those found for alkanes and olefins.

Table III

Typical parallel Fock matrix elements over HAO-s calculated by CNDO/2 for alkanes (in hartrees)

Interacting* orbitals	Methane	Ethane	Propane	Butane
1—1	−0.2580	−0.2628	−0.2631	−0.2624
1—2	−0.5890	−0.5867	−0.5869	−0.5869
1—3	−0.0640	−0.0651	−0.0647	−0.0647
1—5	−0.0640	−0.0609	−0.0598	−0.0595
1—6	−0.0572	−0.0557	−0.0553	−0.0553
2—2	−0.2786	−0.2817	−0.2830	−0.2820
2—3	−0.0828	−0.0857	−0.0861	−0.0861
1—9	—	−0.0277	−0.0270	−0.0270
1—10	—	0.0185	0.0160	0.0160
1—11	—	−0.0930	−0.0927	−0.0927
1—12	—	−0.0148	−0.0149	−0.0150
1—16	—	−0.0181	−0.0180	−0.0180
2—5	—	−0.0734	−0.0749	−0.0750
2—9	—	−0.0629	−0.0626	−0.0625
2—10	—	0.1137	0.1115	0.1117
2—11	—	−0.0861	−0.0868	−0.0871
2—12	—	−0.0277	−0.0276	−0.0276
5—8	—	−0.0862	−0.0871	−0.0867
5—11	—	−0.6655	−0.6642	−0.6644
5—16	—	—	−0.1232	−0.1230
5—17	—	—	0.0299	0.0280
1—15	—	—	−0.0030	−0.0031
1—17	—	—	0.0019	0.0023
2—15	—	—	0.0190	0.0189
2—17	—	—	−0.0179	−0.0176
8—17	—	—	−0.0627	−0.0609
8—18	—	—	0.0181	0.0184
12—14	—	—	0.0187	0.0184
12—17	—	—	−0.0922	−0.0920
12—18	—	—	−0.0179	−0.0176

* The numbering of orbitals is as in Fig. 1.

For transference purposes even fictitious or hypothetical pattern molecules or molecular fragments can effectively be used. In Table VIII some typical Fock matrix elements over AO-s for four heavy centers including fluorine atom in a number of fragments in closed-shell and open-shell states of different spin-multiplicities and in monofluorobenzene and salicylidene-4-fluoro-aniline are collected. Open-shell calculations were carried out by CNDO/2-level spin unrestricted Hartree-Fock (DODS) method. To be able to compare the results of closed-shell and open-

Table IV

Typical parallel Fock matrix elements over AO-s calculated by EHT, INDO and MINDO/1 methodes for alkanes (in hartrees)

Interacting* orbitals	EHT**			INDO			MINDO/1		
	Ethane	Propane	Butane	Ethane	Propane	Butane	Ethane	Propane	Butane
Methyl intragroup									
C_s —C_s	0.2888	0.2645	0.2603	−0.5618	−0.5637	−0.5630	−0.5465	−0.5475	−0.5475
C_{p_x}—C_{p_x}	−0.5464	−0.6264	−0.6209	−0.1780	−0.1799	−0.1789	−0.1640	−0.1658	−0.1657
H_1—H_1	−0.3646	−0.4115	−0.4123	−0.2723	−0.2724	−0.2715	−0.2730	−0.2724	−0.2697
C_s —H	0.2970	0.3215	0.3165	−0.3842	−0.3878	−0.3875	−0.3132	−0.3124	−0.3125
C_{p_z}—H	0.4367	0.4655	0.4723	0.2650	0.2636	0.2639	0.1625	0.1603	0.1603
Methylene intragroup *)**									
C_s —C_s	(0.2888)	0.2613	0.2406	(−0.5618)	−0.5612	−0.5641	(−0.5465)	−0.5588	−0.5599
C_{p_x}—C_{p_x}	(−0.5464)	−0.6341	−0.6938	(−0.1780)	−0.1875	−0.1892	(−0.1640)	−0.1692	−0.1692
H_1—H_1	(−0.3646)	−0.4574	−0.4776	(−0.2723)	−0.2764	−0.2779	(−0.2730)	−0.2695	−0.2691
C_s —H	(0.2970)	0.3041	0.2932	(−0.3842)	−0.3865	−0.3868	(−0.3132)	−0.3124	−0.3122
C_{p_z}—H	(0.4367)	0.5036	0.5088	(0.2650)	0.2590	0.2588	(0.1625)	0.1594	0.1594
First neighbour groups									
C_s —C'_s	0.1060	0.1008	0.1095	−0.3040	−0.3035	−0.3032	−0.2008	−0.2024	−0.2025
C_{p_x}—C'_{p_x}	0.5250	0.5129	0.5194	−0.1696	−0.1748	−0.1736	−0.1232	−0.1190	−0.1191
H —H′	0.1167	0.0848	0.0820	−0.0250	−0.0323	−0.0296	−0.0128	−0.0242	−0.0195
C_s —H′	0.0174	0.0316	0.0339	−0.0728	−0.0706	−0.0702	−0.0436	−0.0462	−0.0450
C_{p_z}—H′	−0.1610	−0.1208	−0.1171	−0.0582	−0.0645	−0.0633	−0.0469	−0.0552	−0.0526
Second neighbour groups									
C_s —C''_s	—	0.0174	0.0142	—	−0.0564	−0.0565	—	−0.0349	−0.0352
C_{p_x}—C''_{p_x}	—	0.0626	0.0631	—	0.0395	0.0388	—	0.0137	0.0140
H —H″	—	0.0307	0.0221	—	−0.0031	−0.0031	—	−0.0075	−0.0075
C_s —H″	—	0.0174	0.0081	—	−0.0219	−0.0219	—	−0.0252	−0.0253
C_{p_z}—H″	—	−0.0738	−0.0528	—	−0.0122	−0.0121	—	−0.0095	−0.0096

* Atomic orbitals with dash and double dash denote those on first and second neighbour group atoms, with respect to the group whose atoms bear on no prime.

** Though the orientations of ethane, propane and butane are identical among themselves in EHT they differ from those in INDO and MINDO/1 calculations.

*** Ethane methylene elements in brackets taken as the corresponding methyl intragroup elements in ethane demonstrate their interchangeability.

Table V

Typical parallel Fock matrix elements over AO-s calculated by CNDO/2 for conjugated hydrocarbons (in hartrees)

Interacting* orbitals	Ethylene	*s-cis*-Butadiene	Benzene
	Intragroup		
C_s—C_s	−0.5239	−0.5238	−0.5235
C_{p_x}—C_{p_x}	−0.1948	−0.2026	−0.2045
H—H	−0.2570	−0.2554	−0.2601
C_s—H	−0.4158	−0.4143	−0.4102
C_{p_x}—H	0.3947	0.3938	0.3928
	First neighbour groups		
C_s—C'_s	−0.3730	−0.3724	−0.3710
C_s—C'_{p_x}	0.3585	0.3563	0.3525
C_{p_x}—C'_{p_x}	0.2169	0.2158	0.2191
C_{p_z}—C'_{p_z}	−0.3671	−0.3548	−0.3540
C_s—H′	−0.0662	−0.0660	−0.0656
	Second neighbour groups		
C_s—C''_s	—	−0.0666	−0.0668
C_s—C''_{p_x}	—	−0.0443	−0.0441
C_{p_x}—C''_{p_x}	—	0.0092	0.0087
C_{p_z}—C''_{p_z}	—	−0.0263	−0.0267
	Third neighbour groups		
C_s—C'''_s	—	−0.0299	−0.0291
C_{p_x}—C'''_{p_x}	—	−0.0106	−0.0096
C_{p_z}—C'''_{p_z}	—	0.0227	0.0199

* Atomic orbitals with prime, double dash and triple dash denote those on first, second and third neighbour group atoms, with respect to the group whose atoms bear on no prime.

shell calculations, the corresponding elements of Fock matrices have been averaged for α and β spins. Though there are better agreements between the corresponding matrix elements of higher members of homologous series or between molecules and molecular fragments of comparable sizes, still acceptable differences occur especially when Fock matrix elements of small fragments assumed to be radicals with one or more unpaired electrons and parts of large molecules are compared.

Usually, matrix elements are decreasing in magnitude with increasing spatial separation of the functions involved. When using hybrid orbitals most matrix elements are negative but at larger separations some elements are positive indicating net repulsions. As a result of our preliminary investigations concerning the changes in the Fock matrix elements over AO-s for mononuclear transition metal complexes and their fragments, containing isoelectronic diatomic ligands (*e.g.* CN^-, NO^+, CO, N_2, *etc.*) arranged around the central metal with the same symmetry, as a function of net charge on the complex molecules, by maintaining other parameters

Table VI

Typical parallel Fock matrix elements over HAO-s calculated by CNDO/2 for conjugated hydrocarbons (in hartrees)

Interacting* orbitals	Ethylene	*s-cis*-Butadiene	Benzene
1—1	−0.3044	−0.2969	−0.3129
1—2	−0.1051	−0.1069	−0.1099
1—3	−0.1224	−0.1236	−0.1099
1—5	−0.6078	−0.6080	−0.6062
1—6	−0.1061	−0.1055	−0.1052
1—7	−0.1003	−0.1011	−0.1029
1—8	0.1201	0.1167	0.1166
1—10	−0.0341	−0.0338	−0.0332
2—5	−0.0506	−0.0489	−0.0501
4—4	−0.1948	−0.2004	−0.2073
4—9	−0.3671	−0.3547	−0.3076
5—5	−0.2575	−0.2513	−0.2648
5—10	−0.0120	−0.0121	−0.0117
1—11	—	−0.0133	−0.0129
1—13	—	0.0299	0.0295
1—15	—	0.0019	0.0018
2—11	—	0.0298	0.0295
2—12	—	−0.0495	−0.0489
2—13	—	−0.1549	−0.1549
5—12	—	−0.0043	−0.0032
5—13	—	−0.0197	−0.0197
5—15	—	0.0013	0.0011

* The numbering of orbitals is as in Fig. 2.

constant, we found that mostly similar matrix elements only appear when the resultant net charges on the molecules to be compared are identical. Less conspicuous changes can be observed in the matrix elements when complexes carrying the same net charges but having ligands different in quality and number are compared. In most cases the use of pattern molecules (fragments) comprising at least three heavy atoms seems to give satisfactory results in semiempirical transference procedures.

The proper criteria for transferability are, of course, lying far more in the results arising from the solutions of the eigenvalue problem, by transferring Fock matrix elements from small pattern molecules or fragments to construct matrices of large target molecules, than in the one by one comparisons of parallel matrix elements for different molecules or fragments, therefore, we completed CNDO/2 calculations for butane in a direct way and also by using synthetic Fock matrices constructed by transference from direct calculations on ethane and propane. When constructing butane from ethane by using Fock matrix element transference, methylene group elements occur in butane which are not found in ethane. On the basis of the similarities of matrix elements in Table II and III it is presumed that the necessary methylene elements can be reasonably approximated by appropriate ethane methyl group elements. Clearly butane elements between non-neighbouring carbon atoms are unavailable from ethane and have been assumed to be negligible, thus all elements

Table VII

Typical parallel Fock matrix elements over AO-s calculated by CNDO/2 for polar carbon molecules (in hartrees)

Interacting orbitals	Formic acid	Acetaldehyde	Acetic acid
	Carbonyl intragroup		
C_s—C_s	−0.5723	−0.5663	−0.5709
C_{p_x}—C_{p_x}	−0.2149	−0.2162	−0.2082
O_s—O_s	−1.1335	−1.1381	−1.1299
O_{p_x}—O_{p_x}	−0.3542	−0.3496	−0.3518
C_s—O_s	−0.4085	−0.4075	−0.4083
C_{p_x}—O_{p_x}	−0.3622	−0.3605	−0.3583
C_{p_z}—O_{p_z}	0.2540	0.2570	0.2532
	Hydroxyl intragroup		
O_s—O_s	−1.1450	—	−1.1391
O_{p_x}—O_{p_x}	−0.6152	—	−0.6135
H—H	−0.2383	—	−0.2345
O_s—H	−0.4568	—	−0.4548
O_{p_x}—H	0.0000	—	0.0000
O_{p_y}—H	−0.4706	—	−0.4688
O_{p_z}—H	−0.1595	—	−0.1639
	Carboxyl intragroup*		
O_s—O'_s	−0.0268	—	−0.0275
O_{p_x}—O'_{p_x}	0.0324	—	0.0329
C_s—O'_s	−0.3347	—	−0.3335
C_s—H	−0.1004	—	−0.1120
	Methyl intragroup*		
C_s—C_s	—	−0.5464	−0.5550
C_{p_x}—C_{p_x}	—	−0.2241	−0.2348
C_s—C_{p_y}	—	0.0024	0.0027
H_i—H_i	—	−0.2750	−0.2776
H_i—H_j	—	−0.0579	−0.0580
C_s—H	—	−0.3890	−0.3891
C_{p_z}—H	—	0.0036	0.0034
	Methyl first neighbour intergroup*		
C_s—C'_s	—	−0.3110	−0.3126
C_{p_x}—C'_{p_x}	—	−0.1727	−0.1714
C_{p_y}—C'_{p_y}	—	−0.1246	−0.1237
C_{p_z}—C'_{p_z}	—	0.3020	0.2997
C_s—C'_{p_x}	—	0.0027	0.0032
C_s—C'_{p_y}	—	0.1172	0.1166
C_s—C_{p_z}	—	0.3317	0.3298
C_{p_y}—C'_{p_z}	—	0.1723	0.1709
H—C'_s	—	−0.0652	−0.0639
H—C'_{p_x}	—	−0.0342	−0.0353
H—C'_{p_y}	—	0.0012	0.0014
H—C'_{p_z}	—	0.0736	0.0747

* Dash denotes orbitals on atoms neighbouring to an atom on which the orbitals bear no dash.

Table VIII

Typical parallel Fock matrix elements over AO-s calculated by CNDO/2 for salicylidene-4-fluoro-aniline and its fragments (in hartrees)*

Interacting** orbitals	Formula 1 singlet	Formula 2 quartet	Formula 3 singlet	Formula 4 quartet	Formula 5 singlet	Formula 6 singlet
$F_s - F_s$	−1.4739	−1.5030	−1.5159	−1.4681	−1.4623	−1.4554
$F_{p_x} - F_{p_x}$	−0.7536	−0.7805	−0.7730	−0.7382	−0.7395	−0.7330
$F_s - F_{p_z}$	0.0132	0.0122	0.0110	0.0120	0.0121	0.0121
$F_s - C_s^3$	−0.3243	−0.3238	−0.3232	−0.3240	−0.3245	−0.3245
$F_s - C_{p_y}^3$	−0.4677	−0.4658	−0.4709	−0.4708	−0.4705	−0.4705
$F_{p_y} - C_{p_y}^3$	0.4201	0.4153	0.4236	0.4235	0.4238	0.4237
$F_{p_y} - C_{p_y}^1$	0.0505	0.0419	0.0302	0.0314	0.0317	0.0317
$F_s - C_{p_y}^2$	−0.0415	−0.0377	−0.0364	−0.0362	−0.0362	−0.0362
$C_s^3 - C_s^3$	−0.5431	−0.5499	−0.6251	−0.5525	−0.5540	−0.5460
$C_{p_y}^3 - C_s^1$	0.1666	0.1770	0.1656	0.1660	0.1666	0.1666
$C_{p_y}^3 - C_{p_y}^1$	−0.1341	−0.1376	−0.1201	−0.1168	−0.1186	−0.1186
$C_{p_z}^3 - C_{p_y}^2$	0.2830	0.2779	0.2786	0.2786	0.2783	0.2783
$C_{p_z}^3 - C_{p_y}^2$	0.1695	0.1765	0.1728	0.1735	0.1746	0.1745
$C_{p_y}^1 - C_{p_z}^1$	−0.1214	−0.1591	−0.2032	−0.2257	−0.2286	−0.2234
$C_s^1 - C_{p_y}^1$	−0.0159	−0.0240	−0.0223	−0.0114	−0.0103	−0.0099
$C_{p_z}^2 - C_{p_z}^2$	−0.1705	−0.2031	−0.2239	−0.2120	−0.2179	−0.2120
$C_{p_z}^2 - C_s^2$	0.0200	0.0179	0.0141	0.0114	0.0108	0.0103
$C_{p_z}^1 - C_{p_z}^2$	−0.0758	−0.0314	−0.0171	−0.0242	−0.0285	−0.0289
$C_{p_z}^1 - C_{p_z}^2$	0.1266	0.1164	0.1139	0.1141	0.1145	0.1145
$H^4 - H^4$	−0.2444	−0.2621	−0.2754	−0.2705	−0.2668	−0.2632
$H^4 - F_s$	−0.0111	−0.0133	−0.0126	−0.0130	−0.0128	−0.0128
$H^4 - F_{p_z}$	0.0127	0.0134	0.0177	0.0125	0.0128	0.0128
$H^4 - C_s^3$	−0.0705	−0.0687	−0.0715	−0.0702	−0.0680	−0.0680
$H^4 - C_{p_z}^1$	0.0109	0.0142	0.0147	0.0157	0.0153	0.0153
$H^4 - C_s^2$	−0.4007	−0.4147	−0.4026	−0.4029	−0.4026	−0.4024

* Only interactions of orbitals on the most critical five atoms are presented.
** The superscripts of orbitals correspond with the numbering of atoms in Fig. 3.

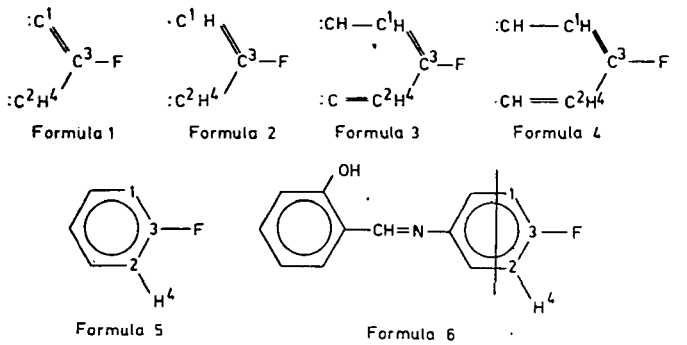

Fig. 3. Structures of fragments and molecules denoted by Formulae 1—6 and numbering of atoms whose orbitals have been considered as interacting orbitals

Table IX

Butane orbital energies (in hartrees)

No.*	Direct CNDO/2 7. step	Simulated CNDO/2**			
		from ethane		from propane	
		non-iterative	2. step	non-iterative	2. step
1.	−1.6646	−1.5605	−1.6675	−1.6573	−1.6647
2.	−1.3901	−1.3996	−1.3896	−1.3975	−1.3900
3.	−1.0883	−1.1408	−1.0874	−1.0884	−1.0879
4.	−1.0651	−1.0145	−1.0665	−1.0650	−1.0652
5.	−0.9840	−0.9542	−0.9847	−0.9831	−0.9836
6.	−0.8399	−0.8471	−0.8408	−0.8392	−0.8410
7.	−0.7879	−0.8075	−0.7882	−0.7930	−0.7875
8.	−0.7814	−0.7754	−0.7800	−0.7822	−0.7805
9.	−0.6618	−0.7010	−0.6627	−0.6611	−0.6630
10.	−0.6205	−0.6448	−0.6195	−0.6190	−0.6198
11.	−0.5727	−0.6242	−0.5741	−0.5712	−0.5721
12.	−0.5588	−0.5354	−0.5596	−0.5588	−0.5585
13.	−0.5434	−0.5331	−0.5431	−0.5366	−0.5440
14.	0.2623	0.2506	0.2612	0.2633	0.2625
15.	0.2771	0.2708	0.2754	0.2784	0.2767
16.	0.2896	0.2854	0.2889	0.2895	0.2891
Total energy	−36.1922	−36.1947	−36.1981	−36.1827	−36.1915
Relative comput. time	1	1/10	1/7	1/10	1/7

* No. 1.—No. 13. orbitals are occupied.

** By using Fock matrix elements over HAO-s of ethane and propane pattern molecules, calculated by CNDO/2 method.

between non-nearest neighbour groups are taken zero. When butane is constructed from propane only the largest distance methyl-methyl (third neighbour) terms have been neglected and some methylene (second neighbour) terms have been approximated by appropriate propane methyl matrix elements, however, all the other terms required in the calculations have directly been taken from propane. In Table IX the orbital energies of butane are presented: in the first column those obtained by direct calculation at the 7. cycle of iterations, in the second and fourth columns those from the non-iterative solution of the synthetic problems constructed from ethane and propane elements and in the third and fifth columns the solutions of the synthetic matrices from ethane and propane elements after the 2. iteration step. The advantages of the semiempirical method transferring Fock matrix elements are most striking when comparing the relative computing times of the calculations in the last row of Table IX. The time requirements of selecting the matrix elements needed and constructing the matrix of the target molecule are not included in the computing times. The gain in computing time is due to the fact that when using the transference method the calculations of molecular orbitals and total energy do not necessitate the repeated lengthy evaluation of two-electron repulsion integrals. It is expected that the benefits of Fock matrix element transferences within semiempirical methods will become much more evident if used to much larger systems but starting with the same pattern molcules. Of such results we will give accounts in following papers of this series after having finished developing our computer library program which would render possible the automatic transfer of matrix elements. The construction of large matrices from elements of pattern molecules by hand is not only exhausting and tedious but also an extensive source of errors.

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ИМИТАЦИОННЫЕ СЕМИЭМПИРИЧЕСКИЕ РАСЧЕТЫ МОЛЕКУЛЯРНЫХ ОРБИТАЛЕЙ, I

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Сравнены конвергированные Фокк матрикс элементы атомных орбиталей типа Слэтера и гибридизированных орбиталей, получаемых семиэмпирическими (РМГ, ППДП, ЧПДП, и МЧПДП) квантово-химическими методами расчетов для алканов, олефинов, кислородсодержащих полярных молекул и различных молекул и молекулярных фрагментов с закрытыми и открытыми электронными оболочками. Хорошее совнадение между параллельными элементами матрикса Фокка, предсказывает их трансферабельность с одной молекулы в другую. Успешно проведена трансферация для алканов. Цель серии работ заключается в представлении принципов, законов, возможностей и ограничений трансферабелбности.