Core and repulsion integrals for Löwdin orthogonalized atomic orbitals in pi-electron systems†

by

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The core integrals and electron repulsion integrals for the $2p\pi$ Slater-type orbitals of the allyl radical, trimethylenemethyl radical, and benzene molecule have been transformed to the corresponding Löwdin orthogonalized basis set of atomic orbitals. All the transformed multi-center non-Coulomb repulsion integrals are found to have reduced in magnitude.

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1. Introduction

In quantum chemistry, orthogonalization of basis functions, when desired, is usually carried out by one of three well-known methods. The most popular is the Schmidt process of orthogonalization [1]. If the orthogonalized orbitals ψ_ℓ is written as

$$\psi_\ell = \sum_k \phi_k T_{k\ell} , \tag{1.1}$$

where $\underset{\sim}{T}$ is the transformation matrix and ϕ_k are the original orbital functions, then the Schmidt transformation has zero $T_{k\ell}$ for $k > \ell$. In the second method of orthogonalization, one diagonalizes the overlap matrix $\underset{\sim}{S}$ by solving the eigenvalue problem

$$[\underset{\sim}{S} - \lambda \underset{\sim}{1}] \underset{\sim}{F} = 0 \tag{1.2}$$

If $\underset{\sim}{F}$ is the eigenfunction matrix, then $\underset{\sim}{T}$ is given by

$$T_{k\ell} = F_{k\ell} \lambda_\ell^{-\frac{1}{2}} \tag{1.3}$$

The third method, developed by Löwdin [2] , starts with normalized orbitals, and $\underset{\sim}{S}^{-\frac{1}{2}}$ is expanded in a power series in $(\underset{\sim}{S} - \underset{\sim}{1})$. The resulting transformation matrix $\underset{\sim}{T}$ is symmetric. Carlson and Keller [3] have shown that the Löwdin orthogonalized orbitals resemble the original non-orthogonal orbitals most by a least

squares criterion, that is

$$\sum_k \int |\psi_k - \phi_k|^2 \, dv = \text{minimum} \qquad (1.4)$$

On the other hand, in theoretical investigations of π-electron systems, the approximation known as zero differential overlap (ZDO) has often been invoked, for example, in the simple Hückel molecular orbital method, or in the Pariser-Parr-Pople semi-empirical approach [4,5].

The connection between the Löwdin orthogonalized atomic orbitals (LOAO) and the ZDO approximation has often been discussed, e.g. by Parr[6], and more recently by Lykos [7] and by Fischer-Hjalmas [8].

In the present investigation, the core integrals calculated by the method of Parr and Mulliken [9] and the electron repulsion integrals for the π-electron systems of the allyl radical CH_2CHCH_2, the trimethylenemethyl radical $C(CH_2)_3$, and benzene C_6H_6 have been transformed to the corresponding LOAO basis. The radicals have been chosen because they represent two of the simplest π-electron systems with non-ionic resonance structures, and the electronic structure of their ground states have been fully investigated by Linnett and coworkers [10-13].

2. Calculations

The Hamiltonian operator in theoretical treatments of π-electron systems is usually written as [14]

$$\mathcal{H} = \sum_i f(i) + \sum_{i<j} g(i,j) \quad , \tag{2.1}$$

where $$f = t + \sum_\nu h_\nu \quad , \tag{2.2}$$

t = kinetic energy operator,

h_ν = potential energy of electron in the sigma framework due to nucleus ν ,

and, $$g(i,j) = 1/r_{ij} \tag{2.3}$$

If ϕ_n is the ordinary $2p\pi$ atomic orbital on nucleus n, the following relation holds [9] :

$$(t + h_n)\,\phi_n = W_{2p}\,\phi_n \tag{2.4}$$

where W_{2p} is the ionization potential of a $2p\pi$ electron in a carbon atom in sp^2 valence state. Let us define the following matrix elements,

$$s_{mn} = \langle \phi_m, \phi_n \rangle \quad , \tag{2.5}$$

$$i_{mn} = \langle \phi_m , \Big(\sum_{\nu \neq n} h_\nu \Big) \phi_n \rangle \quad , \tag{2.6}$$

and,

$$f_{mn} = \langle \phi_m, f , \phi_n \rangle \tag{2.7}$$

Combining eqs. (2.2) to (2.7), one can easily obtain

$$\underset{\sim}{f} = W_{2p} \underset{\sim}{s} + \underset{\sim}{i} \tag{2.8}$$

The matrix elements f_{mn} are called the core integrals [9], and have the values of i_{mn}, relative to W_{2p} as zero of energy. To avoid confusion, we shall call f_{mn} the total core integrals, and i_{mn}, the relative core integrals.

2.1. Relative core integrals

Using the Goeppert-Mayer and Sklar approximation [15], neglecting the hydrogen atoms, the relative core integrals can be evaluated [9] by

$$i_{mn} = -\sum_{r \neq n} \Big[(r : mn) + (mn;rr) \Big] \quad , \tag{2.9}$$

where $(r : mn)$ are the penetration integrals [15], and, the electron repulsion integrals are defined by

$$(ab;cd) = \langle \phi_a(1)\ \phi_c(2)\ ,\ g(1,2)\ \phi_b(1)\ \phi_d(2) \rangle \qquad (2.10)$$

There are available several tables of penetration integrals [16-21], which are either not sufficiently accurate or inconvenient for our use here. Therefore, they are recalculated with Sklar's formula [16], as corrected by Parr and Crawford [17]. The three-center penetration integrals are approximated by

$$(r:k\ell) = s_{k\ell}\ (r : mm)\ , \qquad (2.11)$$

where ϕ_m is a Slater $2p\pi$ atomic orbital located midway between atoms k and ℓ.

Throughout this work, Slater $2p\pi$ atomic orbitals with $Z = 3.18$ are used, and a planar aromatic structure is assumed. The distance between neighboring nuclei is taken to be

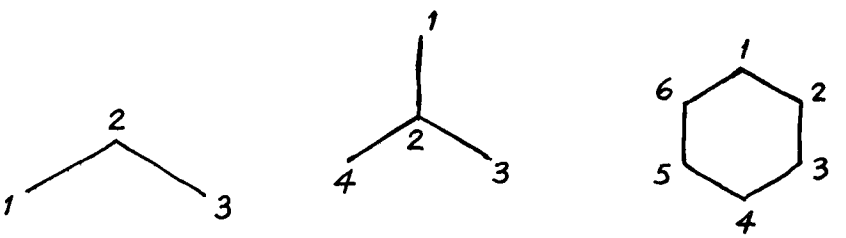
$$\frac{8.37}{3.18} = 2.632075 \text{ bohr}\ ,$$

a choice dictated by the availability [22] of the multi-center repulsion integrals.

The overlap integrals s_{mn}, calculated using Roothaan's formula [23], together with all the two-center penetration integrals needed, are listed in Table 1.

All the repulsion integrals except one have been tabulated in the literature [13,22] . The exception is (11;44) for benzene, which is evaluated with Roothaan's formula [23] to be 0.182605 hartree.

The relative core integrals i_{mn} , computed with eqs. (2.9) and (2.11), are listed in Table 2. The numbering in the three systems is as follows:



2.2. Löwdin orthogonalization

The atomic orbitals are now transformed into LOAO by eq. (1.1), where

$$\underset{\sim}{T} = \underset{\sim}{s}^{-\frac{1}{2}} = \underset{\sim}{1} - \tfrac{1}{2}(\underset{\sim}{s}-\underset{\sim}{1}) + 3/8(\underset{\sim}{s}-\underset{\sim}{1})^2 - 5/16(\underset{\sim}{s}-\underset{\sim}{1})^3 + \cdots \qquad (2.12)$$

The series is continued until the transformed overlap matrix is a unit matrix to better than 1×10^{-7} , that is

$$\underset{\sim}{S} = \underset{\sim}{T}\,\underset{\sim}{s}\,\underset{\sim}{T} = \underset{\sim}{1} \qquad (2.13)$$

All distinct elements of $\underset{\sim}{T}$ are listed in Table 2.

2.3. Transformed integrals

The transformed integrals in the LOAO basis, corresponding to $\underset{\sim}{i}$ and $\underset{\sim}{f}$, are defined by

$$I_{ij} = \langle \psi_i , (\sum_{\nu \neq j} h_\nu) \psi_j \rangle \quad , \tag{2.14}$$

$$F_{ij} = \langle \psi_i , f \psi_j \rangle \quad , \tag{2.15}$$

and

$$[ab;\ cd] = \langle \psi_a(1)\psi_c(2) , g(1,2)\psi_b(1)\psi_d(2) \rangle \ . \tag{2.16}$$

It follows that the transformed integrals are given simply by

$$\underset{\sim}{I} = \underset{\sim}{T}\,\underset{\sim}{i}\,\underset{\sim}{T} \quad , \tag{2.17}$$

$$\underset{\sim}{F} = \underset{\sim}{T}\,\underset{\sim}{f}\,\underset{\sim}{T} = W_{2p}\,\underset{\sim}{1} + \underset{\sim}{I} \quad , \tag{2.18}$$

and

$$[ab;cd] = \sum_{k}' \sum_{\ell}' \sum_{m} \sum_{n} (k\ell\ ;\ mn)\ T_{ka} T_{\ell b} T_{mc} T_{nd} \quad . \tag{2.19}$$

The transformed relative core integrals I_{mn} are listed in Table 3, and the transformed repulsion integrals $[ab;cd]$ in Tables 4 to 6 .

3. Discussion

The results on repulsion integrals confirm the findings of McWeeny [24] that [ab;cd] is quite small except for the Coulomb type [aa;cc] . This justifies the neglect of non-Coulomb-type repulsion integrals in the Pariser-Parr-Pople approach, which is applied with ZDO approximation.

The one-center core integrals show a dependence on the position of the center as well as on the particular molecule. This may cast doubt on the assumption of a single value for the parameter α in the semi-empirical approach. Further work is planned in this direction, as well as in making use of the present results in other calculations, such as starting with LOAO in Coulson-Fischer [25] type wave functions, or in non-paired spatial orbital functions [10,13] .

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Table 1 Input integrals

R_{mn}	s_{mn}	(m ; nn) hartrees	(m ; mn) hartrees
A †		0.3010320	
2A	0.2599520	0.0314152	0.0693913
$\sqrt{7}$A		0.0054776	
3A		0.0019693	
$2\sqrt{3}$A	0.03886876	0.0004879	0.0040005
$\sqrt{13}$A		0.0003155	
4A	0.01772265	0.0000914	0.0013565

† $2A = \frac{8.37}{3.18}$ bohr

Table 2. Intermediate results

Matrix	m	n	Allyl radical	Trimethylene-methyl radical	Benzene
	2	2	-0.726506	-1.089760	
	1	1	-0.572126	-0.780999	-1.326948
$\underset{\sim}{i}$ hartrees	1	2	-0.260763	-0.330380	-0.433872
	1	3	-0.045723	-0.055801	-0.075074
	1	4			-0.031044
	2	2	1.0543215	1.0830548	
	1	1	1.0268716	1.0270909	1.0549169
$\underset{\sim}{T}$	1	2	-0.1377590	-0.1398510	-0.1402838
	1	3	0.0068517	0.0070710	0.0094137
	1	4			-0.0063760

Table 3 Transformed relative core integrals, hartrees†

Matrix	m	n	Allyl radical	Trimethylene-methyl radical	Benzene
	2	2	-0.679535	-1.030421	
	1	1	-0.543477	-0.750688	-1.275621
$\underset{\sim}{I}$	1	2	-0.100593	-0.096919	-0.099020
	1	3	+0.004214	+0.003837	+0.002430
	1	4			-0.002002

† The sixth decimal place may contain accumulative rounding-off errors.

Table 4 Transformed repulsion integrals for allyl radical, hartrees †

a	b	c	d	[ab;cd]	a	b	c	d	[ab;cd]
1	1	1	1	0.634403	1	1	1	3	-0.000218
2	2	2	2	0.647147	1	1	2	3	-0.001863
1	1	2	2	0.325417	1	2	1	3	-0.000105
1	1	3	3	0.205116	1	2	2	3	-0.000166
1	2	1	2	0.003575	1	3	1	3	0.000051
1	1	1	2	-0.003415	1	3	2	2	-0.001168
1	2	2	2	-0.003526					

† See footnote, Table 3

Table 5 Transformed repulsion integrals for trimethylenemethyl radical, hartrees †

a	b	c	d	[ab;cd]	a	b	c	d	[ab;cd]
1	1	1	1	0.634457	1	1	2	3	-0.001921
2	2	2	2	0.661220	1	1	3	4	-0.000854
1	1	2	2	0.328231	1	2	1	3	-0.000126
1	1	3	3	0.205104	1	2	2	3	-0.000072
1	2	1	2	0.003745	1	2	3	4	-0.000096
1	1	1	2	-0.003526	1	3	1	3	0.000054
1	2	2	2	-0.004065	1	3	1	4	0.000013
1	1	1	3	-0.000205	1	3	2	2	-0.001086

† See footnote, Table 3

Table 6 Transformed repulsion integrals for benzene, hartrees†

a	b	c	d	[ab;cd]	a	b	c	d	[ab;cd]
1	1	1	1	0.647337	1	1	3	5	0.000744
1	1	2	2	0.328156	1	2	1	3	-0.000130
1	1	3	3	0.205545	1	2	1	4	0.000058
1	1	4	4	0.179853	1	2	1	5	0.000091
1	2	1	2	0.003672	1	2	1	6	-0.000176
1	3	1	3	0.000045	1	3	1	4	0.000001
1	4	1	4	0.000015	1	3	1	5	-0.000001
1	1	1	2	-0.003698	1	2	3	4	0.000244
1	1	1	3	0.000100	1	2	3	5	0.000010
1	1	1	4	-0.000940	1	2	3	6	0.000057
1	1	2	3	-0.002118	1	2	4	5	0.000092
1	1	2	4	0.000878	1	3	2	4	0.000019
1	1	2	5	0.000314	1	3	2	5	0.000008
1	1	2	6	-0.001068	1	3	4	6	0.000005
1	1	3	4	0.000771	1	4	2	5	0.000003

† See footnote, Table 3

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CORE AND REPULSION INTEGRALS FOR LÖWDIN ORTHOGONALIZED ATOMIC ORBITALS IN PI-ELECTRON SYSTEMS[+]

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A mistake has been discovered in one of the input cards for the case of the trimethylenemethyl radical. This error has led to inaccurate values for most of the integrals for trimethylenemethyl. They should be corrected as follows:

In Table 2 on page 12, the core integral i_{14} should be -0.054641. The column of entries for trimethylenemethyl in Table 3 should read -1.030285, -0.750656, -0.097256, and +0.005078. Finally, the entire Table 5 should be replaced by the following one.

Table 5 Transformed repulsion integrals for trimethylenemethyl radical, hartrees[+]

a	b	c	d	[ab;cd]	a	b	c	d	[ab;cd]
1	1	1	1	0.634454	1	1	2	3	-0.001907
2	2	2	2	0.660782	1	1	3	4	-0.000856
1	1	2	2	0.328157	1	2	1	3	-0.000113
1	1	3	3	0.205102	1	2	2	3	-0.000145
1	2	1	2	0.003671	1	2	3	4	-0.000082
1	1	1	2	-0.003512	1	3	1	3	0.000052
1	2	2	2	-0.003752	1	3	1	4	0.000011
1	1	1	3	-0.000207	1	3	2	2	-0.001159

[+] See footnote, Table 3