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Studies in Molecular Structure. II. LCAO-MO-SCF Wave Functions for Selected First-Row Diatomic Molecules*

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I. GLOSSARY OF GENERAL TERMS AND SYMBOLS[1,2]

AO—Atomic orbital.

STO—Slater-type AO: $S_{nlm}=N_n(\zeta)r^{n-1}e^{-\zeta r}Y_l^m(\theta,\varphi)$.

ζ—Orbital exponent of an AO or STO and a variable parameter.

MO—Molecular orbital.

LCAO-MO, LCSTO-MO—Molecular orbitals approximated as a linear combination of AO's or STO's of like m.

CI—Configuration interaction.

SCF—Self-consistent field.

SCF-AO, SCF-MO—Self-consistent field AO's or MO's. The terms "accurate SCF-AO" and "accurate SCF-MO" are used to denote the best possible one-electron wave functions (which are solutions to the Hartree-Fock self-consistent field equations). These terms are synonomous with Hartree-Fock AO and and Hartree-Fock MO.

Free atom AO's (free atom ζ's)—Terms used to describe AO's or ζ's which are suitable (e.g., Slater AO's and Slater ζ's) or optimal (best atom AO's and best atom ζ's) in describing AO's of free atoms.

Slater AO's (Slater ζ's)—A specific type of free atom AO; STO's in which the ζ's (Slater ζ's) are those obtained from the empirical scheme devised by Slater.[3]

Slater MO's—Molecular orbitals constructed as linear combinations of STO's.

Best atom AO's (best atom ζ's)—Another specific type of free atom AO; these are STO's, the ζ's of which (best atom ζ's) are determined by a variational procedure. Best atom AO's have been reported by Roothaan[4] for first-row atoms (inner and valence shells) in a single determinantal approximation.

Best atom MO—Molecular orbitals constructed as linear combinations of best atom AO's.

Best MO—A term referring either to AO's or MO's meaning only that the ζ's have been determined so as to minimize the molecular energy.

Limited MO's—Molecular orbitals constructed from a basis set of STO's comprising only inner and valence shell STO's.

Extended MO's—Molecular orbitals constructed from inner shell, valence shell and extra-valence shell STO's.

Best limited MO's—Molecular orbitals constructed from inner and valence shell STO's only, the ζ's of which have been optimized with respect to the molecular energy by a variational procedure.

Best extended MO's—Same as the preceding except that extra-valence shell STO's are used in constructing the MO's.

Definitions

A. An SCF–LCAO–MO as discussed in this paper is defined as

$$\varphi_i=\sum_p c_{ip}\chi_p(\zeta) \tag{1}$$

(1) where the $\chi(\zeta)$'s are STO's centered on each atom,

$$\chi_p(\zeta)=Nr^{n-1}e^{-\zeta r}Y_l^m(\theta,\phi). \tag{2}$$

(2) ζ, the orbital exponent, is preferably determined by a variational procedure. According to a scheme for the empirical determination of the orbital exponents devised by Slater[5] (and later given a theoretical basis by Gombás and Gáspár[6]), ζ is defined as

$$\zeta=Z^*/n^*, \tag{3}$$

where Z^* is an effective nuclear charge and n^* an effective principal quantum number of the AO. If the ζ's are determined by Slater's rules, the $\chi(\zeta)$ are called simply "Slater orbitals"; if determined by minimizing the atomic or molecular total energy in a single determinantal approximation they are called "best atom AO's" and "best MO AO's," respectively.

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[1] The Glossary given here for the most part follows the Glossary recently compiled by R. S. Mulliken with some assistance and critical comment by the author. While the merits of the latter Glossary are many, it unfortunately does not provide a simple nomenclature for the single determinant functions given here, which fall under the classification STO-ζ. The author has therefore introduced a few new terms where necessary.

[2] The Glossary is compiled with a single determinantal function in mind; if the labels are to serve their purpose, their use should be limited to those AO's and MO's determined in the manner described using the Roothaan SCF procedure.

[3] J. C. Slater, Phys. Rev. **37**, 57 (1930).

[4] C. C. J. Roothaan, Tech. Rept., Laboratory of Molecular Structure and Spectra, University of Chicago (1955).

[5] J. C. Slater, footnote 3.

[6] P. Gombás and R. Gáspár, Acta Phys. Acad. Sci. Hung. **3** 317 (1952).

(3) The c_{ip} are MO coefficients determined by the Roothaan SCF procedure.[7]

B. The N-electron, normalized single-determinantal wave function for a singlet closed-shell ground state in terms of SCF–LCAO–MO's is given symbolically by

$$\Psi=(\varphi_1\alpha)(\varphi_1\beta)(\varphi_2\alpha)\cdots(\varphi_n\alpha)(\varphi_n\beta). \tag{4}$$

($2n=N$, the total number of electrons.) The corresponding total energy is

$$E=\int\Psi^*H\Psi dv. \tag{5}$$

C. The N-electron wave function denoted by the term *Slater LCAO–MO* is a normalized single-determinantal function [Eq. (4)] for which

(1) the MO coefficients c_{ip} have been determined by solution of the secular equation[7]

$$(F-\epsilon_i S)C_i=0 \tag{6}$$

(2) employing the Roothaan SCF procedure, and the ζ's are Slater ζ's.

D. The N-electron wave function *best atom LCAO–MO* is a single-determinantal wave function calculated as in Sec. C except that the ζ's are best atom rather than Slater ζ's.

E. The N-electron wave function denoted as *best limited LCAO–MO* is a single-determinantal function calculated in the same manner as C and D except that the energy has been minimized with respect to the ζ's (as well as the c_{ip}); these optimized ζ's are a function of the internuclear distance and differ from the Slater and best atom ζ's.

F. The term *extended LCAO–MO* identifies a normalized single-determinantal N-electron wave function which meets the description D, except that the MO expansions include STO's of higher principal quantum number than those of the valence shells of the constituent atoms.

Dissociation Energy: The experimental dissociation energies referred to are D_e, the sum of an observed dissociation energy $D_0{}^0$, and the zero-point vibrational energy. A summary of experimental data consulted for this study is given in Paper I, Table VII.[8] Calculated dissociation energies are obtained by taking the difference between the calculated total molecular energy and the sum of atomic energies calculated by the same procedure: $E_M(AB)-E_A-E_B$.

Total Energy: The total molecular energy (E_M) of a diatomic molecule AB is defined as the sum of the energy required to remove the electrons to rest at infinity (i.e., the electronic energy E_e) and the energy of the two nuclei of charge Z_A and Z_B, respectively, fixed a distance R_{AB} from each other (Z_AZ_B/R_{AB}): $E_M=E_e+Z_AZ_B/R_{AB}$.

Units[9]

1 a.u. = 27.210 ev.

1 a.u. = 0.5291 A.

1 a.u. = 2.5415 debye.

All energies and internuclear distances are given in atomic units (a.u.) unless clearly marked otherwise. Dipole moments are given in debye units.

II. BASIS FUNCTIONS

Because the atomic integrals were expressed and calculated in terms of STO's which constitute a nonorthogonal basis set and because the observables calculated here are invariant under the transformation to an orthogonal basis set, the wave functions and energies were also computed in terms of the STO's.

The tabulated MO's consequently are those for a nonorthogonal basis set. A table of the overlap integrals [Sec. VI, Table C] necessary for conversion to MO's in terms of orthogonal AO's if it is desired is given. MO's tabulated for the orthogonal basis set are on file at the Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago.

Atomic Integrals

The atomic integrals (in terms of nonorthogonal, complex STO's) were obtained from digital computer programs developed by the personnel of the Laboratory of Molecular Structure and Spectra, University of Chicago.[10]

Atomic Orbital Indexing

The MO coefficient subscript p indexes the atomic orbitals. The numbering of orbitals differs from the hydride to homopolar and heteropolar cases: The two cases are given below.

Hydride[11]

Atom \ x	$1s$	$2s$	$2p\sigma$	$2p\pi$	$2p\bar{\pi}$
A	1	2	3	5	6
B	4	...	...	...	...

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[7] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).

[8] Bernard J. Ransil, Revs. Modern Phys. **32**, 239 (1960), this issue.

[9] E. R. Cohen, J. W. M. Dumond, T. W. Layton, and J. S. Rollett, Revs. Modern Phys. **27**, 363 (1955).

[10] The analyses for most of the integral programs are based, to some extent, on the following papers: C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951); K. Ruedenberg, ibid. **19**, 1459 (1951); K. Ruedenberg, C. C. J. Roothaan, and W. Jaunzemis, ibid. **24**, 201 (1956); and C. C. J. Roothaan, ibid. **24**, 947 (1956). Publication of the new analyses is planned by C. C. J. Roothaan. The programing and coding of all but the exchange integrals was done by M. Yoshimine and C. C. J. Roothaan. The greater part of the analyses and the programing and coding of the exchange integrals was the work of A. D. McLean.

[11] Atom B is always hydrogen.

Homopolar and Heteropolar

Atom \ χ	$1s$	$2s$	$2p\sigma$	$2p\pi$	$2p\bar{\pi}$
A	1	2	3	7	9
B	4	5	6	8	10

Choice of Internuclear Distance

The wave functions tabulated here have been computed for the best values of the spectroscopic internuclear distances R_e available when the computations were begun. All values of R_e and the orbital exponents (ζ's) are given with the tables of wave functions.

An attempt at computing R_e has been made for H_2 completely optimizing the ζ's and for HF, LiH, Li_2, N_2, and F_2 using the best-MO ζ's for the experimental R_e. The calculated R_e differs from experimental usually by 0.05 to 0.1 a.u. The limited experience with CI in the field today indicates that it probably corrects in the right direction.

III. COMPUTATIONAL ACCURACY OF THE WAVE FUNCTIONS

Because of the loss of figures encountered in computing certain hybrid integrals, their accuracy is limited at times (depending on the ζ and R values) to five decimal places, rather than the usual six to eight. Obviously, the accuracy of the computed energies and wave functions can never exceed five decimal accuracy when this occurs. Because the ζ and R values lie in a trouble-free range, this source of computational error is never serious in the calculations tabulated here.

Another, and more drastic limitation to the accuracy of the wave function is the convergence criterion which is imposed while iterating the MO's. Because higher accuracy seemed unnecessary (in view of the foregoing remarks on integral accuracy and the well-known deficiency of the initial approximation), convergence was defined, and iteration automatically interrupted, when two successive sets of coefficients agreed in the fifth decimal place.

In practice, convergence was rapidly reached for the hydrides and homopolars; in a few cases, so rapidly that consistency between two successive sets of coefficients reached the seventh or eighth decimal place before iteration was interrupted. By that time the total and orbital energies agreed to the tenth significant figure. Repetition of any of these runs produced an exact duplicate in integrals, coefficients, and energies. Usually, however, duplication yielded total energies differing in the eighth significant figure and coefficients differing in the sixth decimal place.

For the heteropolars, convergence was usually from three to ten times slower. Consequently the coefficients are accurate to the fifth or sixth decimal place and the total energies to about the eighth significant figure. Repetition of any of these calculations produced results which begin to differ in the fifth or sixth decimal place in the coefficients and in the eighth significant figure in the total energy.

Dipole moments are very sensitive to the MO coefficients and are probably accurate to about the third significant figure for heteropolar molecules. Probably six significant figures are reliable in the case of the homopolars and hydrides.

IV. ACKNOWLEDGMENTS

The backbone of a research undertaking of this character is an extensive digital computer library, which implies years of programing and preparation involving many workers. Without the continuing cooperative effort of the group comprising the LMSS staff from roughly 1955 on, this research and its continuing phases could not have been, and continue to be, carried out to the degree of completeness indicated here.

The author particularly acknowledges the extensive analytic foundations laid by Professor C. C. J. Roothaan and Professor K. Ruedenberg, the programing achievements of Professor Roothaan, A. D. McLean, S. Fraga, A. Weiss, and M. Yoshimine, and the invariably reliable desk calculations of Mr. T. Kinyon. He is further indebted to Professor R. S. Mulliken and Professor Roothaan for their continuing interest, ever-stimulating suggestions and support, and to Dr. M. Krauss (National Bureau of Standards) and Professor J. W. Richardson (Purdue University) for their careful reading and constructive criticism of the manuscript.

Finally, the past and continuing cooperation of the staff of the Computation Section, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, is gratefully acknowledged.

V. TABLES OF MOLECULAR WAVE FUNCTIONS

TABLE I. Molecule: Li_2; state: ${}^1\Sigma_g^+$ $(1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2)$; R_e: 2.672_5 A, 5.051 a.u.

		Slater LCAO-MO		Best atom LCAO-MO		Best limited LCAO-MO	
ζ_{1s}		2.70		2.6865		2.6894	
ζ_{2s}		0.65		0.6372		0.6335	
$\zeta_{2p\sigma}$		0.65		0.6372		0.7609	
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
	$c_{11}=c_{14}$	0.70442		0.70476		−0.70477	
$1\sigma_g$	$c_{12}=c_{15}$	0.01050	−2.42666	0.00922	−2.43582	−0.00950	−2.43551
	$c_{13}=c_{16}$	0.00074		0.00077		−0.00033	
	$c_{21}=-c_{24}$	0.70501		0.70541		0.70544	
$1\sigma_u$	$c_{22}=-c_{25}$	0.03310	−2.42653	0.03000	−2.43565	0.02090	−2.43523
	$c_{23}=-c_{26}$	0.01140		0.01027		0.00315	
	$c_{31}=c_{34}$	0.14919		0.14603		0.14397	
$2\sigma_g$	$c_{32}=c_{35}$	−0.52597	−0.17892	−0.52172	−0.18062	−0.52979	−0.18134
	$c_{33}=c_{36}$	−0.11913		−0.12368		−0.11438	
	$c_{41}=-c_{44}$	0.11835		0.11389		0.11404	
$2\sigma_u$	$c_{42}=-c_{45}$	−0.74974	0.02907	−0.75904	0.02530	−0.95612	0.02755
	$c_{43}=-c_{46}$	0.28653		0.28271		0.15828	
	$c_{51}=c_{54}$	−0.00288		0.00526		0.00002	
$3\sigma_g$	$c_{52}=c_{55}$	−0.30758	0.09168	0.31088	0.08668	0.26479	0.10791
	$c_{53}=c_{56}$	0.67398		−0.67796		−0.63690	
	$c_{61}=-c_{64}$	0.03685		−0.02570		0.01313	
$3\sigma_u$	$c_{62}=-c_{65}$	−2.19314	0.35792	2.33160	0.34868	−1.61268	0.39592
	$c_{63}=-c_{66}$	−1.66708		1.72737		−1.40974	
E_M (a.u.)		−14.84075		−14.84111		−14.84149	

TABLE II. Molecule: Be_2; state: ${}^1\Sigma_g^+$ $(1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2)$; R_e: 2.0 A, 3.78 a.u.

		Slater LCAO-MO		Best atom LCAO-MO		Best limited LCAO-MO	
ζ_{1s}		3.70		3.6847		3.6845	
ζ_{2s}		0.975		0.9562		0.9577	
$\zeta_{2p\sigma}$		0.975		0.9562		1.1286	
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
	$c_{11}=c_{14}$	0.70462		−0.70493		0.70493	
$1\sigma_g$	$c_{12}=c_{15}$	0.00894	−4.70522	−0.00776	−4.72673	0.00795	−4.70933
	$c_{13}=c_{16}$	0.00133		−0.00136		0.00125	
	$c_{21}=-c_{24}$	−0.70463		0.70508		−0.70518	
$1\sigma_u$	$c_{22}=-c_{25}$	−0.02568	−4.70529	0.02333	−4.72671	−0.01853	−4.70918
	$c_{23}=-c_{26}$	−0.01109		0.01022		−0.00641	
	$c_{31}=c_{34}$	0.15794		0.15447		0.15355	
$2\sigma_g$	$c_{32}=c_{35}$	−0.51869	−0.42687	−0.51318	−0.43118	−0.52381	−0.42562
	$c_{33}=c_{36}$	−0.16369		−0.16892		−0.16167	
	$c_{41}=-c_{44}$	0.14150		0.13640		−0.13878	
$2\sigma_u$	$c_{42}=-c_{45}$	−0.83502	−0.21930	−0.84809	−0.22437	0.91363	−0.22080
	$c_{43}=-c_{46}$	0.19109		0.18457		−0.14353	
	$c_{51}=c_{54}$	0.02492		−0.02263		−0.02774	
$3\sigma_g$	$c_{52}=c_{55}$	−0.34356	0.04064	0.34769	0.03176	0.30889	0.05549
	$c_{53}=c_{56}$	0.64104		−0.64310		−0.61817	
	$c_{61}=-c_{64}$	0.07370		0.06643		−0.05551	
$3\sigma_u$	$c_{62}=-c_{65}$	−1.50193	0.48519	−1.58863	0.46917	1.15406	0.54412
	$c_{63}=-c_{66}$	−1.39548		−1.43807		1.21764	
E_M (a.u.)		−29.05645		−29.05612		−29.05825	

TABLE III. Molecule: C_2; state: $^1\Sigma_g^+$ $(1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 2\sigma_u^2\, 1\pi_u^4)$; R_e: 1.2422 A, 2.3475 a.u.

		Slater LCAO-MO		Best atom LCAO-MO		Best limited LCAO-MO	
ζ_{1s}		5.70		5.6726		5.6738	
ζ_{2s}		1.625		1.6082		1.6332	
$\zeta_{2p\sigma}$		1.625		1.56805		1.9735	
$\zeta_{2p\pi}$		1.625		1.56805		1.6080	
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
$1\sigma_g$	$c_{11}=c_{14}$	0.70443	−11.36560	0.70488	−11.45152	0.70470	−11.33876
	$c_{12}=c_{15}$	0.00864		0.00716		0.00781	
	$c_{13}=c_{16}$	0.00123		0.00124		0.00109	
$1\sigma_u$	$c_{21}=-c_{24}$	−0.70457	−11.36414	0.70505	−11.44999	−0.70504	−11.33696
	$c_{22}=-c_{25}$	−0.02095		0.01814		−0.01460	
	$c_{23}=-c_{26}$	−0.00856		0.00775		−0.00441	
$2\sigma_g$	$c_{31}=c_{34}$	0.17342	−1.03337	0.17124	−1.06469	0.17228	−1.02837
	$c_{32}=c_{35}$	−0.51467		−0.50913		−0.52447	
	$c_{33}=c_{36}$	−0.18460		−0.18992		−0.18586	
$2\sigma_u$	$c_{41}=-c_{44}$	0.15683	−0.48984	0.15356	−0.51609	0.16220	−0.48312
	$c_{42}=-c_{45}$	−0.76802		−0.76401		−0.85274	
	$c_{43}=-c_{46}$	0.24962		0.25061		0.19646	
$3\sigma_g$	$c_{51}=c_{54}$	0.03938	−0.04977	0.03766	−0.08076	−0.04798	−0.02220
	$c_{52}=c_{55}$	−0.36099		−0.37038		0.32490	
	$c_{53}=c_{56}$	0.62980		0.63513		−0.60734	
$3\sigma_u$	$c_{61}=-c_{64}$	−0.09793	0.99277	0.09636	0.92410	0.08235	1.12990
	$c_{62}=-c_{65}$	1.39700		−1.49400		−0.98006	
	$c_{63}=-c_{66}$	1.31834		−1.36737		−1.09702	
$1\pi_u$	$c_{77}=c_{78}$	−0.61638	−0.43579	0.61123	−0.45999	0.61486	−0.42033
$1\pi_g$	$c_{87}=-c_{88}$	0.85500	0.25506	0.86927	0.21706	0.85912	0.26473
E_M (a.u.)		−75.21122		−75.19880		−75.22381	

TABLE IV. Molecule: N_2; state: $^1\Sigma_g^+$ $(1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 2\sigma_u^2\, 1\pi_u^4\, 3\sigma_g^2)$; R_e: 1.094 A, 2.068 a.u.

		Slater LCAO-MO		Best atom LCAO-MO		Best limited LCAO-MO	
ζ_{1s}		6.70		6.6652		6.6675	
ζ_{2s}		1.95		1.9236		1.9170	
$\zeta_{2p\sigma}$		1.95		1.9170		2.2524	
$\zeta_{2p\pi}$		1.95		1.9170		1.9090	
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
$1\sigma_g$	$c_{11}=c_{14}$	0.70447	−15.72176	0.70493	−15.80452	0.70480	−15.64705
	$c_{12}=c_{15}$	0.00842		0.00688		0.00743	
	$c_{13}=c_{16}$	0.00182		0.00184		0.00203	
$1\sigma_u$	$c_{21}=-c_{24}$	−0.70437	−15.71965	−0.70494	−15.80219	0.70494	−15.64423
	$c_{22}=-c_{25}$	−0.01972		−0.01656		0.01502	
	$c_{23}=-c_{26}$	−0.00857		−0.00744		0.00567	
$2\sigma_g$	$c_{31}=c_{34}$	0.16890	−1.45241	−0.16618	−1.47922	−0.16328	−1.42106
	$c_{32}=c_{35}$	−0.48828		0.48390		0.49029	
	$c_{33}=c_{36}$	−0.23970		0.24276		0.24824	
$2\sigma_u$	$c_{41}=-c_{44}$	0.16148	−0.73066	−0.15799	−0.75409	−0.15963	−0.71370
	$c_{42}=-c_{45}$	−0.74124		0.74773		0.80527	
	$c_{43}=-c_{46}$	0.26578		−0.26068		−0.23244	
$3\sigma_g$	$c_{51}=c_{54}$	−0.06210	−0.54451	−0.05986	−0.56759	−0.06640	−0.55548
	$c_{52}=c_{55}$	0.40579		0.40879		0.38257	
	$c_{53}=c_{56}$	−0.60324		−0.60431		−0.58527	
$3\sigma_u$	$c_{61}=-c_{64}$	−0.10969	1.100865	0.10547	1.04956	0.09239	1.22618
	$c_{62}=-c_{65}$	1.20696		−1.25520		−0.96578	
	$c_{63}=-c_{66}$	1.21625		−1.24382		−1.07595	
$1\pi_u$	$c_{77}=c_{78}$	−0.62450	−0.57951	0.62200	−0.60486	−0.62139	−0.54540
$1\pi_g$	$c_{87}=-c_{88}$	0.83452	0.27290	0.84059	0.24041	0.84211	0.30021
E_M (a.u.)		−108.57362		−108.55808		−108.63359	

Table V. Molecule: F_2; state: $^1\Sigma_g^+$ $(1\sigma_u^2\, 1\sigma_g^2\, 2\sigma_g^2\, 2\sigma_u^2\, 1\pi_u^4\, 3\sigma_g^2\, 1\pi_g^4)$; R_e: 1.418 A, 2.680 a.u.

		Slater LCAO-MO		Best atom LCAO-MO		Best limited LCAO-MO	
	ζ_{1s}	8.70		8.6501		8.6504	
	ζ_{2s}	2.60		2.5639		2.5776	
	$\zeta_{2p\sigma}$	2.60		2.5498		2.4934	
	$\zeta_{2p\pi}$	2.60		2.5498		2.5688	
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
$1\sigma_u$	$c_{11}=-c_{14}$	0.70451	−26.21758	0.70509	−26.38210	0.70506	−26.35953
	$c_{12}=-c_{15}$	0.01092		0.00865		0.00874	
	$c_{13}=-c_{16}$	0.00158		0.00135		0.00140	
$1\sigma_g$	$c_{21}=c_{24}$	0.70483	−26.21721	0.70535	−26.38193	0.70530	−26.35934
	$c_{22}=c_{25}$	0.00912		0.00717		0.00726	
	$c_{23}=c_{26}$	−0.00022		−0.00011		−0.00014	
$2\sigma_g$	$c_{31}=c_{34}$	0.17327	−1.58408	0.16892	−1.63270	0.17048	−1.62585
	$c_{32}=c_{35}$	−0.67160		−0.66881		−0.66955	
	$c_{33}=c_{36}$	−0.08540		−0.08450		−0.08350	
$2\sigma_u$	$c_{41}=-c_{44}$	0.18643	−1.31728	0.18233	−1.36795	0.18374	−1.36128
	$c_{42}=-c_{45}$	−0.75834		−0.76066		−0.75916	
	$c_{43}=-c_{46}$	0.07461		0.07102		0.07242	
$3\sigma_g$	$c_{51}=c_{54}$	−0.03841	−0.50371	0.03784	−0.55685	−0.03841	−0.54610
	$c_{52}=c_{55}$	0.17685		−0.18035		0.18357	
	$c_{53}=c_{56}$	−0.65244		0.65032		−0.64770	
$3\sigma_u$	$c_{61}=-c_{64}$	−0.04303	0.38634	0.04257	0.32801	0.04403	0.34242
	$c_{62}=-c_{65}$	0.20640		−0.21279		−0.22057	
	$c_{63}=-c_{66}$	0.78597		−0.79297		−0.80001	
$1\pi_u$	$c_{77}=c_{78}$	0.69104	−0.56445	0.68958	−0.61427	0.69015	−0.60792
$1\pi_g$	$c_{87}=-c_{88}$	0.72434	−0.43181	0.72604	−0.47932	0.72538	−0.47444
E_M (a.u.)		−197.85686		−197.87409		−197.87694	

Table VI. Molecule: LiH; state: $^1\Sigma^+$ $(1\sigma^2\, 2\sigma^2)$; R_e: 1.5953_5 A, 3.015 a.u.

		Slater LCAO-MO		Best atom LCAO-MO		Best limited LCAO-MO	
		Li	H	Li	H	Li	H
	ζ_{1s}	2.70	1.00	2.6875	1.00	2.6909	0.9766
	ζ_{2s}	0.65		0.6372		0.7075	
	$\zeta_{2p\sigma}$	0.65		0.6372		0.8449	
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
1σ	c_{11}	0.99658	−2.44695	0.99703	−2.45412	0.99581	−2.42568
	c_{12}	0.01605		0.01384		0.01738	
	c_{13}	−0.00514		−0.00506		−0.00729	
	c_{14}	0.00600		0.00615		0.00627	
2σ	c_{21}	0.13097	−0.30350	0.12908	−0.30379	0.14056	−0.29858
	c_{22}	−0.32335		−0.32298		−0.30778	
	c_{23}	−0.23106		−0.22951		−0.21144	
	c_{24}	−0.68526		−0.68757		−0.70388	
3σ	c_{31}	0.13433	0.01668	0.12900	0.01324	0.16164	0.05004
	c_{32}	−0.80523		−0.80287		−0.88948	
	c_{33}	0.59916		0.60122		0.49500	
	c_{34}	0.14750		0.14531		0.27388	
4σ	c_{41}	−0.02386	0.34924	0.01881	0.33885	−0.03451	0.44639
	c_{42}	0.86883		−0.86285		0.84249	
	c_{43}	1.11663		−1.10939		1.19011	
	c_{44}	−1.28580		1.27455		−1.30139	
E_M (a.u.)		−7.96666		−7.96598		−7.96992	

TABLE VII. Molecule: BH; state: $^1\Sigma^+$ $(1\sigma^2\, 2\sigma^2\, 3\sigma^2)$; R_e: 1.2325 A, 2.329 a.u.

		Slater LCAO-MO		Best atom LCAO-MO		Best limited LCAO-MO	
		B	H	B	H	B	H
	ζ_{1s}	4.70	1.00	4.6794	1.00	4.6805	1.1860
	ζ_{2s}	1.30		1.33825		1.2955	
	$\zeta_{2p\sigma}$	1.30		1.21055		1.3168	
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
1σ	c_{11}	0.99664		0.99680		0.99707	
	c_{12}	0.01818	−7.69969	0.01646	−7.71395	0.01506	−7.66412
	c_{13}	0.00600		0.00572		0.00458	
	c_{14}	−0.00734		−0.00688		−0.00479	
2σ	c_{21}	−0.16773		−0.17665		−0.16703	
	c_{22}	0.57039	−0.64749	0.58613	−0.65371	0.60348	−0.63820
	c_{23}	0.21778		0.20368		0.24477	
	c_{24}	0.48162		0.47576		0.45490	
3σ	c_{31}	−0.14454		−0.14841		−0.14227	
	c_{32}	0.81788	−0.34594	0.78871	−0.34478	0.76543	−0.32767
	c_{33}	−0.55368		−0.57431		−0.59282	
	c_{34}	−0.44488		−0.41873		−0.37269	
4σ	c_{41}	0.09172		−0.10384		−0.08724	
	c_{42}	−0.92769	0.46730	0.95452	0.45679	0.81025	0.58388
	c_{43}	−1.14539		1.17594		1.07989	
	c_{44}	1.42270		−1.46719		−1.33298	
E_M (a.u.)		−25.06210		−25.05509		−25.07460	

TABLE VIII. Molecule: NH; state: $^1\Sigma^+$ $(1\sigma^2\, 2\sigma^2\, 1\pi^4)$; R_e: 1.045_5 A, 1.976 a.u.

		Slater LCAO-MO		Best atom LCAO-MO		Best limited LCAO-MO	
		N	H	N	H	N	H
	ζ_{1s}	6.70	1.00	6.6652	1.00	6.6703	1.4096
	ζ_{2s}	1.95		1.9236		1.9442	
	$\zeta_{2p\sigma}$	1.95		1.9170		2.0959	
	$\zeta_{2p\pi}$	1.95		1.9170		1.7697	
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
1σ	c_{11}	0.99601		0.99675		0.99699	
	c_{12}	0.01862	−15.31801	0.01547	−15.38799	0.01357	−15.58738
	c_{13}	0.00199		0.00167		0.00079	
	c_{14}	−0.00593		−0.00491		−0.00328	
2σ	c_{21}	0.20908		0.20717		0.21586	
	c_{22}	−0.76582	−0.87022	−0.78259	−0.88830	−0.84062	−0.96322
	c_{23}	−0.14156		−0.14645		−0.15340	
	c_{24}	−0.34297		−0.31910		−0.27502	
3σ	c_{31}	0.14182		−0.13460		−0.11821	
	c_{32}	−0.79870	0.00293	0.78563	−0.01543	0.62262	−0.03215
	c_{33}	0.42444		−0.43378		−0.56154	
	c_{34}	0.76336		−0.76029		−0.60654	
4σ	c_{41}	0.07125		−0.06922		−0.07076	
	c_{42}	−0.58658	0.58475	0.59905	0.55857	0.52433	0.72254
	c_{43}	−1.03867		1.04242		0.95360	
	c_{44}	1.03595		−1.06409		−1.05184	
$1\pi, 1\bar{\pi}$	c_π	1.00000	−0.23778	1.00000	−0.25774	1.00000	−0.31111
E_M (a.u.)		−54.25984		−54.27581		−54.32459	

Table IX. Molecule: HF; state: $^1\Sigma^+$ $(1\sigma^2\,2\sigma^2\,3\sigma^2\,1\pi^4)$; R_e: 0.9171 A, 1.733 a.u.

		Slater LCAO-MO		Best atom LCAO-MO		Best limited LCAO-MO	
		F	H	F	H	F	H
	ζ_{1s}	8.70	1.00	8.6501	1.00	8.6533	1.3163
	ζ_{2s}	2.60		2.5639		2.5551	
	$\zeta_{2p\sigma}$	2.60		2.5498		2.6693	
	$\zeta_{2p\pi}$	2.60		2.5498		2.4965	
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
1σ	c_{11}	0.99627	−26.13948	0.99709	−26.25971	0.99713	−26.26612
	c_{12}	0.01632		0.01301		0.01273	
	c_{13}	0.00243		0.00210		0.00209	
	c_{14}	−0.00460		−0.00366		−0.00332	
2σ	c_{21}	0.24346	−1.47646	0.23918	−1.50298	0.23719	−1.48860
	c_{22}	−0.93218		−0.94111		−0.93992	
	c_{23}	0.09066		−0.09787		−0.09042	
	c_{24}	−0.16060		−0.14232		−0.15365	
3σ	c_{31}	−0.08394	−0.56559	−0.07888	−0.59073	−0.07566	−0.60558
	c_{32}	0.47149		0.45526		0.42221	
	c_{33}	−0.68695		−0.70538		−0.71146	
	c_{34}	−0.57613		−0.54961		−0.51612	
4σ	c_{41}	−0.08000	0.47711	−0.07766	0.44756	−0.07691	0.66916
	c_{42}	0.55994		0.57012		0.53922	
	c_{43}	0.80646		0.79565		0.80463	
	c_{44}	−1.05015		−1.07819		−1.07437	
$1\pi, 1\bar{\pi}$	c_π	1.00000	−0.46455	1.00000	−0.49005	1.00000	−0.46863
E_M (a.u.)		−99.47854		−99.49147		−99.53614	

Table X.[a] Molecule: CO; state: $^1\Sigma^+$, $(1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,1\pi^4\,5\sigma^2)$; R_e: 1.1281_9 A, 2.132 a.u.

		Slater LCAO-MO		Best atom LCAO-MO	
		C	O	C	O
	ζ_{1s}	5.70	7.70	5.6726	7.6580
	ζ_{2s}	1.625	2.275	1.6082	2.2461
	$\zeta_{2p\sigma}$	1.625	2.275	1.56805	2.22625
	$\zeta_{2p\pi}$	1.625	2.275	1.56805	2.22625
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
1σ	c_{11}	−0.00021	−20.70597	0.00014	−20.81172
	c_{12}	0.00694		−0.00586	
	c_{13}	0.00626		−0.00524	
	c_{14}	−0.99603		0.99683	
	c_{15}	−0.02018		0.01661	
	c_{16}	−0.00576		0.00505	
2σ	c_{21}	0.99643	−11.35323	0.99708	−11.44369
	c_{22}	0.01707		0.01413	
	c_{23}	0.00587		0.00521	
	c_{24}	−0.00024		−0.00030	
	c_{25}	−0.00542		−0.00453	
	c_{26}	−0.00069		−0.00031	
3σ	c_{31}	−0.11522	−1.49881	0.11397	−1.53348
	c_{32}	0.24006		−0.22414	
	c_{33}	0.16874		−0.15542	
	c_{34}	−0.21481		0.21170	
	c_{35}	0.75883		−0.76872	
	c_{36}	0.22322		−0.23892	
4σ	c_{41}	0.14683	−0.73234	−0.14563	−0.75993
	c_{42}	−0.53827		0.53638	
	c_{43}	−0.06682		0.05995	
	c_{44}	0.12625		0.12315	
	c_{45}	0.65294		−0.65264	
	c_{46}	−0.63503		0.63639	
5σ	c_{51}	−0.14025	−0.48078	−0.13573	−0.50698
	c_{52}	0.75786		0.76218	
	c_{53}	−0.56582		−0.56148	
	c_{54}	0.00215		0.00184	
	c_{55}	0.03656		0.04066	
	c_{56}	−0.43792		−0.45046	
6σ	c_{61}	−0.09155	0.93222	0.08903	0.85994
	c_{62}	0.96935		−1.00957	
	c_{63}	1.25088		−1.28576	
	c_{64}	0.11970		−0.11681	
	c_{65}	−1.12888		1.17759	
	c_{66}	−0.94147		0.94646	
1π	c_{77}	−0.46864	−0.58308	−0.46058	−0.61240
	c_{78}	−0.77124		−0.77140	
2π	c_{87}	−0.92245	0.26082	0.93131	0.22143
	c_{88}	0.68973		−0.69601	
E_M (a.u.)		−112.34357		−112.32604	

[a] No values for best limited LCAO-MO.

TABLE XI.[a] Molecule: BF; state: $^1\Sigma^+$ $(1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,1\pi^4\,5\sigma^2)$; R_e: 1.262 A, 2.385 a.u.

		Slater LCAO-MO		Best atom LCAO-MO	
		B	F	B	F
	ζ_{1s}	4.70	8.70	4.6794	8.6501
	ζ_{2s}	1.30	2.60	1.33825	2.5639
	$\zeta_{2p\sigma}$	1.30	2.60	1.21055	2.54985
	$\zeta_{2p\pi}$	1.30	2.60	1.21055	2.54985
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
	c_{11}	−0.00023		0.00020	
	c_{12}	0.00410		−0.00331	
1σ	c_{13}	0.00482	−26.36560	−0.00390	−26.46924
	c_{14}	−0.99616		0.99699	
	c_{15}	−0.01767		0.01418	
	c_{16}	−0.00290		0.00244	
	c_{21}	0.99659		0.99680	
	c_{22}	0.01558		0.01387	
2σ	c_{23}	0.00425	−7.65211	0.00385	−7.68511
	c_{24}	−0.00037		−0.00038	
	c_{25}	−0.00256		−0.00221	
	c_{26}	0.00192		0.00187	
	c_{31}	0.06237		0.06288	
	c_{32}	−0.10525		−0.09248	
3σ	c_{33}	−0.09502	−1.64128	−0.07656	−1.66403
	c_{34}	0.24323		0.23925	
	c_{35}	−0.92713		−0.93934	
	c_{36}	−0.12339		−0.13519	
	c_{41}	0.11198		0.11758	
	c_{42}	−0.35804		−0.35503	
4σ	c_{43}	−0.17849	−0.72778	−0.15237	−0.74802
	c_{44}	−0.07464		−0.07118	
	c_{45}	0.40521		0.39294	
	c_{46}	−0.81910		−0.82789	
	c_{51}	0.18001		0.18709	
	c_{52}	−0.89287		−0.89163	
5σ	c_{53}	0.45204	−0.35362	0.45647	−0.36217
	c_{54}	−0.01864		−0.01662	
	c_{55}	0.09208		0.07781	
	c_{56}	0.28407		0.30782	
	c_{61}	0.08444		0.09456	
	c_{62}	−0.64000		−0.66600	
6σ	c_{63}	−1.12175	0.60736	−1.13904	0.54930
	c_{64}	−0.10605		−0.10309	
	c_{65}	0.82366		0.84797	
	c_{66}	0.63634		0.61054	
1π	c_{77}	−0.29531	−0.61982	−0.28354	−0.63940
	c_{78}	−0.90257		−0.90499	
2π	c_{87}	0.97360	0.21018	0.97957	0.18309
	c_{88}	−0.46954		−0.47006	
E_M (a.u.)		−123.61550		−123.60373	

[a] No values for best limited LCAO-MO.

TABLE XII.[a] Molecule: LiF; state: $^1\Sigma^+$ $(1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,1\pi^4)$; R_e: 1.51 A, 2.85 a.u.

		Slater LCAO-MO		Best atom LCAO-MO	
		Li	F	Li	F
	ζ_{1s}	2.70	8.70	2.6865	8.6501
	ζ_{2s}	0.65	2.60	0.6372	2.5639
	$\zeta_{2p\sigma}$	0.65	2.60	0.6372	2.5498
	$\zeta_{2p\pi}$	0.65	2.60	0.6372	2.5498
		c_{ip}	ϵ_i (a.u.)	c_{ip}	ϵ_i (a.u.)
	c_{11}	−0.00017		0.00017	
	c_{12}	−0.00228		0.00177	
1σ	c_{13}	−0.00324	−26.04530	0.00250	−26.12619
	c_{14}	0.99629		−0.99710	
	c_{15}	0.01606		−0.01280	
	c_{16}	0.00075		−0.00061	
	c_{21}	0.99415		0.99458	
	c_{22}	0.01865		0.01610	
2σ	c_{23}	−0.00302	−2.42511	−0.00357	−2.43092
	c_{24}	−0.00798		−0.00781	
	c_{25}	0.02696		0.02724	
	c_{26}	0.01734		0.01715	
	c_{31}	0.07912		0.07925	
	c_{32}	−0.05250		−0.04296	
3σ	c_{33}	−0.06044	−1.33902	−0.04834	−1.34426
	c_{34}	0.25248		0.24769	
	c_{35}	−0.98783		−0.99524	
	c_{36}	−0.04173		−0.04596	
	c_{41}	0.08745		−0.08815	
	c_{42}	−0.11874		0.10478	
4σ	c_{43}	−0.09605	−0.39981	0.08303	−0.40308
	c_{44}	−0.02339		0.02166	
	c_{45}	0.12722		−0.11824	
	c_{46}	−0.97846		0.98274	
	c_{51}	0.15911		0.15336	
	c_{52}	−0.89939		−0.89717	
5σ	c_{53}	0.46059	0.02964	0.46436	0.02409
	c_{54}	−0.01288		−0.01185	
	c_{55}	0.06330		0.05940	
	c_{56}	0.07384		0.06751	
	c_{61}	0.05627		0.05399	
	c_{62}	−0.54355		−0.55028	
6σ	c_{63}	−0.99198	0.26989	−0.99248	0.25785
	c_{64}	−0.08754		−0.08247	
	c_{65}	0.60783		0.59843	
	c_{66}	0.21674		0.19728	
1π	c_{77}	−0.35981	−0.34088	−0.33756	−0.34835
	c_{78}	−0.88890		−0.89867	
2π	c_{87}	0.94158	0.16462	0.95030	0.15604
	c_{88}	−0.47528		−0.45761	
E_M (a.u.)		−106.36521		−106.38126	

[a] No values for best limited LCAO-MO.

VI. APPENDIX

TABLE A. First-row orbital exponents.

	Slater ζ		Best atom ζ		
	$1s$	$2s=2p\sigma=2p\pi$	$1s$	$2s$	$2p\sigma=2p\pi$
H	1.0		1.0		
He	1.7		1.6875		
Li	2.7	0.65	2.6865	0.6372	(0.6372)
Be	3.7	0.975	3.6847	0.9562	(0.9562)
B	4.7	1.3	4.6794	1.33825	1.21055
C	5.7	1.625	5.6726	1.6082	1.56805
N	6.7	1.95	6.6652	1.9236	1.9170
O	7.7	2.275	7.6580	2.2461	2.22625
F	8.7	2.6	8.6501	2.5639	2.54985

TABLE B. SCF input information.

		Electron configuration[a]			Internuclear distance R_e[b]	
Molecule	State	s	$+p$	$-p$	A	a.u.
Li_2	$^1\Sigma_g^+$	3	0	0	2.672_5	5.051
Be_2	$[^1\Sigma_g^+]$	4	0	0	2.0	(3.780)
C_2	$^1\Sigma_g^+$	4	1	1	1.2422	2.3475
N_2	$^1\Sigma_g^+$	5	1	1	1.094	2.068
F_2	$^1\Sigma_g^+$	5	2	2	1.418	2.680
LiH	$^1\Sigma^+$	2	0	0	1.5953_5	3.015
BH	$^1\Sigma^+$	3	0	0	1.2325	2.329
NH*	$^1\Sigma^+$	2	1	1	$[1.045_5]$	1.976
HF	$^1\Sigma^+$	3	1	1	0.9171	1.733
CO	$^1\Sigma^+$	5	1	1	1.1281_9	2.132
BF	$^1\Sigma^+$	5	1	1	1.262	2.385
LiF	$^1\Sigma^+$	4	1	1	1.51	2.85

[a] s, $+p$, and $-p$ refer to MO's of l value 0, +1, and −1, respectively.
[b] 1 a.u.=0.5291 A.

TABLE C. One-center overlap integrals.

Molecule	Overlap integral	Slater LCAO-MO	Best atom LCAO-MO	Best limited LCAO-MO
LiH	S_{12}	0.1662 6484	0.1620 4403	0.1930 7013
BH	S_{12}	0.2099 1853	0.2216 0079	0.2101 5522
NH	S_{12}	0.2279 2130	0.2248 6784	0.2284 5502
FH	S_{12}	0.2377 1090	0.2346 3500	0.2332 2147
Li_2	$S_{12}=S_{45}$	0.1662 6484	0.1620 4403	0.1601 1469
Be_2	$S_{12}=S_{45}$	0.1937 9309	0.1888 9342	0.1894 0733
C_2	$S_{12}=S_{45}$	0.2204 7827	0.2185 0310	0.2239 2555
N_2	$S_{12}=S_{45}$	0.2279 2130	0.2248 6784	0.2235 0663
F_2	$S_{12}=S_{45}$	0.2377 1090	0.2346 3500	0.2366 1054
CO	S_{12}	0.2204 7827	0.2185 0310	
	S_{45}	0.2334 4716	0.2307 4713	
BF	S_{12}	0.2099 1853	0.2216 0079	
	S_{45}	0.2377 1090	0.2346 3500	
LiF	S_{12}	0.1662 6484	0.1620 4403	
	S_{45}	0.2377 1090	0.2346 3500	

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Role of Coulomb Energy in the Valence-Bond Theory*,†

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I. INTRODUCTION

IN VB (valence-bond) theory calculations using covalent structures only, the binding energy is regarded as the sum of two terms, namely, a Coulomb term and an exchange term.[1,2] For the hydrogen molecule the computed energy at the r value at which it is a maximum (about 1.0 A) is about 12% of the experimental binding energy at that r value. (At the equilibrium internuclear distance in H_2, however, the contribution of the Coulomb energy to the binding energy is only about 1%.) It has very often been assumed that the ratio of Coulomb to total binding energy is about 12% in any chemical bond.

There are relatively few accurate calculations on this subject. Rosen and Ikehara[3] computed the Coulomb and exchange binding energies for the interaction between a pair of identical neutral atoms, each having one ns electron, for $n=1, 2, 3, 4, 5$. The results showed that both energies decrease with increasing n, but that the proportion of Coulomb energy in the total binding energy increases with increasing n. On extrapolating beyond $n=5$ they found greater values for the Coulomb than for the exchange binding energy. It has been shown also that for p electron bonds the Coulomb binding energy can have larger values than for s electron bonds.[4] The same is true for bonds formed by $2s-2p$ hybrid orbitals; the calculations of Woods[5] on CH_4 showed a Coulomb binding energy greater than 50% of the total binding energy.[6] A few unpublished calculations made some time ago in this Laboratory by C.W. Scherr also indicated large Coulomb energies. Fischer[7] too has made some calculations of Coulomb energies, but in a modified way directed toward the evaluation of hybridizations.

These few calculations raise the serious question

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[1] Cf. J. H. Van Vleck and A. Sherman, Revs. Modern Phys. **7**, 167 (1935); L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935); H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York); C. A. Coulson, *Valence* (Clarendon Press, Oxford, England, 1957).

[2] R. S. Mulliken, J. Phys. Chem. **56**, 295 (1952).

[3] N. Rosen and S. Ikehara, Phys. Rev. **43**, 5 (1953).

[4] J. H. Bartlett, Phys. Rev. **37**, 507 (1931).

[5] H. J. Woods, Trans. Faraday Soc. **28**, 877 (1932).

[6] For more references on the subject cf. reference 2, Sec. XIII.

[7] I. Fischer-Hjalmars, Arkiv Fysik **5**, 349 (1952); **7**, 165 (1953).