On the d Orbital of the Sulfur Atom in Thiophene

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(Received June 17, 1959)

The idea of *pd* hybridization in thiophene has been used successfully in accounting for the general similarity between thiophenes and their benzene analogues[1-3]. In hybridizing the *p*- and *d*-orbitals on the sulfur atom, the fundamental procedure was that the two hybridized orbitals which conjugate with $2p\pi$ orbitals on the carbon atoms are defined so as to be non-orthogonal to each other. A problem which has to be solved, however, results from adopting the *d* orbitals in bonding; it follows what values should be used for nuclear charge parameters of the *d* orbitals. If the use of the free atom parameter required by Slater's rule[4] for an electron in the *d* orbital is to be retained at all, the orbital becomes too diffuse and weakly bound to participate substantially in bonding. For example, when an electron of an unshared pair on the sulfur atom is considered to be in the *d* state, it bears the value 1 as the effective nuclear charge; this fact gives a small value of overlap integral with the $2p\pi$ orbital on the carbon atom, of the order of 0.1[5] and suggests the level of its energy much higher than the ground state. Under this condition, one might not expect the appreciable participation in bonding to occur through the hybridization, from the point of overlap criterion on bonding[6] and from balancing of energy. The eigenfunction of the electron, however, has its radial function whose maximum lies at 9 atomic units. The orbital, therefore, may be regarded as including the full carbon skeleton of thiophene, so that it would be impossible to avoid the influence of the nuclear charges of neighboring carbon atoms. The charges may distort the orbital, contracting it and allowing its participation in the hybridization, as suggested by Craig and Magnusson[7].

In this paper, the influence of perturbing potentials of the charges will be examined, and the possibility of the participation in the hybridization will be inquired into, following the treatment by Craig and Magnusson, who presented a model to represent *d* electrons in an octahedral molecule, and applied it to the consideration of actual examples.

Orbital Contraction.—Let us now consider the system in which a bivalent sulfur atom combines with two carbon atoms at an angle. In this model, a single *d* electron will be supposed to move in the field of the sulfur nucleus of charge Z_s, and upon this hydrogen-like atom system will be superposed a perturbation consisting of two positive charges of the carbon atoms of magnitude Z_c at the distance of σ atomic units. Furthermore, the central hydrogen-like atom will be considered to be surrounded, not by two hydrogen-like atoms of carbon, but just by point charges of magnitude Z_c. The actual potential of perturbation consists of the attraction of the surrounding nuclei minus the

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[1] H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

[2] K. Kikuchi, *Sci. Repts. Tohoku Univ. Series I*, **40**, 133 (1956).

[3] K. Kikuchi, ibid., **41**, 35 (1957).

[4] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

[5] H. H. Jaffé, *J. Chem. Phys.*, **21**, 258 (1953).

[6] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, **1954**, 332.

[7] D. P. Craig and E. A. Magnusson, ibid., **1956**, 4895.

coulomb repulsions of their electrons plus exchange terms; hence the dependence on distance of this composite potential will not follow the r^{-1} law at all closely. The system being thus too complicated, the point charge approximation is employed as approximation in this paper; the charge Z_c will be treated rather as a parameter relevant to making up for the imperfection of the approximation, values plausible in wider range being involved. As for the angle between two C–S bonds, θ, the following three cases will be considered apart from the thiophene in question, from a more general point of view, 90°, 120° and further 180°. For $Z_c=0$, the eigenfunction for d electron is, of course, that of the hydrogen-like atom of charge Z_s. As the d electron wave function, two of the usual Slater-type atomic functions are taken up for consideration, as follows:

$$\begin{aligned}\psi_{xz}&=(\sqrt{2}/81\sqrt{\pi})\alpha^{7/2}r^2\exp(-\alpha r/3)\\&\quad\times\sin\vartheta\cos\vartheta\cos\varphi\\\psi_{yz}&=(\sqrt{2}/81\sqrt{\pi})\alpha^{7/2}r^2\exp(-\alpha r/3)\\&\quad\times\sin\vartheta\cos\vartheta\sin\varphi\end{aligned}$$

where, α, as will be mentioned later, is a parameter to be determined with respect to energy. Further, the influence upon $3p$ Slater atomic function will be examined in comparison with the case of the d orbitals.

The potential by the outlying charges may be expanded as a sum in the usual $1/r$ series8), which reduces to the following expressions for the three cases respectively.

$\theta=90°$:

$$\begin{aligned}V_{r<\sigma}&=-(2Z_c/\sigma)-(Z_c/\sigma)(r/\sigma)\\&\quad\times(\cos\varphi+\sin\varphi)\sin\vartheta\\&\quad-(Z_c/2\sigma)(r/\sigma)^2(3\sin^2\vartheta-2)+\cdots\cdots\\V_{r>\sigma}&=-(2Z_c/r)-(Z_c/r)(\sigma/r)\\&\quad\times(\cos\varphi+\sin\varphi)\sin\vartheta\\&\quad-(Z_c/2r)(\sigma/r)^2(3\sin^2\vartheta-2)+\cdots\cdots\end{aligned}$$

$\theta=120°$:

$$\begin{aligned}V_{r<\sigma}&=-(2Z_c/\sigma)-(Z_c/\sigma)(r/\sigma)\\&\quad\times\cos(\varphi-\pi/3)\sin\vartheta\\&\quad-(Z_c/2\sigma)(r/\sigma)^2\{(15/4)\cos^2\varphi\sin^2\vartheta\\&\quad+(3\sqrt{3}/2)\sin\varphi\cos\varphi\sin^2\vartheta\\&\quad+(9/4)\sin^2\varphi\sin^2\vartheta-2\}+\cdots\cdots\\V_{r>\sigma}&=-(2Z_c/r)-(Z_c/r)(\sigma/r)\\&\quad\times\cos(\varphi-\pi/3)\sin\vartheta-(Z_c/2r)(\sigma/r)^2\\&\quad\times\{(15/4)\cos^2\varphi\sin^2\vartheta\\&\quad+(3\sqrt{3}/2)\sin\varphi\cos\varphi\sin^2\vartheta\\&\quad+(9/4)\sin^2\varphi\sin^2\vartheta-2\}+\cdots\cdots\end{aligned}$$

$\theta=180°$:

$$\begin{aligned}V_{r<\sigma}&=-(2Z_c/\sigma)-(Z_c/\sigma)(r/\sigma)^2\\&\quad\times(3\cos^2\varphi\sin^2\vartheta-1)+\cdots\cdots\\V_{r>\sigma}&=-(2Z_c/r)-(Z_c/r)(\sigma/r)^2\\&\quad(3\cos^2\varphi\sin^2\vartheta-1)+\cdots\cdots\end{aligned}$$

Each expression shows that the perturbing potential has its symmetrical plane bisecting the angle between two C–S bonds, θ. The perturbation energy due to the outlying potential is given by $\int\psi V\psi\mathrm{d}\tau$, where ψ and V are both shown above. Hence, after integrating over the angular parts excepting the radial one, it is found that the expressions for $3p_z$ orbitals have the same forms, and that the $3d_{xz}$ and $3d_{yz}$ orbitals are exposed respectively to the same fields of the outlying potentials when $\theta=90°$. Both of these can naturally be expected from their symmetric characters. In integrating with respect to the radial part, the terms higher than 2nd may be neglected because of their small contribution to the potential. Hence, the perturbation energy E' is given by the following, for example, for $3d_{xz}$ when $\theta=180°$;

$$\begin{aligned}E'&=(8Z_c/81^2\times15)\int_0^\sigma\alpha^7r^6\{-2/6-(2/7)\\&\quad\times(r^2/\sigma^3)\}\exp(-2\alpha r/3)\mathrm{d}r\\&\quad+(8Z_c/81^2\times15)\int_\sigma^\infty\alpha^7r^5\{-2-(2/7)\\&\quad\times(\sigma^2/r^2)\}\exp(-2\alpha r/3)\mathrm{d}r\\&=-(2Z_c/\sigma)(2\alpha\sigma/3)^7(1/6)[\{6!(3/2\alpha\sigma)^7\\&\quad-A_6(2\alpha\sigma/3)+A_5(2\alpha\sigma/3)\}\\&\quad+(1/7)\{8!(3/2\alpha\sigma)^9-A_8(2\alpha\sigma/3)\\&\quad+A_3(2\alpha\sigma/3)\}]\end{aligned}$$

where

$$A_n(\omega)=\int_1^\infty r^n\exp(-\omega r)\mathrm{d}r$$

Hereupon, using the auxiliary function presented by Craig and Magnesson7),

$$\begin{aligned}R^p{}_{nn}(\alpha\sigma)&=(1/\sigma)(2\alpha\sigma/n)^{2n+1}\{1/(2n)!\}\\&\quad\times\{(2n+p)!(n/2\alpha\sigma)^{2n+p+1}\\&\quad-A_{2n+p}(2\alpha\sigma/n)+A_{2n-p-1}(2\alpha\sigma/n)\}\end{aligned}$$

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8) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry", John Wiley & Sons, Inc., New York (1944), p. 369.

$$E' = -(2Z_c/\sigma)\{\sigma R^0_{33}(\alpha\sigma) - (1/7)\sigma R^2_{33}(\alpha\sigma)\}$$

For $3d_{yz}$ when $\theta = 180°$,

$$E' = -(2Z_c/\sigma)\{\sigma R^0_{33}(\alpha\sigma) - (2/7)\sigma R^2_{33}(\alpha\sigma)\}$$

Similarly, when $\theta = 120°$, for $3d_{xz}$

$$E' = -(2Z_c/\sigma)\{\sigma R^0_{33}(\alpha\sigma) - (1/56)\sigma R^2_{33}(\alpha\sigma)\}$$

and also for $3d_{yz}$,

$$E' = -(2Z_c/\sigma)\{\sigma R^0_{33}(\alpha\sigma) - (1/8)\sigma R^2_{33}(\alpha\sigma)\}$$

As mentioned above, the $3d_{xz}$ and the $3d_{yz}$ orbitals have the same potentials of perturbation when $\theta = 90°$, and so their energies are given in the same form,

$$E' = -(2Z_c/\sigma)\{\sigma R^0_{33}(\alpha\sigma) - (1/14)\sigma R^2_{33}(\alpha\sigma)\}$$

In the case of the $3p$ orbitals, they have the same energies for three cases of the angle θ because of their symmetric characters, that is;

$$E' = -(2Z_c/\sigma)\{\sigma R^0_{33}(\alpha\sigma) - (1/5)\sigma R^2_{33}(\alpha\sigma)\}$$

The total energy is the sum of the perturbation energy E' and the unperturbed given by

$$W = (\alpha/3^2)(\alpha/2 - Z_s)$$

for the hydrogen-like orbital of free atom parameter Z_s.

The procedure to be performed now is to find the new value of effective nuclear charge for which the total energy is a minimum for given magnitude of σ, Z_c and Z_s, i.e. to minimize the energy with respect to the exponent α. The increase in α over Z_s corresponds to a contraction of the orbital and the decrease to an expansion, since Slater radial functions have their maxima at $r_m = n^2/\alpha$. As the value of Z_s, the following two are chosen, 1 and 2 for $3d$ orbital, and 5 and 6 for $3p$. The distance σ is assigned to three values, 4, 3 and 2 atomic units, the first two come from actual examples containing the sulfur atoms, and the last is taken for the purpose of comparison with the first two. With respect to the value of Z_c, it is difficult to determine the straightforwardly equivalent parameter of the outlying potential, because, as mentioned above, the real field is not truly coulombic but much more complicated. Furthermore, there is, in general, a considerable difference between so-called potential- and field-determined nuclear charges on the same atom[9]. Therefore, in this paper, three values are assumed, $Z_c = 1$, 2 and 3, which are of course treated as tentative parameters, and the last is introduced from the well-known value of Slater's rule for the $2p$ orbital of carbon. In finding the minimum of the total energy, it is necessary to evaluate the values of $\sigma R^p_{nn}(\alpha\sigma)$, which are tabulated in *Appendix*.

In Tables I and II are given the results. It is shown in these tables that the $3d$ orbitals are largely contracted, while the $3p$ orbitals are little affected by the outlying perturbing charges, and that the contraction is more sensitive to the bond distance σ than to the effective charge Z_c. The magnitude of the contraction is less for a greater bond distance and for a greater value of Z_s. This may be expected for the model employed here. Fig. 1 illustrates the rapid decrease in increment $(\alpha - Z_s)$ with increasing σ and

TABLE I. EFFECTIVE NUCLEAR CHARGE α OF $3d$ ORBITAL WHEN $\theta = 180°$ AND $120°$

I. $3d_{xz}$

θ	Z_s	Z_c	$\sigma=2$	$\sigma=3$	$\sigma=4$
180°	1	1	2.85	2.50	2.15
〃	〃	2	3.76	3.00	2.45
〃	〃	3	4.20	3.25	2.50
〃	2	1	3.66	2.96	2.64
〃	〃	2	4.25	3.48	2.93
〃	〃	3	4.50	3.65	3.10
120°	1	1	2.63	2.30	2.09
〃	〃	2	3.56	2.93	2.48
〃	〃	3	4.14	3.20	2.70
〃	2	1	3.40	2.94	2.58
〃	〃	2	4.14	3.42	2.90
〃	〃	3	4.60	3.60	3.05

II. $3d_{yz}$

θ	Z_s	Z_c	$\sigma=2$	$\sigma=3$	$\sigma=4$
180°	1	1	2.30	2.10	1.95
〃	〃	2	3.12	2.68	2.24
〃	〃	3	3.78	3.05	2.62
〃	2	1	3.08	2.84	2.59
〃	〃	2	3.75	3.14	2.96
〃	〃	3	4.10	3.06	3.15
120°	1	1	2.54	2.20	1.98
〃	〃	2	3.45	2.80	2.51
〃	〃	3	3.90	3.16	2.65
〃	2	1	3.28	2.87	2.68
〃	〃	2	3.95	3.27	2.84
〃	〃	3	4.40	3.56	2.94

TABLE II. EFFECTIVE NUCLEAR CHARGE α OF $3p_z$ ORBITAL

Z_s	Z_c	$\sigma=2$	$\sigma=3$	$\sigma=4$
5	1	5.47	5.22	5.15
〃	2	5.93	5.52	5.20
〃	3	6.20	5.55	5.24
6	1	6.32	6.13	6.00
〃	2	6.63	6.20	6.12
〃	3	6.90	6.25	6.18

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[9] For example, see: F. W. Brown, *Phys. Rev.*, **44**, 214 (1933).

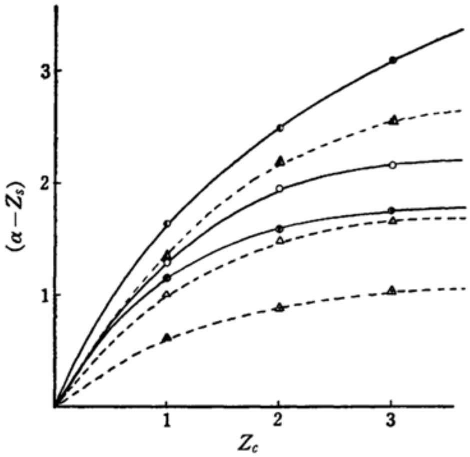

Fig. 1. Values of the increment $(\alpha - Z_s)$ for $3d_{xz}$ and $3d_{yz}$ orbitals when $\theta = 90°$.

—◐— $Z_c = 1$ $\sigma = 2$
—○— 〃 $\sigma = 3$
—⊙— 〃 $\sigma = 4$
--▲-- $Z_s = 2$ $\sigma = 2$
--△-- 〃 $\sigma = 3$
--◬-- 〃 $\sigma = 4$

Z_s, when $\theta = 90°$ (the case of thiophene[10]). The figure also shows that the increment of effective nuclear charge by the perturbation is little altered by Z_c in the range $Z_c = 2 \sim 3$ which are most plausible as the equivalent parameter, $\sigma = 3$ and 4 corresponding to the actual molecule containing the sulfur atom.

From these results, it might be inferred in any case that in hybridizing the d orbital on the sulfur atom as in thiophene the effective nuclear charge for the d orbital would not bear the free atom parameter, but it should bear at least a greater value, for example, $\alpha \fallingdotseq 3$ for that in thiophene. Of course, it must be emphasized that this discussion on the effective value for α is by all means tentative under the point charge approximation. Furthermore, the value of α appropriate to the real system should be determined precisely with respect to the whole energy of the molecule. The value obtained through the approximation, however, may be used as the first step of the calculation about the molecular energy.

On the other hand, for the $3p$ orbital, the free atom parameter may be used directly in calculating the molecular energy, because it is little affected by the surrounding nuclei. In general, the contraction of orbital is large only when the orbital with highly screened and loosely bound electrons lies under the perturbation. For the $2p\pi$ orbital of carbon, an argument similar to the case for $3p$ orbital can be applied as follows; the perturbation energy E' for the $2p$ orbital with nuclear charge $Z = 3$ is given as

$$E' = -(2Z_c/\sigma)\{\sigma R_{22}^{0}(\alpha\sigma) - (1/5)\sigma R_{22}^{2}(\alpha\sigma)\}$$

when $\theta = 120°$. Using the values σR_{22}^{0} and σR_{22}^{2} (see *Appendix*), the perturbed nuclear charge can be obtained, which is given in Table III for $\sigma = 2$, 3 and 4 atomic units. It is seen that the orbital is not altered at all. The free atom parameter for the $2p$ orbital of carbon may be used securely as usual in the molecular energy calculation.

TABLE III. EFFECTIVE NUCLEAR CHARGE α OF $2p_z$ ORBITAL WHEN $\theta = 120°$

Z	Z_c	$\sigma = 2$	$\sigma = 3$	$\sigma = 4$
3	1	3.26	3.14	3.07
〃	2	3.46	3.22	3.10
〃	3	3.64	3.33	3.14

It is of interest to notice that the radial maxima of the $3d$ orbitals contracted lie nearly at the bond distance σ.

Overlap Integral.—The overlap criterion[6] may be used conveniently in discussing the bond formation, because it is generally impracticable to calculate accurately the energy of formation of a bond between two centers, and, as much used and discussed by Mulliken and his collaborators[11], it gives some measure of the concentration of electronic charge between the nuclei. It can be used not only for the discussion of covalent bond, but also can be well applied to that of π bonding. An amount of increase in overlap integral means to strengthen the bond to some extent. Further the increase in overlap integral of a d orbital with an orbital on the neighboring atom will be associated by large contribution to the hybridization in which the d orbital participates, because the integral of the hybrid orbital may be written as a sum of those of participating orbitals.

The values of the integral for the contracted and unperturbed $3d\pi$ orbitals with the $2p\pi$ orbitals of carbon are summarized in Table IV, together with those for $3p\pi$ orbitals. In calculating these values, numerical tables given by Jaffé[5] and

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[10] Y. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1779 (1939).

[11] For example, F. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

TABLE IV. OVERLAP INTEGRALS OF 3*d* ORBITALS WITH 2*p* ORBITALS OF CARBON, WHEN $\theta=90°$*

Z_s	Z_c	$\sigma=2$	$\sigma=3$	$\sigma=4$
I. $3d_{xz}$ and $3d_{yz}$				
1	0	0.109	0.129	0.127
1	1	0.438	0.425	0.290
1	2	0.537	0.428	0.309
1	3			
2	0	0.319	0.326	0.279
2	1	0.525	0.426	0.308
2	2	0.566	0.439	0.315
2	3			
II. $3p_z$				
5	0	0.492	0.242	0.109
5	1	0.484	0.241	0.099
5	2	0.477	0.220	0.098
5	3			
6	0	0.477	0.202	0.081
6	1	0.444	0.192	0.079
6	2	0.426	0.192	0.074
6	3			

* In calculating the overlap integral involving *d* orbital, one must pay some attention to the special symmetric character of the orbital; in this table are given only the values when $\theta=90°$, because both other cases may cause some confusion in the calculation. Cf. Ref. 2.

Mulliken et al.[12] were used. The results show that the values of integral for the contracted 3*d* orbitals are enlarged without exception. Although it does not necessarily signify a very great possibility of bonding by the *d* orbital, it may be said at least that such $d\pi-p\pi$ bonding is likely to be more commom and important than has ever been considered, and that, therefore, the participation of the *d* orbitals in the hybridization is more probable than expected through the direct employment of free atom parameter by Slater's rule. In an actual system such as the sulfur atom in thiophene, the extent to which the *d* orbital participates in bonding will be of the order same as, or less than, that of the 3*p* orbital, despite the greater value of the integral. Because the mixing coefficient of the *d* orbital in the hybridization is not great, and also the balancing of energy is unfavorable; this will be examined in the next section.

Balancing of Energy.—Slater's rule seems to be insufficient for the accurate calculation of energy levels of an atom, although it suffices for the discussion of orbital size and overlap of atoms. For example, according to the rule, one has the values 45 and 1.5 eV. for 3*p* and 3*d* orbitals on the sulfur atom, respectively. They are very different from spectroscopic data[13], though these data are not always precisely corresponding to the so-called valence states of the atom. Spectroscopically the ionization energy of the atom is 10.36 eV. and the difference between 3*p* and 3*d* states is about 8.5 eV.

The discussion dealing with the final determining factor in bonding, i. e. the energy, can not be free from some ambiguity, since the general relationships between the overlap and the bond energy, and between the effective nuclear charge and the energy level, are not yet well established. If one should be allowed to assume that the free atom parameters $Z_s=5.45$ and 1 may correspond to the energy values 10.36 and 1.86 eV., respectively, the levels of the contracted *d* orbitals will be settled at about 5 eV. above the ground state. Of course, this estimation is merely tentative. However, it might be said that the level of energy of the *d* orbital will be drawn to some extent near to that of the 3*p* orbital as the result of the contraction by the perturbation, so that the possibility of participation in the hybridization will become greater, setting aside the question of extra promotion energy suggested by Craig and Magnusson[7], who estimated the energy directly by Slater's rule. It is well known that the closer the two energy levels are drawn to each other, the greater the interaction between them[14].

All the discussions above are those under the point charge approximation. It is more or less inevitable that the results obtained in this paper are not so readily available for an accurate discussion of bond formation in the real system. Further, in thiophene, there are two other perturbing charges which are included by the diffuse *d* orbital on the sulfur atom.

Nevertheless, the results will be sufficiently valid for approximate and semiquantitative discussion on the possibility of participation of the *d* orbital in hybridization.

Summary

The influence of neighboring atoms upon the diffuse *d* orbital on the sulfur atom

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[12] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[13] C. E. Moore, *Natl. Bur. Standards* (*U. S.*), *Circ.* **467**, 181 (1949).

[14] C. A. Coulson, "Valence", Oxford University Press, London (1952), p. 195.

and the possibility of the participation in the hybridization were examined. It might be expected that, with respect to the sulfur atom in thiophene, the participation of *d* orbitals in the hybridization would take place to a greater extent than predicted by the direct application of free atom parameter by Slater's rule, owing to the contraction by the perturbation of neighboring carbon atoms.

The author wishes to express his sincere thanks to Dr. S. Nagakura for his kind advice and helpful discussions. Thanks are also due to Dr. K. Saito for his kind inspection and revision of this manuscript.

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Appendix THE VALUES OF AUXILIARY FUNCTIONS

$\alpha\sigma$*	σR_{22}^{0}	σR_{22}^{2}	σR_{33}^{0}	σR_{33}^{2}
1.5			0.1665	0.0082
2.0	0.4799	0.1693		
2.25			0.2498	0.0269
3.0	0.6702	0.2287	0.3323	0.0611
3.75			0.4133	0.1088
4.0	0.8046	0.4517		
4.5			0.4915	0.1698
5.0	0.8908	0.4958		
5.25			0.5656	0.2368
6.0	0.9417	0.4843	0.6341	0.3061
6.75			0.6961	0.3714
7.0	0.9701	0.4412		
7.5			0.7511	0.4286
8.0	0.9851	0.3863		
8.25			0.7988	0.4752
9.0	0.9928	0.3313	0.8394	0.5098
10.0	0.9966	0.2817		
10.5			0.9011	0.5433
11.0	0.9984	0.2396		
12.0	0.9993	0.2045	0.9416	0.5373
13.0	0.9996	0.1758		
13.5			0.9667	0.5053
14.0	0.9999	0.1524		
15.0	1.0004	0.1364	0.9817	0.4598
18.0			0.9949	0.3616
21.0			0.9987	0.2850
24.0			0.9997	0.2169
27.0			0.9999	0.1725

* The values for $\alpha\sigma$ in the table given by Craig and Magnusson should be multiplied by 1.5.