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Justification of the Mataga-Nishimoto Approximation

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Coulson's expression for the two-centre Coulombic integral, (*pp/qq*), obtained by use of Saturno's operator, is shown to yield values almost identical to those given by the empirical relationship of Mataga and Nishimoto.

In a recent communication Saturno [1] proposed the use of the operator $1/(r_1+r_2)$, in place of the customary $1/r_{12}$, for the evaluation of the one-centre Coulombic integral. The result, $(pp/pp)=2\zeta/(4l+5)$, for Slater type orbitals, has since been obtained more simply by Coulson [2], who also used the operator $1/(r_1+r_2+R)$ to find the $2p\pi-2p\pi$ two-centre integral, (pp/qq), for the case $p=q$, deriving the expression

$$(pp/qq)=2\zeta e^{2\zeta R}E_{4l+6}(2\zeta R)$$

where $E_n(x)=\int_1^\infty e^{-xt}t^{-n}dt$.

We have determined (pp/qq) in the case of carbon, using $2\zeta=3.25$ as given by Slater's rules, for a range of R values and the results are shown in the Table. For high values of n, tables of the generalised exponential integral are not readily available and we therefore made use of the recursion formula $E_{n+1}(x)=1/n\cdot(e^{-x}-xE_n(x))$, together with $E_1(x)=-Ei(-x)$, the required values of the latter being taken from the B. A. Tables [3]. The results agree extremely closely with

Table. *Variation of the two-centre integral with R*

R (Å)	(pp/qq) eV Coulson-Saturno	(pp/qq) eV Mataga-Nishimoto	(pp/qq) eV Ohno
0.000	9.820	9.820	9.820
0.489	7.211	7.368	9.320
0.651	6.660	6.801	8.978
0.814	6.156	6.316	8.588
1.140	5.378	5.526	7.755
1.303	5.061	5.201	7.343
1.384	4.916	5.053	7.142
1.466	4.780	4.912	6.947
1.628	4.529	4.654	6.572
2.443	3.593	3.684	5.055
2.768	3.319	3.401	4.600
3.257	2.972	3.049	4.032
4.885	2.227	2.267	2.823

those derived using the empirical relationship of Mataga and Nishimoto [4], $(pp/qq) = 1/(R + a_{pq})$ where $a_{pq} = 2/((pp/pp) + (qq/qq))$, which are tabulated for comparison together with those obtained from Ohno's [5] equation, $(pp/qq) = 1/(R^2 + a_{pq}^2)^{\frac{1}{2}}$.

Recently Chojnacki [6] produced evidence for the superiority of the Mataga-Nishimoto procedure over that of Ohno for the calculation of singlet state excitation energies but found the opposite to be true for triplet states. This result is though to be expected if, as has been suggested [7], the generally poor performance of the Mataga-Nishimoto relationship for triplet states is due to its empirical allowance for electron correlation. Thus since the form of Saturno's operator is clearly such as to impose theoretically the necessary constraint to take into account the effects of correlation, the use of the Mataga-Nishimoto formula for singlet states can be fully justified, and its unsuitability for triplet states readily understood. Similarly the inclusion of correlation is responsible for both the drastic reduction in the value of the one-centre integral and the much more rapid decrease of (pp/qq) with R as compared with the values calculated using the $1/r_{12}$ operator [8]. Incidentally, the value of 9.82 eV found [1] for (pp/pp) agrees almost exactly with Julg's [9] figure of 9.87 eV obtained from an empirical attempt to allow for electron correlation.

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