443. *The Study of π-Electron States by the Valence-bond Method.*

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By using Mulliken's type of approximation in computing many-centre atomic integrals the standard valence-bond technique is modified to include overlap and exchange integrals of all orders. The range of applicability to π-electron energetics is extended and a procedure is indicated for calculating dipole and transition moments at the same time.

By reference to an example the errors introduced by neglecting overlap and higher-order exchange integrals are discussed in relation to the more exact calculations by the new method.

(I) IN the valence-bond method[1,2] the molecular wave-functions, characterizing each state of a many-electron system, are represented in a basis of " structures," *i.e.*, many-electron functions corresponding to a distribution of " bonds " between a given set of atomic orbitals $a_i(r_i;\ \theta_i;\ \phi_i)$, whose form will be supposed to be quite general.

These " structures " are linear combinations of determinantal wave-functions (1):

$$A_n = (n!)^{-\frac{1}{2}}\,\text{det.}\,|\,\bar{a}_1\bar{a}_2\,.\,.\,.\,a_n\,| \qquad (1)$$

where the bar indicates β-spin. It follows that each matrix element of the secular equation for a many-electron problem is a linear combination of integrals (2)

$$\int A_i\mathrm{F}A_j\mathrm{d}\tau \equiv (A_i\mathrm{F}A_j) \qquad (2)$$

where the operator F is either the Hamiltonian H or the unit operator.

To make the calculation, the integrals (2) must be expanded in exchange integrals of all orders, and then expressed in terms of atomic integrals.

As a result, the complexity of an n-electron problem increases very rapidly with n, and, if the usual π-approximation is adopted, only a few molecules can be comprehensively studied. For instance, even if only " structures " with one charge separation at the most are considered (and this is not an assumption made later in this paper), the number of integrals (2) which occur in an n-electron problem and in the absence of symmetry is given by:

$$(\Gamma_n + n\Gamma_{n-2})^2 \quad \text{where} \quad \Gamma_k = k!/[(k/2)!]^2$$

and bearing in mind that each integral (2) yields $[(n/2)!]^2$ exchange integrals it is readily seen that the order of complexity with which one can reasonably expect to cope is given by $n \leqslant 4$. To overcome these difficulties a number of approximations is usually adopted (for example, the neglect of exchange integrals of order higher than the second), but none is really satisfactory.

In what follows a method will be described in which the complexity of the valence-bond technique * is reduced by assuming only the validity of Mulliken's approximation[3] in computing many-centre atomic integrals.

The types of Mulliken's approximations employed here are:

$$(\phi_k\phi_l\,|\,\phi_m\phi_n) = \int\phi_k(1)\phi_m(2)\frac{1}{r_{12}}\phi_l(1)\phi_n(2)\mathrm{d}\tau = \frac{S_{kl}S_{mn}}{4}[(\phi_k\phi_k\,|\,\phi_m\phi_m) + (\phi_k\phi_k\,|\,\phi_n\phi_n) + (\phi_l\phi_l\,|\,\phi_m\phi_m) + (\phi_l\phi_l\,|\,\phi_n\phi_n)] \qquad (3)$$

$$(\phi_kV_r\phi_l) = \int\phi_kV_r\phi_l\mathrm{d}\tau = \frac{S_{kl}}{2}[(\phi_kV_r\phi_k) + (\phi_lV_r\phi_l)] \qquad (4)$$

* Another kind of approach, in which however the chemical analogy of the valence-bond method is lost, has been used by McWeeny.[4]

[1] Eyring, Walter, and Kimball, " Quantum Chemistry," J. Wiley, New York, Chap. 13.

[2] Pauling and Wilson, " Introduction to Quantum Mechanics," McGraw-Hill, New York, Chap. 13.

[3] Mulliken, *J. Chim. phys.*, 1949, **46**, 500, 521.

[4] McWeeny, *Proc. Roy. Soc.*, 1954, *A*, **223**, 306.

V_r being the nuclear potential of atom r with $r \neq k,\ l$ and S_{kl} the overlap integral of ϕ_k and ϕ_l.

The symbol ϕ_i has been used here to denote the sub-group of the class of functions a_i which satisfy the following condition:

(i) the ϕ_i's form an orthonormal and complete set around one centre.

A theoretical justification for Mulliken's approximation has been given by Ruedenberg:[5] the cases relevant to the present study are discussed in the Appendix.

Eqn. (2) can be written in the form:

$$(A_i\mathrm{F}A_j) = (-1)^{P_j}\begin{Bmatrix}\bar{a}_1\bar{a}_2 & \ldots & a_{n-1}a_n \\ \bar{a}_3\bar{a}_1 & \ldots & a_{k+1}a_k\end{Bmatrix}_{\mathrm{F}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

the upper row representing A_i, the lower A_j, and the atomic orbitals with β-spin grouped together on the left-hand side of the parenthesis: here P_j is the number of permutations which, when applied to the lowest row of (5), gives the standard form of A_j.* For convenience, $(-1)^{-P_j}(A_i\mathrm{F}A_j)$ will be used in the following.

When $\mathrm{F} = 1$ it is always possible to factorise eqn. (5) in two terms,[6] each a function only of atomic orbitals with the same spin:

$$\begin{Bmatrix}\bar{a}_1\bar{a}_2 & \ldots & a_{n-1}a_n \\ \bar{a}_3\bar{a}_1 & \ldots & a_k a_{k+1}\end{Bmatrix}_1 = \begin{Bmatrix}\bar{a}_1\bar{a}_2 & \ldots \\ \bar{a}_3\bar{a}_1 & \ldots\end{Bmatrix}_1 \begin{Bmatrix}\ldots & a_{n-1}a_n \\ \ldots & a_{k+1}a_k\end{Bmatrix}_1 = \mathbf{S}_\beta\mathbf{S}_\alpha \quad . \quad . \quad . \qquad (6)$$

When $\mathrm{F} = \mathrm{H}$ such a factorization is no longer possible but by using eqns. (3) and (4) a formula analogous to (6) can be obtained.

For this purpose a function T_{kl}, which contains ϕ_k and ϕ_l only, will be defined as follows:

$$T_{kl} = \frac{1}{S_{kl}}[(\phi_k V_k \phi_l) + (\phi_k V_l \phi_l) + (\phi_k \,|\, -\Delta \,|\, \phi_l)] - \tfrac{1}{2}[(\phi_k \,|\, -\Delta + V_k \,|\, \phi_k) +$$
$$(\phi_i \,|\, -\Delta + V_l \,|\, \phi_l) + (\phi_k V_l \phi_k) + (\phi_l V_k \phi_l) + (\phi_k\phi_k \,|\, \phi_l\phi_l)] + \frac{1}{2S^2_{kl}}(\phi_k\phi_l \,|\, \phi_k\phi_l) \qquad (7)$$

here

$$(\phi_i \,|\, -\Delta + V_i \,|\, \phi_i) = (\phi_i \,|\, -\Delta \,|\, \phi_i) + (\phi_i V_i \phi_i) \quad . \quad . \quad . \quad . \qquad (8)$$

Δ is the kinetic-energy operator.

It can be seen that by using eqns. (3) and (4) any exchange integral (EI) derived from (2) may be written as:

$$\mathrm{EI} = s_\alpha s_\beta[(Q^j + Q^i + 2k)/2] + s_\alpha s_\beta(T_{12} + T_{23} + \ldots + T_{kl}) \quad . \quad . \qquad (9)$$

where Q^i and Q^j are the coulomb integrals of the " structures " to which A_i and A_j electron respectively belong, T's subscripts represent atomic orbitals occupied by the same electron and s_μ (with $\mu = \alpha,\ \beta$) the product of overlap integrals among the atomic orbitals with the same spin function occurring in the exchange integral, so that $s_\alpha s_\beta = S$, S being the value of the exchange integral when $\mathrm{F} = 1$. Here k (see p. 2206 for its complete definition) is a function which depends only upon the atomic orbitals not contained in both rows of eqn. (5), thus being the same for all exchange integrals derived from an integral (2). Since $T_{kl} = 0$ when $k = l$, atomic orbitals not involved in the exchange do not appear in expression (9).

Now, when T's derived from atomic orbitals with the same spin function are grouped together, eqn. (9) becomes:

$$\mathrm{EI} = s_\alpha s_\beta[(Q^i + Q^j + 2k)/2] + s_\alpha(s_\beta T_\beta) + s_\beta(s_\alpha T_\alpha) \quad . \quad . \quad . \quad . \qquad (10)$$

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* The standard form of A_j is referred to the primary choice of the order in which the atomic orbitals are arranged in expression (1).

[5] Ruedenberg, *J. Chem. Phys.*, 1951, **19**, 1433.

[6] Mangini and Zauli, *J.*, 1956, 4960.

and the sum over all the exchange integrals derived from (2) leads to equation (11):

$$(-1)^{-P_j}(A_i\mathrm{H}A_j) = \boldsymbol{S}_\alpha\boldsymbol{S}_\beta[(Q^i + Q^j + 2k)/2] + \boldsymbol{S}_\alpha\mathbf{H}_\beta + \boldsymbol{S}_\beta\mathbf{H}_\alpha \quad . \quad . \quad (11)$$

where $\mathbf{H}_\mu$ has the form

$$\mathbf{H}_\mu = \sum^{P_\mu} S_{12}S_{23} \ . \ . \ . \ S_{kl}(T_{12} + T_{23} + \ . \ . \ . \ + T_{kl}) \quad . \quad . \quad . \quad . \quad (12)$$

P_μ being the number of permutations among the atomic orbitals with the same spin function.

The form of the k-function will now be specified: when A_i and A_j differ in one atomic orbital (*e.g.*, ϕ_r in A_j is absent in A_i and replaced by ϕ_p) its form is given by (13):

$$k_{r,p} = \tfrac{1}{8}[2(\phi_r\phi_r \,|\, \phi_p\phi_p) - (\phi_r\phi_r \,|\, \phi_r\phi_r) - (\phi_r\phi_p \,|\, \phi_p\phi_p)] \quad . \quad . \quad . \quad . \quad (13)$$

If A_i and A_j differ in two atomic orbitals (*e.g.*, ϕ_r and ϕ_s in A_j replaced by ϕ_p and ϕ_q in A_i) the k-function is given by (13*a*):

$$k_{rs,pq} = k_{r,p} + k_{s,q} + \tfrac{1}{4}[(\phi_p\phi_p \,|\, \phi_s\phi_s) + (\phi_q\phi_q \,|\, \phi_r\phi_r) - (\phi_r\phi_r \,|\, \phi_q\phi_q) - (\phi_r\phi_r \,|\, \phi_s\phi_s)] \quad (13a)$$

the last term appearing in order to ensure the invariance of (13*a*) under an exchange of ϕ_r with ϕ_s (or ϕ_p with ϕ_q). Eqns. (11), (13), and (13*a*) show that, when the charge distributions in the structures, to which A_i and A_j belong, differ, the mean value of the coulombic integral is $(Q^i + Q^j + 2k)/2$; moreover, since k is always negative the energy is lowered by an amount that increases with the distance of the negative centres in A_i and A_j, if both belong to polar structures, or with the displacement of negative charge, if either A_i or A_j belongs to a covalent structure.

(II) So far the use of eqn. (4) has been restricted by the condition $r \neq k, l$ (see Appendix). Now the case in which the approximation (14) is adopted will be discussed:

$$(\phi_k \,|\, -\Delta + V_l \,|\, \phi_l) = \frac{S_{kl}}{2}[(\phi_l \,|\, -\Delta + V_l \,|\, \phi_l) + (\phi_k \,|\, -\Delta + V_k \,|\, \phi_k)] \quad . \quad . \quad (14)$$

Substituting (14) in eqn. (8) gives eqn. (15):

$$T_{kl} = \frac{(\phi_k V_k \phi_l)}{S_{kl}} - \tfrac{1}{2}[(\phi_k V_l \phi_k) + (\phi_l V_k \phi_l) + (\phi_k\phi_k \,|\, \phi_l\phi_l)] + \frac{1}{2S^2_{kl}}(\phi_k\phi_l \,|\, \phi_k\phi_l) \quad . \quad (15)$$

Now eqn. (15) is no longer invariant to exchange of k with l.* This means that the hermitean character of $(A_i\mathrm{H}A_j)$ is lost,† therefore when approximation (14) is employed it is necessary to compute both $(A_i\mathrm{H}A_j)$ and $(A_i\mathrm{H}A_j)$ because they are now different. However, by defining a new integral

$$\overline{(A_i\mathrm{H}A_j)} = \tfrac{1}{2}[(A_i\mathrm{H}A_j) + (A_j\mathrm{H}A_i)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

it is possible to avoid doubling the computation, if eqn. (17) is used instead of (7):

$$(-1)^{-P_j}\overline{(A_i\mathrm{H}A_j)} = \boldsymbol{S}_\alpha\boldsymbol{S}_\beta[(Q^i + Q^j + 2k)/2] + \boldsymbol{S}_\alpha\overline{\mathbf{H}}_\beta + \boldsymbol{S}_\beta\overline{\mathbf{H}}_\alpha \quad . \quad . \quad . \quad (17)$$

in which $\overline{\mathbf{H}}_\mu$ is formally the same as given by expression (11) when the T's are replaced by the new $\overline{T}$'s defined as follows:

$$\overline{T}_{kl} = \frac{(\phi_k V_k \phi_l) + (\phi_k V_l \phi_l)}{2S_{kl}} - \tfrac{1}{2}[(\phi_k V_l \phi_k) + (\phi_l V_k \phi_l) + (\phi_k\phi_k \,|\, \phi_l\phi_l)] + \frac{1}{2S^2_{kl}}(\phi_k\phi_l \,|\, \phi_k\phi_l) \quad (18)$$

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* Only when ψ_k and ψ_l are exactly equivalent does the relation $T_{kl} = T_{lk}$ still hold.

† The problem that here arises is the same as that discussed by Moffitt[7] in the method of " Atoms in Molecules."

[7] Moffitt, *Proc. Roy. Soc.*, 1951, *A*, **210**, 261.

Since the matrix element in the secular equations always contain terms such as (16) the use of eqn. (17) is justified.

(III) If, instead of dealing with the Hamiltonian operator H, we are concerned with a one electron-operator M the factorization of an integral

$$\overline{(A_i\mathrm{M}A_j)} = \tfrac{1}{2}[(A_i\mathrm{M}A_j) + (A_j\mathrm{M}A_i)] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (19)$$

can be accomplished without loss in accuracy as in the case $\mathrm{M} = 1$.

When dealing with a more general case (for instance, when M represents electron co-ordinates) a procedure similar to outlined for H may be followed. In fact, by using $\bar{N}_{kl}$ functions (corresponding to the $\bar{T}_{kl}$'s) written as:

$$\bar{N}_{kl} = \frac{(\phi_k\mathrm{M}\phi_l) + (\phi_l\mathrm{M}\phi_k)}{2S_{kl}} - \tfrac{1}{2}[(\phi_k\mathrm{M}\phi_k) + (\phi_l\mathrm{M}\phi_l)] \quad . \; . \; . \; . \; . \quad (20)$$

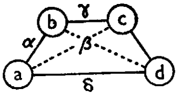
in the way described in (I) we can derive an equation corresponding to (11) or (18) which has the form

$$(-1)^{-P_j}\overline{(A_i\mathrm{M}A_j)} = \boldsymbol{S}_\alpha\boldsymbol{S}_\beta\bar{Q} + \boldsymbol{S}_\alpha\bar{\mathbf{M}}_\beta + \boldsymbol{S}_\beta\bar{\mathbf{M}}_\alpha \quad . \; . \; . \; . \; . \; . \; . \quad (21)$$

The $\bar{\mathbf{M}}_\mu$'s are of the same form as $\bar{\mathbf{H}}_\mu$'s in which the $\bar{T}$'s are substituted by the $\bar{N}$'s and the substitution $\bar{Q} = \tfrac{1}{2}(Q^i + Q^j)$ is made, Q^k being the coulomb integral with H replaced by M.

(IV) In order to make the calculations for an eigen-value problem once the atomic integrals have been tabulated, the procedure is as follows: first the T's have to be computed for all possible pairs of atomic orbitals by using eqn. (7). The second step consists in calculating $\boldsymbol{S}_\mu$ and $\mathbf{H}_\mu$ by using eqn. (12). It is worth noticing that eqn. (12) gives the $\boldsymbol{S}_\mu$ values also provided that the sum of T_{kl} is put equal to unity in each permutation P_μ. The number of $\mathbf{H}_\mu$'s (or $\boldsymbol{S}_\mu$'s) which have to be calculated is generally related to the symmetry of the molecule but is always very much less than the number of integrals (2) occurring in a given problem. Moreover the number of permutations P_μ is the square root of those occurring in the expansion of eqn. (2). This extends the range of applicability to $n = 6$ and possibly, in some favourable cases where a high degree of symmetry is present, to $n = 8$.

The final step consists in the tabulation of integrals (2) by using expression (11) after the k-functions have been calculated with eqns. (13) and (13*a*). From here the procedure follows the standard pattern: it is possible to introduce all the structures desired, since their energies are merely a sum of integrals (2). Each matrix element can be obtained and the solution of the secular equations gives energy values and the corresponding molecular wave-functions. On the other hand, the similarity between eqns. (11) and (21) suggests that it may be possible to carry out at the same time and with only a little extra labour the calculation of dipole moments in the different states and transition moments. There exists then the possibility of checking readily the degree of accuracy of the wave functions obtained, by comparison with experimental data such as dipole moments and oscillator strengths.



(I)

(V) It is of interest to get an approximate idea of the effect of neglecting overlap integrals and exchange integrals of order higher than the second in the energy of a state. In the simple case of the 4-equivalent π-electron problem as shown in (I), the energy corresponding to the " structure " $\psi_{ab,cd}$[1,2] is

$$E = \frac{\int \psi_{ab,cd}\mathrm{H}\psi_{ab,cd}\mathrm{d}\tau}{\int [\psi_{ab,cd}]^2\mathrm{d}\tau} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

If overlap integrals and exchange integrals of order higher than the second are neglected, then eqn. (23) is obtained:

$$E = Q + 2\alpha - \beta - \tfrac{1}{2}\gamma - \tfrac{1}{2}\delta \; . \; . \; . \; . \; . \; . \; . \; . \quad (23)$$

where α, β, γ, and δ are the second-order exchange integrals as indicated in (I). On the other hand, a complete calculation by the proposed method, which makes it possible to express high-order exchange integrals in second-order exchange integrals, leads to the results:

$$E_s = Q + 1{\cdot}9\alpha - 1{\cdot}5\beta - 0{\cdot}5\gamma - 1{\cdot}33\delta \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$E_k = Q + 1{\cdot}7\alpha - 2{\cdot}2\beta - 0{\cdot}5\gamma - 1{\cdot}15\delta \quad . \quad . \quad . \quad . \quad . \quad (24a)$$

where the subscripts *s* and *k* refer to calculations made with an exponential factor for the $2p_\pi$-atomic orbitals of 1·625 and 1·044 (Slater's and Kohlrausch's value respectively) for the carbon atom. Here the coefficients of the exchange integrals depend on the exponential factor chosen, partly because the normalisation coefficient in expression (22) is no longer unity and partly because the expansion of high-order in terms of second-order exchange integrals is a function of the overlap integrals among the various atomic orbitals. For instance, by applying eqn. (9) to the exchange integral[1] $\begin{pmatrix} abcd \\ badc \end{pmatrix}$ the following result is obtained:

$$\begin{pmatrix} abcd \\ badc \end{pmatrix} - S_{ab}{}^4Q = 2S_{ab}{}^2[\alpha - S_{ab}{}^2Q] \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Now

$$E - E_s = \Delta E_s = 0{\cdot}1\alpha + 1{\cdot}5\beta + 0{\cdot}8\delta \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$E - E_k = \Delta E_k = 0{\cdot}3\alpha + 1{\cdot}2\beta + 0{\cdot}6\delta \quad . \quad . \quad . \quad . \quad . \quad (26a)$$

From (26) and (26*a*) it can be seen that neglecting overlap and higher-order exchange integrals leads, for the case under consideration to: (i) an overestimate of the exchange energy to an extent depending upon the exponential factor value, the error being in inverse relation to it (a rough calculation showed that ΔE_s is ~10% and ΔE_k ~50% of the total exchange energy), and (ii) an overestimate of the contribution by neighbouring electrons to the exchange energy and a large underestimate of second- and third-neighbour electrons.

(VI) *Conclusions.*—The technique presented possesses some advantages which are summarized as follows.

(1) The only approximation used is Mulliken's and accordingly the error in the determination of π-energies is likely to be small,* of the order of some tenths of an ev. Moreover, its theoretical meaning is not vague,[5] but represents a first stage of a series development (see Appendix). (2) It makes possible the introduction of all the exchange integrals deriving from expression (2) with comparatively little computation. (3) The range of applicability is extended. (4) Dipole and transition moments can be calculated at the same time, providing a check on the wave-functions obtained.

APPENDIX

The atomic functions ϕ_k appearing in (3) and (4) may be written

$$\phi_k(n, l, m) = R_{n,l}(r_k)Y_{lm}(\theta_k, \phi_k) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

The Y_{lm} are spherical harmonics and, if the internuclear axis for a chosen pair of atoms is the *z* axis we have, for the π electrons, $m \neq 0$. Now suppose we represent by $\phi_k{}^i$ a complete set of functions centred at nucleus *k*, where the superscript *i* stands for the set of quantum numbers *n*, *l*, and *m*. We shall continue to denote by ϕ_k the chosen function belonging to the set of $\phi_k{}^i$ concerned in π-bonding at *k*.

Then:
$$\phi_k = \sum_{i=0}^{\infty} S(\phi_k;\ \phi_l{}^i)\phi_l{}^i \quad \text{and} \quad \phi_l = \sum_{i=0}^{\infty} S(\phi_l;\ \phi_k{}^i)\phi_k{}^i \quad . \quad . \quad . \quad . \quad (28)$$

with
$$S(\phi_k{}^i;\ \phi_l{}^i) = \int \phi_k{}^i\phi_l{}^i \mathrm{d}\tau$$

so that
$$\phi_k\phi_l = \tfrac{1}{2}S(\phi_k;\ \phi_l)[\phi_k\phi_k + \phi_l\phi_l] + \tfrac{1}{2}\sum_{i=0}^{\infty} [S(\phi_k;\ \phi_l{}^i)\phi_k\phi_l{}^i + S(\phi_l;\ \phi_k{}^i)\phi_k{}^i\phi_l] \quad . \quad (29)$$

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* Some kind of approximation is always used when computing many-centre integrals.

where the largest term [5] in most problems is the one abstracted from the sum, and the primed summation sign omits the term concerned.

Since $S(\phi_k^i, \phi_l^j) = 0$ for $m_k^i \neq m_l^j$, and since also $m \neq 0$, many terms vanish and the neglect of all but the first term in expression (29) should leave a close approximation.[3,8]

In could be interesting to assess the accuracy of eqn. (3) and (4) in the particular case of equicentre, Slater's atomic orbitals $\phi_k = (2,1,1)_k$ and $\phi_l = (2,1,1)_l$ (which is the most frequent to occur in π-electron problems) and the importance of higher terms in eqn. (29), in this case expected to be:

$$\tfrac{1}{2}S(2\pi_k;\ 3\pi_l)[(2\pi_l 3\pi_l) + (2\pi_k 3\pi_l)] + \tfrac{1}{2}S(2\pi_k;\ 3\delta_l)[(2\pi_k 3\delta_k) + (2\pi_l 3\delta_l)] \quad . \quad (30)$$

for $n\pi_k = \phi_k(n,1,1)_k$ and $n\delta_k = \phi_k(n,2,1)_k$.

At present this is not feasible, since the two-centre integrals originated by including expression (30) in the expansion of an electron-repulsion or potential-energy integral are not to be found in the literature. Moreover, only two-centre integrals involving 2π Slater's atomic orbitals are tabulated, so that an accuracy test of eqns. (3) and (4) would be possible only in this limiting case where Mulliken's type of approximation is expected to be at its worst since monocentric integrals will appear and their values are very unlikely to fall off rapidly with increasing quantum number. However, by using a few reasonable assumptions to estimate the values of some integrals involving 3π and 3δ atomic orbitals, the contribution to the value of the two-centre repulsion integrals $(2\pi_k 2\pi_l \mid 2\pi_k 2\pi_k)$ and $(2\pi_k 2\pi_l \mid 2\pi_k 2\pi_l)$, due to the inclusion of (30) in addition to the first term of eqn. (29), has been computed. The results are collected in Table 1: the entries $Z^{-1}(2\pi)$ are the values obtained by using only the first term of eqn. (29), *viz.*, by using Mulliken's approximation. $Z^{-1}(3\pi)$ is the increment due to including the $3p\pi$ function, and $Z^{-1}(3\delta)$ due to including $3d\pi$. $Z^{-1}(ht)$ is the lumped contribution by higher terms. The difference between the exact value of the integral and (2π) is also given and indicated by Δ.

TABLE 1.

	$(2\pi_k 2\pi_l \mid 2\pi_k 2\pi_k)$				$(2\pi_k 2\pi_l \mid 2\pi_k 2\pi_l)$			
$ZR/2$	2	3	4	5	2	3	4	5
$Z^{-1}\Delta$	0·0013	0·0005	−0·0006	−0·0011	0·0026	0·0018	0·0007	0·0002
$Z^{-1}(2\pi)$	0·1230	0·0764	0·0436	0·0235	0·0854	0·0358	0·0125	0·0039
$Z^{-1}(3\pi)$	−0·0126	−0·0161	−0·0155	−0·0129	−0·0151	−0·0122	−0·0056	−0·0015
$Z^{-1}(3\delta)$	0·0052	0·0058	0·0051	0·0038	0·0076	0·0059	0·0031	0·0014
$Z^{-1}(ht)$	0·0087	0·0109	0·0098	0·0070	0·0088	0·0089	0·0042	0·0009

From this Table the following points arise: (1) The contributions by terms after the first in expressions (29) and (30) decrease rapidly. Moreover, the error Δ involved in using eqn. (3) is small in the region of main interest. (2) The error in the examples considered does not decrease monotonically on including more terms, but oscillates owing to the negative contribution of the 3π-atomic orbital (here orthogonalized to the 2π). (3) The estimated contribution by still higher terms with $n > 3$ is not therefore necessarily small, although it must fall off rapidly with increasing principal quantum number.

Some calculations were also made for $(2\pi_k 2\pi_l \mid 2\pi_j 2\pi_j)$ with k, h, j equidistant and are reported in Table 2. They suggest that the error of Mulliken's approximation is generally similar, and probably smaller than, for two-centre cases.

TABLE 2.

	$(2\pi_k 2\pi_l \mid 2\pi_j 2\pi_j)$			
$ZR/2$	2	3	4	5
$Z^{-1}(2\pi)$	0·1100	0·0636	0·0310	0·0149
$Z^{-1}(3\pi)$	−0·0093	−0·0079	−0·0038	−0·0006
$Z^{-1}(3\delta)$	0·0046	0·0047	0·0036	0·0025

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[8] Baker *et al.*, *J. Chem. Phys.*, 1954, **22**, 699, 1177, 1182, 2072.