
ATTI ACCADEMIA NAZIONALE DEI LINCEI
CLASSE SCIENZE FISICHE MATEMATICHE NATURALI
RENDICONTI

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**Simple approximate evaluation of two-center
Coulomb integrals**

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche,
Matematiche e Naturali. Rendiconti, Serie 8, Vol. 42 (1967), n.3, p. 402–414.*

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1967_8_42_3_402_0>

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Chimica. — *Simple approximate evaluation of two-center Coulomb integrals.* Nota di GIOVANNI CIULLO e CLAUDIO FURLANI (*), presentata(**) dal Corrisp. G. SARTORI.

RIASSUNTO. — In considerazione dell'attuale stato dei calcoli SCF—LCAO—MO per molecole inorganiche complesse, si propone una semplice approssimazione per gli integrali coulombiani bicentrici, basata sulla sostituzione di una delle due distribuzioni di carica interagenti con un appropriato sistema di cariche puntiformi. Alcune possibilità di miglioramento sono contenute in questo semplice modello e sono discusse e valutate in una serie di confronti fra valori approssimati e teorici di integrali su autofunzioni di Slater. La conseguente ottimizzazione del calcolo permette una esattezza dell'1% per la maggior parte dei casi di interesse pratico.

INTRODUCTION.

Molecular problems require knowledge of two-center Coulomb integrals even if simplifying assumptions, e.g. the Wolfsberg-Helmholz approximation for non-diagonal elements [1], and the zero differential overlap concept [2], are adopted. Exact calculation of such integrals is feasible [3, 4, 5, 6, 7], but usually rather complicated, especially for high principal quantum numbers n of the involved AO's, so that even in organic problems, where mostly only $n = 2$ occurs, Coulomb integrals are often evaluated through roughly simplified models like the charged spheres model [8], or through semiempirical relationships [2, 9, 10, 11]; another approximation, however not largely generalizable, is the multipole method by Mason and Hirschfelder [12]. We are interested in self-consistent MO calculations of metal complexes, where principal quantum numbers 3 or 4 are frequently encountered; exact calculation of Coulomb integrals, although possible, becomes then so complicated, that it would take the largest part of the calculative effort of the molecular problem. On the other hand, MO methods for coordination compounds employ, in their present status, several types of rather drastic approximations, and suffer also from uncertainty in the knowledge of the exact form of the atomic orbitals, so that the high accuracy attainable from exact analytical calculation of Coulomb integrals is here probably superfluous. With this in mind, we propose here a method for simplified evaluation of two-center Coulomb integrals for any n , based upon replacement of one of the two interacting charge distributions through an appropriate distribution of point charges, which does not probably lower the overall accuracy of the current MO methods for complex inorganic molecules, and requires no more reckoning effort than is needed for nuclear attraction integrals.

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(**) Nella seduta dell'11 marzo 1967.

THE MODEL.

The Coulomb interaction between a charge distribution $\psi_a^* \psi'_a$ centered on nucleus a and a charge element $dq_b = \psi_b^* \psi_b d\tau$ belonging to a charge distribution $\psi_b^* \psi_b$ centered on nucleus b is given by:

$$(1) \quad dq_b \int \psi_a^*(1) \frac{1}{r_1} \psi'_a(1) d\tau_1.$$

The whole Coulomb interaction between the electronic charge $\psi_a^* \psi'_a$ and the electron in ψ_b is given as the result of the integration of (1) over the whole coordinate space of electron 2:

$$(2) \quad (\psi_a^* \psi'_a | \psi_b^* \psi_b) = \iint \psi_a^*(1) \psi'_a(1) \frac{1}{r_{12}} \psi_b^*(2) \psi_b(2) d\tau_1 d\tau_2$$

this integration can be performed analytically, but we prefer instead to do it approximately, as a finite sum of terms, after replacing the continuous charge distribution $\psi_b^* \psi_b$ through a discontinuous distribution of point charges q_{ib} ($\sum_i q_{ib} = 1$):

$$(3) \quad (\psi_a^* \psi'_a | \psi_b^* \psi_b) = \sum_i q_{ib} (\psi_a^* | \psi'_a)$$

with

$$(3') \quad (\psi_a^* | \psi'_a) = \int \psi_a^*(1) \frac{1}{r_{1ib}} \psi'_a(1) d\tau_1.$$

Clearly, the choice of the assumed distribution of point charges q_{ib} is the basic feature of our model, and is essential for the validity of the proposed approximation.

Let us first discuss the case of orbitals with nodeless radial parts, i.e. with charge radial density comprised under one "bell" only. Taking care to retain as far as possible the multipole character of the orbital charge distribution, the proposed fractionation of charge is, for different types of orbitals, as follows:

s : 14 charges $-1/14e$ at the vertices of a tetrakisshexahedron;

p : two charges $-1/2e$ along the axis of the orbital;

d (except d_{z^2}): four charges $-1/4e$ on the two appropriate axes at right angles;

d_{z^2} : two charges $-0.30755e$ on the z -axis plus four charges $-0.09623e$ on the x and y axes.

In all above cases, the fractional charges are supposed to lie all at the same appropriate distance from the nucleus. A physically plausible choice for such a distance may be e.g. the mean orbital radius ($\bar{r} = \frac{n+0.5}{\alpha}$ for Slater orbitals) or the radius of maximum density ($r_{\max} = n/\alpha$ for Slater orbitals);

since this choice also has some influence on the validity of the approximation, we shall discuss it later in more detail.

It is to be remarked that the above charge fractionation preserves the multipole character of the orbitals in all cases except s , where the charge distribution is improperly assigned a 64-pole character like that of f -electrons; nevertheless, the accuracy of reproduction of the actual charge distribution turns out after all to be better for s than for p or d orbitals, owing to the finer subdivision into fractional charges, and we shall take particular advantage of this favourable circumstance in the optimization of our approximation, as will be discussed below.

If the charge distribution $\psi_a^* \psi_b$ has any radial nodes, we shall replace it, with obvious extension of the above model of fractionation, through as many sets of point charges of the symmetry above described as there are "bells" in the charge radial distribution curve, each set comprising the fraction of the electronic charge lying under the corresponding "bell". The point-charge approximation will be particularly good here because of the finer subdivision; furthermore, it will be better the narrower the "bells" are. By the same token, when dealing with nodeless charge distributions (one radial "bell" only), the approximation will be better the less the charge distribution is expanded; if therefore a Coulomb integral between two nodeless orbitals ψ_a and ψ_b is to be calculated by our approximation, it will be more convenient to replace the less expanded one through point charges, except possibly when the more expanded of the two orbitals is of s -type, since the better fractionation of s -charge distributions, according to the proposed model, can overcome the disadvantages arising from the point-charge simulation of the broader of the two charge distributions. In any case, the point-charge approximation obviously works better the larger the internuclear distances are; we shall discuss below the possible occurrence of lower limits of applicability of the point-charge model.

EVALUATION OF THE INTEGRALS.

In our approximation, the essential step in the calculation of a Coulomb integral is the evaluation of the integrals (3'), having the form of a nuclear attraction integral. ψ_a and ψ_b can in principle be any kind of atomic orbitals, i.e. hydrogenic, Slater-type, SCF type or else, but we shall deal here in larger detail with the case of nodeless Slater orbitals (radial part $R_{nl} = (2\alpha)^{(n+0.5)} \cdot [(2n)!]^{-0.5} r^{n-1} \exp(-\alpha r)$, r in a.u.), since they represent a very simple type of charge distribution where the general aspects of our model can be most easily exemplified and discussed; on the other hand, SCF orbitals are often expressed through linear combinations of Slater orbitals [13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25]; so their use in integrals (3') can be reduced again to the calculation of integrals of the same type, but with Slater radial parts.

Since the fractional charges q_{ib} do not in general lie on the axes of the functions ψ_a or ψ'_a , it is not convenient to evaluate (3') in elliptic coordinates; instead, we use polar coordinates centered on nucleus a , and expand $1/r_{1ib}$ in series of surface harmonics according to:

$$(4) \quad \frac{1}{r_{1ib}} = \sum_{k=0}^{\infty} \sum_{m'=-k}^{+k} \frac{(k-|m'|)!}{(k+|m'|)!} \frac{r <^k}{r >^{(k+1)}} P_k^{|m'|}(\cos \vartheta_1) P_k^{|m'|}(\cos \vartheta_{ib}) \cdot \exp [im'(\varphi_1 - \varphi_{ib})].$$

Expansion (4) allows useful group-theoretical simplifications: namely only those terms of (4) which belong to the identical representation of the symmetry group of the distribution of the q_{ib} 's, or contain the same representation among their reduction products, give non-vanishing contributions to (3); further simplifications arise in the calculation of group Coulomb integrals in complex molecules, when summing (3) over all atoms surrounding a . By the use of the proposed model, we can therefore fully exploit the possibility of group theoretical aids in the computation of interatomic Coulomb integrals. We notice by the way that the present type of reasoning closely follows the basic ideas of the crystal-field model.

Confining ourselves to the case where ψ_a and ψ'_a are real Slater orbitals of the same n and same angular part, we obtain after inclusion of (4) into the expression of the integrals (3'):

$$(5) \quad \left\{ \begin{aligned} (s | s') &= I_{0ib} \\ (p_z | p'_z) &= I_{0ib} + \frac{1}{5} (3 \cos^2 \vartheta_{ib} - 1) I_{2ib} \\ (p_x | p'_x) &= I_{0ib} - \frac{1}{10} (3 \cos^2 \vartheta_{ib} - 1) I_{2ib} + \frac{3}{10} \sin^2 \vartheta_{ib} \cos 2 \varphi_{ib} I_{2ib} \\ (p_y | p'_y) &= I_{0ib} - \frac{1}{10} (3 \cos^2 \vartheta_{ib} - 1) I_{2ib} - \frac{3}{10} \sin^2 \vartheta_{ib} \cos 2 \varphi_{ib} I_{2ib} \\ (d_{z^2} | d'_{z^2}) &= I_{0ib} + \frac{1}{7} (3 \cos^2 \vartheta_{ib} - 1) I_{2ib} + \frac{1}{28} (35 \cos^4 \vartheta_{ib} - 30 \cos^2 \vartheta_{ib} + 3) I_{4ib} \\ (d_{xz} | d'_{xz}) &= I_{0ib} + \frac{1}{14} [2 - 3 \sin^2 \vartheta_{ib} (\cos 2 \varphi_{ib} + 1)] I_{2ib} + \left[\frac{5}{42} \cos 2 \varphi_{ib} \sin^2 \vartheta_{ib} \cdot \right. \\ &\quad \left. \cdot (1 - 7 \cos^2 \vartheta_{ib}) - \frac{5}{6} \cos^4 \vartheta_{ib} + \frac{5}{7} \cos^2 \vartheta_{ib} - \frac{1}{14} \right] I_{4ib} \\ (d_{yz} | d'_{yz}) &= I_{0ib} + \frac{1}{14} [3 \sin^2 \vartheta_{ib} (\cos 2 \varphi_{ib} - 1) + 2] I_{2ib} + \left[\frac{5}{42} \cos 2 \varphi_{ib} \sin^2 \vartheta_{ib} \cdot \right. \\ &\quad \left. \cdot (7 \cos^2 \vartheta_{ib} - 1) - \frac{5}{6} \cos^4 \vartheta_{ib} + \frac{5}{7} \cos^2 \vartheta_{ib} - \frac{1}{14} \right] I_{4ib} \\ (d_{x^2-y^2} | d'_{x^2-y^2}) &= I_{0ib} - \frac{1}{7} (3 \cos^2 \vartheta_{ib} - 1) I_{2ib} + \left(\frac{5}{24} \cos^4 \vartheta_{ib} - \frac{5}{28} \cos^2 \vartheta_{ib} + \frac{1}{56} - \right. \\ &\quad \left. - \frac{5}{24} \sin^4 \vartheta_{ib} \cos 4 \varphi_{ib} \right) I_{4ib} \\ (d_{xy} | d'_{xy}) &= I_{0ib} - \frac{1}{7} (3 \cos^2 \vartheta_{ib} - 1) I_{2ib} + \left(\frac{5}{24} \cos^4 \vartheta_{ib} - \frac{5}{28} \cos^2 \vartheta_{ib} + \frac{1}{56} + \right. \\ &\quad \left. + \frac{5}{24} \sin^4 \vartheta_{ib} \cos 4 \varphi_{ib} \right) I_{4ib} \end{aligned} \right.$$

where:

$$I_{kib} = I_k(n_a, \alpha_a, \alpha'_a, R_{ib}) = \alpha_m \left(\frac{\sqrt{\alpha_a \alpha'_a}}{\alpha_m} \right)^{2n_a+1} \left\{ \frac{(2n_a+k)!}{(2n_a)! 2^k X_{ib}^{(k+1)}} + \right. \\ \left. + \frac{2^{(2n_a+1)}}{(2n_a)!} \exp(-2X_{ib}) \left[\sum_{v=0}^{2n_a-k-1} (-1)^v \frac{(2n_a+k;-1;v) - (2n_a-k-1;-1;v)}{(-2)^{(v+1)}} X_{ib}^{(2n_a-v-1)} + \right. \right. \\ \left. \left. + \sum_{v=2n_a-k-1}^{2n_a+k} (-1)^v \frac{(2n_a+k;-1;v)}{(-2)^{(v+1)}} X_{ib}^{(2n_a-v-1)} \right] \right\}$$

with $X_{ib} = \alpha_m R_{ib}$, $\alpha_m = \frac{\alpha_a + \alpha'_a}{2}$ and R_{ib} equal to the distance between the point charge q_{ib} and the nucleus a .

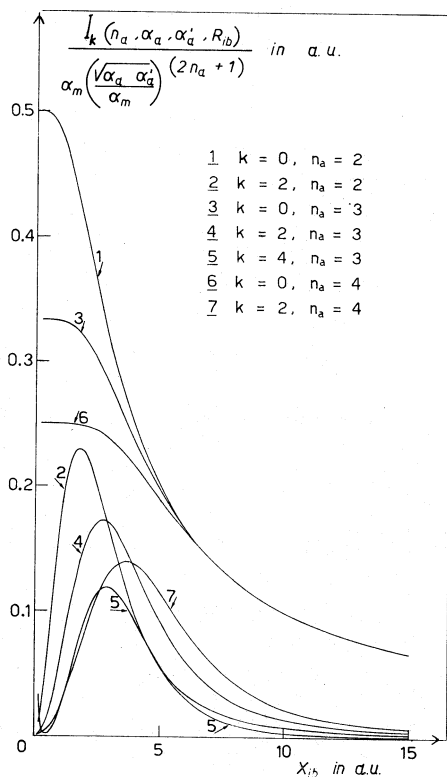


Fig. 1.

Quite analogous formulas can be easily derived for the case $n_a \neq n'_a$. fig. 1 shows the curves of

$$\frac{I_k(n_a, \alpha_a, \alpha'_a, R_{ib})}{\alpha_m \left(\frac{\sqrt{\alpha_a \alpha'_a}}{\alpha_m} \right)^{(2n_a+1)}}$$

against X_{ib} for some k and n_a .

Before passing to illustrate the results of some actual calculations carried out with the application of formulas (3) and (5), we want to discuss briefly the

physical meaning of the terms in (5), together with some additional possibilities of improving the proposed approximation without requiring any more involved calculations than those of nuclear attraction integrals already employed in formulas (5).

As is evident from (5), all Coulomb integrals $(\psi_a \psi'_a | \psi_b^2)$ contain a term $\sum_i q_{ib} I_0(n_a, \alpha_a, \alpha'_a, R_{ib})$ representing the electrostatic interaction of the point charges q_{ib} with the monopole of the charge distribution $\psi_a \psi'_a$; for s_a orbitals, this is the only non-vanishing term. Terms with $k > 0$ represent interactions of the q_{ib} 's with the higher multipoles (of order 2^k) of the charge distribution $\psi_a \psi'_a$; they are presumably smaller and often vanish, e.g. the last terms in the expressions for p_x or p_y in (5), with $k = 2$, containing $\cos 2\varphi_{ib}$, vanish if the system of the point charges q_{ib} has at least a C_4 axis along the internuclear axis.

According to (3) and (5), the said monopole interaction term is expressed as:

$$(6) \quad \sum_i \frac{q_{ib}}{R_{ib}} = \alpha_m \sum_i q_{ib} \exp(-2X_{ib}) f(X_{ib})$$

where $f(X_{ib})$ is a polynomial of X_{ib} and $1/X_{ib}$. Since the sum over the index i replaces, in our approximation, integration over the whole volume of the charge distribution ψ_b^2 of electron 2, the first term of (6) represents the point-charge approximation of $\int \psi_b(2) \frac{1}{r_{2a}} \psi_b(2) d\tau_2$; we can then calculate the exact value of the latter integral according to the appropriate formula of type (5), after merely interchanging indexes $a, b, 1$ and 2 , and replace the first term of the approximate expression (6) through its exact value. This leads in general to a significant improvement in the accuracy of the whole Coulomb integral, provided the first term of (6) is large with respect to the second one, as it is usually the case, since the second term of (6) tends to zero when the point charges q_{ib} tend to be external, or at least to lie on the tail of the charge distribution $\psi_a \psi'_a$ of electron 1. However the same procedure is not applicable, when one of the point charges q_{ib} falls very close to the nucleus a ; then the absolute values of both terms of (6) tend to infinite for $X_{ib} \rightarrow 0$, while their difference remains finite and is still a good approximation to the value of the monopole interaction; under such circumstances, clearly an improvement in the first term alone would make the overall result worse.

Furthermore, turning to the case $\alpha_a = \alpha'_a$, the monopole interaction term corresponds to the integral $(\psi_{as}^2 | \psi_b^2)$, where ψ_{as} is an s -type orbital, centered on nucleus a , and having the same n and α as ψ_a ; this integral, which is part of all integrals $(\psi_a^2 | \psi_b^2)$, can be evaluated according to optimization rules found for the integrals $(s_a^2 | \psi_b^2)$, e.g. taking advantage of the better approximation for the charge distribution s_a^2 , and then approximating ψ_{as}^2 .

Referring hereafter to the case $\alpha_a = \alpha'_a$, we shall discuss below, with regard to the above problems, the limits of validity and the optimal conditions for our point-charge model. We compared, in some selected cases, exactly calculated

values of Coulomb integrals with the approximate ones, making use of the different possibilities discussed above, in order to decide what parametrization procedure ensures the best agreement. We performed such a comparison for some cases where numerical tables or at least master formulas for exact calculation of the Coulomb integrals were given in the literature, namely mostly for $n_a=n_b=2$ [26] and also for a few integrals involving $n_a=n_b=3$ with the restriction $\alpha_a=\alpha_b$ [6]. The final conclusions as to the optimal procedure, emerging from the comparison between approximate and exact Coulomb integrals with $n=2$, can be made valid also for higher quantum numbers n , provided we replace, in the expressions given below for the validity limits of different approximations, α of the considered Slater orbital through $\alpha_2 = \frac{2\alpha}{n}$. This extensional method has been checked for the quantum numbers $n=2$ and 3.

We present here a concise list of the results for the most relevant cases and illustrate them by a few numerical examples; a more ample and detailed description and discussion of all calculations, whose results are epitomized below, will be given elsewhere.

RESULTS.

(a) $s_a - s_b$ Coulomb interaction.

Optimization of the point-charge approximation requires that the less expanded of the two orbital charge distributions, namely the one with smaller $\bar{r}$ (hereafter indexed b), be approximated by point charges. The distance of the point charges from the nucleus is better set equal to $\bar{r}_b$, except if $R_{ab} \gg \gg (r_{\max,a} + r_{\max,b})$, when $r_{\max,b}$ gives slightly better results. Substitution of the first term of (6) by its exact value always improves the approximation, unless one of the point charges falls too close to the nucleus a (i.e. in this case, unless $X_{2ib} = \alpha_{2a} R_{ib} \leq 1.45$ for any of the i 's), as discussed in the preceding section; if such is the case with $\bar{r}_b$ but not with $r_{\max,b}$, use of $r_{\max,b}$ and substitution of the first term of (6) gives better results than use of $\bar{r}_b$ without substitution; if substitution with the use of $\bar{r}_b$ is possible, this procedure yields the best solution. Following the above rules for optimization, the agreement between exactly and approximately calculated Coulomb integrals is better than 1%. Table I shows some characteristic examples of the above case.

(b 1) $\psi_a - s_b$ Coulomb interaction ($\psi \neq s$; radial part of s_b equally or less expanded than that of ψ_a).

In this case, s_b^2 has to be approximated by point charges. The Coulomb integral is here a sum of two terms: a monopole-monopole interaction term $(\psi_a^2 | s_b^2)$ which is again equivalent to an $s-s$ Coulomb interaction, and will therefore be calculated according to the rules given above under (a), and the interaction of the higher multipoles of ψ_a^2 with s_b^2 , for which the best results are usually obtained with $r_{\max,b}$, except when the distance from any of the

point charges to the positions of maximum density of ψ_a^2 is small; $\bar{r}_b$ is namely to be preferred in a region of α_{2b} ($R_{ab} - R_{\max,a} - R_{\max,b}$) grossly limited between -1.3 and 1.65 , the actual limits varying slightly with the type of the orbital ψ_a . Accuracy is generally better than 2% , but somewhat poorer for $\psi_a = d_\sigma$ and $\alpha_a = \alpha_b$ at short internuclear distances.

TABLE I.

ψ_a	α_a	ψ_b	α_b	R_{ab}	$(\psi_a^2 \psi_b^2)$				
					Exact	Approximate methods			
						$\bar{r}$	$\bar{r} + \text{substitution}$	$r_{\max}$	$r_{\max} + \text{substitution}$
2s	1.8	2s	2.7	4.0	.24988	.24995	<i>.24992</i>	.24995	.24994
»	1.0	»	1.5	3.5	.26697	.26938	<i>.26748</i>	.27238	.27136
»	1.0	»	1.5	2.08	.35235	<i>.35565</i>	.26543	.36914	.33236
3s	2.0	3s	2.0	4.5	.22156	.22223	<i>.22190</i>	.22220	.22204
»	1.0	»	1.0	5.0	.17981	.18178	<i>.16837</i>	.18633	<i>.17918</i>
»	4.0	»	4.0	0.5	.96371	<i>.96643</i>	1.07710	1.03194	.92048
»	2.0	»	2.0	1.6	.43832	<i>.43944</i>	.08246	.46210	— .16749
2s	1.0	2s	1.5	0.8	.41441	<i>.41894</i>	.52009	.44310	.38391

Note.—In this and the other tables, all the quantities are expressed in a.u., and the values of the integrals in best agreement with the theoretical ones are shown in italics.

(b 2) $s_a - \psi_b$ Coulomb interaction ($\psi \neq s$; radial part of ψ_b less expanded than that of s_a).

In this case, it does not appear obvious which one of the two charge distributions s_a^2 and ψ_b^2 has to be simulated through point charges since the finer subdivision of s_a^2 into fractional charges contrasts with the smaller expansion of ψ_b . If we approximate s_a^2 , we must change just a little the rules under (b1), and calculate the monopole-monopole interaction by replacing, on the contrary, the less expanded charge distribution ψ_b^2 by point charges. A survey of many numerical examples has shown that the point-charge approximation of s_a^2 gives better results if ψ_b is of p rather than d type, and if n_a, α_a are not vastly different from n_b, α_b ; on the contrary, it is more convenient to have ψ_b^2 replaced through point charges if the two principal quantum numbers and the two radial exponents are very different, and if ψ_b is of d rather than p type. In the latter case, the rules of parameter choice are slightly modified

TABLE II.

ψ_a	α_a	ψ_b	α_b	R_{ab}	$(\psi_a^2 \psi_b^2)$						
					Exact	Approximate methods					
						ψ_b^2 approximated				s_a^2 approximated	
						$\bar{r}$	$\bar{r} + \text{substitution}$	$r_{\max}$	$r_{\max} + \text{substitution}$	$\bar{r}$	$r_{\max}$
2 s	1.48	$2 p_\sigma$	1.48	5.0	.21011	.22516	.21031	.21550	.21065	.21074	.21074
»	»	$2 p_\pi$	»	»	.19445	.18947	.19451	.19306	.19451	.19442	.19442
»	1.0	$2 p_\sigma$	1.0	2.7	.30654	.34587	—1.83796	.35256	—0.05578	.30055	.31629
»	»	$2 p_\pi$	»	»	.27879	.26541	.29562	.28685	.29120	.28650	.27863
»	1.0	$2 p_\sigma$	1.5	1.9	.37215	.38628	—1.30401	.39636	—0.04788	.36690	.36949
»	»	$2 p_\pi$	»	»	.35840	.35386	.39553	.37254	.37905	.36582	.36452
»	1.0	$2 p_\sigma$	1.0	0.8	.35778	.36040	.45758	.39975	.34733	.34970	.35086
»	»	$2 p_\pi$	»	»	.35383	.34526	.42818	.38799	.38764	.35059	.35001
»	1.0	$2 p_\sigma$	1.5	2.08	.36277	.38004	—	.41473	.38758	.11980	.35613
»	»	$2 p_\pi$	»	»	.34714	.34174	.37762	.35894	.36526	.35540	.35227
»	1.8	$2 p_\sigma$	2.7	4.0	.25619	.26390	.25618	.25873	.25629	.25646	.25638
»	»	$2 p_\pi$	»	»	.24673	.24354	.24676	.24579	.24676	.24665	.24669
3 s	3.0	$3 p_\sigma$	3.0	3.5	.29979	.32114	.29993	.31098	.30009	.30028	.30021
»	»	$3 p_\pi$	»	»	.27842	.27105	.27845	.27472	.27845	.27835	.27838
»	»	$3 d_\sigma$	»	»	.29759	.30186	.29801	.29702	.29810	.29830	.29819
»	»	$3 d_\pi$	»	»	.28938	.29214	.28945	.29073	.28946	.28942	.28943
»	»	$3 d_\delta$	»	»	.27568	.27105	.27570	.27472	.27569	.27560	.27563
»	2.0	$3 p_\sigma$	2.0	1.0	.49082	.50773	.41572	.52867	.08515	.48102	.48603
»	»	$3 p_\pi$	»	»	.47737	.46813	.54490	.50545	.52366	.48431	.48180
»	»	$3 d_\sigma$	»	»	.49559	.49249	.55432	.51974	.34281	.48702	.48695
»	»	$3 d_\pi$	»	»	.48017	.49211	.54208	.52302	.47899	.47884	.48307
»	»	$3 d_\delta$	»	»	.47667	.46813	.52754	.50545	.50630	.50662	.50144
»	1.0	$3 p_\sigma$	1.0	3.4	.22567	.23902	—4.50793	.24455	—0.75806	.21968	.22693
»	»	$3 p_\pi$	»	»	.20966	.20058	.22583	.21349	.22313	.21360	.20998
»	»	$3 d_\sigma$	»	»	.22251	.22422	—2.63580	.23259	—0.33030	.25629	.21925
»	»	$3 d_\pi$	»	»	.21888	.22562	.22156	.23470	.21191	.19189	.22263
»	»	$3 d_\delta$	»	»	.20736	.20058	.21747	.21349	.21478	.22457	.21098
»	3.0	$3 p_\sigma$	3.0	2.2	.47952	.56159	.43895	.53571	.47254	.48560	.48967
»	»	$3 p_\pi$	»	»	.42209	.40130	.42510	.41341	.42499	.41949	.41745
»	»	$3 d_\sigma$	»	»	.47359	.49989	.46842	.48864	.48904	.48072	.48627
»	»	$3 d_\pi$	»	»	.45156	.46408	.45413	.46393	.45545	.45212	.45182
»	»	$3 d_\delta$	»	»	.41473	.40130	.41612	.41341	.41600	.41207	.40925

with respect to case (a), in such a way as to avoid, whenever possible, bringing any of the point charges q_{ib} too close to the positions of maximum density of s_a^2 : $\bar{r}_b$ is to be preferred to $r_{\max,b}$ whenever $R_{ab} < (r_{\max,a} + r_{\max,b})$ if ψ_b is p_σ , d_σ or d_π , or $R_{ab} < r_{\max,a}$ if ψ_b is p_π or d_δ ; furthermore, replacement of $\sum_i \frac{q_{ib}}{R_{ib}}$ through its exact value seems to have a less beneficial effect than in the $s_a - s_b$ and in the $\psi_a - s_b$ case; it really improves the approximation only if all X_{2ib} 's are relatively large (≥ 3.5 – 4.5 , depending on l and λ of ψ_b), is practically without effect for smaller X_{2ib} 's (3.5 – $4.5 \geq X_{2ib} \geq 1.5$ – 3.4) and, as in case (a), is not applicable for even smaller X_{2ib} 's. Following the above rules for optimization, the accuracy is generally better than 2%, except if $\psi_b = p_\sigma$, where the error may be somewhat larger, especially for short distances ($< \frac{1.9}{\alpha_{2b}}$) between one or two of the charges q_{ib} and the positions of maximum density of s_a^2 (error 7–8%). Table II shows some characteristic examples for the cases (b 1) and (b 2).

(c) $\psi_a - \psi_b$ *Coulomb interaction (both ψ different from s).*

Point-charge approximation will be applied to replace the less expanded of the two orbital distributions (still indexed b). The complete integral $(\psi_a^2 | \psi_b^2)$ can be separated into two terms: the interaction of the monopole of ψ_a^2 with the point charge system simulating ψ_b^2 , represented by $\sum_i q_{ib} I_0(n_a, \alpha_a, R_{ib})$, namely by the point-charge approximation of $(\psi_{as}^2 | \psi_b^2)$, to be calculated according to paragraph (b 2), and the interaction of the higher multipoles of ψ_a^2 with the point charges q_{ib} ; in the latter term $r_{\max,b}$ gives the better results, except for $-1.6 < \alpha_{2b}(R_{ab} - R_{\max,a} - R_{\max,b}) < 0$, when use of $\bar{r}_b$ instead of $r_{\max,b}$ gives slightly better accuracy. Here too, the case of $\psi_b = p_\sigma$ is unfavourable for short distances between one ($< \frac{1.9}{\alpha_{2b}}$; error 4–6%) or two ($< \frac{1.7}{\alpha_{2b}}$; error 10%) of the charges q_{ib} 's and the positions of maximum density of ψ_a^2 .

An alternative way (c 1) to evaluate $(\psi_a^2 | \psi_b^2)$ may follow from the reduction of ψ^2 to basic charge distributions [3, 26] and results in the approximate relationship:

$$(7) \quad (\psi_a^2 | \psi_b^2) \approx (\psi_a^2 | \psi_{bs}^2) + (\psi_{as}^2 | \psi_b^2) - (\psi_{as}^2 | \psi_{bs}^2)$$

where the three terms of the right-hand side can be evaluated according to (a), (b 1) and/or (b 2). If e.g. both ψ_a and ψ_b are $2p$ orbitals, the two members of eq. (7) are identical except for a term corresponding to interactions of two basic charge distributions of type $3D$, which should be added to the right-hand side, but which, by direct calculation, turns out to be negligible for $R_{ab} \left(\frac{\alpha_a + \alpha_b}{2} \right) \geq 2$; the same limit, expressed as $R_{ab} \left(\frac{\alpha_{2a} + \alpha_{2b}}{2} \right) \geq 2$, was found to hold for orbitals of higher n . This method is particularly useful in case of proximity of one (always $R_{ab} \left(\frac{\alpha_{2a} + \alpha_{2b}}{2} \right) > 2$) or two of the point charges q_{ib}

TABLE III.

ψ_a	α_a	ψ_b	α_b	R_{ab}	$(\psi_a^2 \psi_b^2)$			
					Exact	Approximate methods		
						$\bar{r}$	$r_{\max}$	formula (7)
$2p_\sigma$	1.0	$2p_\sigma$	1.5	0.8	.44184	.48670	.47636	.42623
$2p_\sigma$	»	$2p_\pi$	»	»	.41351	.39951	.41031	.42492
$2p_\pi$	»	$2p_\sigma$	»	»	.40298	.38300	.38817	.41323
$2p_\pi$	»	$2p_\pi$	»	»	.43346	.48563	.47419	.41193
$2p_\sigma$	1.0	$2p_\sigma$	1.5	3.5	.31794	.34156	.34137	.31315
$2p_\sigma$	»	$2p_\pi$	»	»	.29242	.28841	.29445	.29754
$2p_\pi$	»	$2p_\sigma$	»	»	.26149	.25716	.25726	.25880
$2p_\pi$	»	$2p_\pi$	»	»	.24729	.24937	.24484	.24319
$2p_\sigma$	1.8	$2p_\sigma$	4.2	3.0	.37295	.37780	.37563	.37316
$2p_\sigma$	»	$2p_\pi$	»	»	.36021	.35867	.35987	.36128
$2p_\pi$	»	$2p_\sigma$	»	»	.32060	.31939	.32047	.32422
$2p_\pi$	»	$2p_\pi$	»	»	.31446	.31531	.31141	.31235
$3d_\delta$	4.0	$3d_\pi$	4.0	4.0	.24774	.24765	.24770	.24787
$3d_\delta$	»	$3d_\sigma$	»	»	.24997	.24984	.25001	.25039
$3p'_\pi$	»	$3d_\pi$	»	»	.24881	.24870	.24877	.24898
$3p_\sigma$	»	$3d_\delta$	»	»	.25112	.25089	.25107	.25161
$3p_\pi$	»	$3d_\delta$	»	»	.24366	.24377	.24368	.24341
$3d_\delta$	2.0	$3d_\pi$	2.0	3.1	.29736	.29523	.29098	.29815
$3d_\delta$	»	$3d_\sigma$	»	»	.30860	.30808	.30780	.31637
$3p'_\pi$	»	$3d_\pi$	»	»	.29800	.28990	.29037	.30694
$3p_\sigma$	»	$3d_\delta$	»	»	.31319	.30929	.31377	.32096
$3p_\pi$	»	$3d_\delta$	»	»	.27917	.28024	.27799	.28045
$3d_\delta$	3.0	$3d_\pi$	3.0	0.7	.71685	.76222	.75311	.68980
$3d_\delta$	»	$3d_\sigma$	»	»	.70252	.69563	.69938	.71036
$3p'_\pi$	»	$3d_\pi$	»	»	.68616	.63737	.63547	.71144
$3p_\sigma$	»	$3d_\delta$	»	»	.71295	.67960	.69455	.70124
$3p_\pi$	»	$3d_\delta$	»	»	.70747	.70382	.69635	.69301

to the positions of maximum density of ψ_a^2 , since it does not give even under the unfavourable condition errors larger than 5-6 %, whereas both the methods (c) and (c 1), in their respective favourable cases, give results of comparable accuracy (better than 2 %). Table III shows some examples of cases (c) and (c 1).

CONCLUDING REMARKS

The approximation here proposed gives results of fairly uniform quality in all investigated cases; the attained accuracy becomes poor ($\geq 5\%$) only for very low values of X_{ib} , i.e. for unusually short internuclear distances or for unusually expanded orbital charge distributions. In most cases of practical interest, namely for valence orbitals and for distances close to or larger than the usual order of magnitude of bond distances, the agreement between exactly and approximately calculated values of two-center Coulomb integrals is never worse than 1 %, the higher limit occurring with p orbitals; from some cases where comparison with exactly calculated values could be made for both quantum numbers $n = 2$ and 3, we observed that the accuracy, at equal α_2 values, is even slightly better for the higher n , and we therefore reached the conclusion that the proposed extension to higher quantum numbers n of validity limits, actually checked for $n = 2$, can be regarded as entirely feasible. We thus confidently assume that our model can give results accurate within $\pm 1\%$ for any principal quantum number in most cases of practical interest.

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