

APPROXIMATE FORMULAS FOR MANY-CENTER INTEGRALS
IN THE THEORY OF MOLECULES AND CRYSTALS[†]

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FUNDAMENTAL PROBLEM in the theory of molecules and crystals is the evaluation of
atomic many-center integrals of the type

$$(ab|cd) = \iint \psi_a(1)\psi_b(1)[e^2/r_{12}]\psi_c(2)\psi_d(2)d\tau_1d\tau_2, \quad (1)$$

where the ψ -functions are normalized atomic orbitals associated with the nuclei a, b, c, and d, which in special cases also may coincide. Useful approximate formulas for these integrals have been given intuitively by Sklar¹ and by Mulliken², who have expressed them in terms of overlap integrals³

$$\Delta_{ab} = \int \psi_a\psi_b d\tau = \delta_{ab} + S_{ab} \quad (2)$$

and two-center integrals of the Coulomb type. Recently Ruedenberg⁴ has shown rigorously that the Mulliken formula may be considered as being the first term in an infinite expansion of (1).

At the Shelter Island Conference, 1951, J. E. Mayer pointed out that charge densities (expressed in atomic units with $e = 1$) of the form $\psi_a\psi_b - \Delta_{ab}\psi_a^2$ do not give

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¹A. L. Sklar, J. Chem. Phys. **7**, 984 (1939); A. London, J. Chem. Phys. **13**, 396 (1945).

²R. S. Mulliken, J. chim. phys. **46**, 497, 675 (1949), see particularly Eqs. (63) and (154b).

³Note the different meanings of the symbol S in papers by different authors; we have always used this notation for the deviation from normality and orthogonality for a set of functions, and, for $a = b$, we have therefore $S_{aa} = 0$.

⁴K. Ruedenberg, J. Chem. Phys. **19**, 1433 (1951).

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MANY-CENTER INTEGRALS

any contribution to the total charge and that these "quasi-dipoles" may be used in the interpretation of the energy expression⁵. The purpose of this note is to show that it is possible to use quantities of a similar type for deriving a generalization of the Sklar-Mulliken formulas.

For the sake of simplicity, let us assume that the charge distribution $\psi_a\psi_b$ has a "center of gravity" T, which is situated on the line connecting the nuclei a and b with respective distances α and β from them, and that similarly $\psi_c\psi_d$ has a center T' on the line connecting c and d with the distances γ and δ from them. We will then determine the coefficients in the expression $\lambda_a\psi_a^2 + \lambda_b\psi_b^2$ from the condition that this quantity should have the same total charge and total moment as the density $\psi_a\psi_b$, which gives

$$\lambda_a = \Delta_{ab}(1+\alpha/\beta)^{-1}, \quad \lambda_b = \Delta_{ba}(1+\beta/\alpha)^{-1} \quad (3)$$

with $\Delta_{ab} = \Delta_{ba}$. In comparison to Mayer's idea this means that we are here considering a quantity $\psi_a\psi_b - \lambda_a\psi_a^2 - \lambda_b\psi_b^2$ which does not contribute to the total charge, nor to the total moment. Neglecting the influence of higher moments, we obtain the approximate formula

$$\psi_a\psi_b \approx \lambda_a\psi_a^2 + \lambda_b\psi_b^2, \quad (4)$$

and similarly

$$\psi_c\psi_d \approx \lambda_c\psi_c^2 + \lambda_d\psi_d^2. \quad (5)$$

Substituting these expressions into (1), we get finally

$$(ab|cd) = \lambda_a\lambda_c(aa|cc) + \lambda_a\lambda_d(aa|dd) + \lambda_b\lambda_c(bb|cc) + \lambda_b\lambda_d(bb|dd). \quad (6)$$

Hence it is possible to evaluate the many-center integral (1) approximately in terms of the overlap integrals Δ_{ab} and Δ_{cd} , the quotients α/β and γ/δ , and the Coulomb integrals.

For symmetrical charge distributions with $\alpha = \beta$ and $\gamma = \delta$ the right-hand side of (6) will reduce to the Mulliken formula. However, in the case of unsymmetrical charge distributions, as for instance in ionic crystals, formula (6) seems to be an essential improvement of the previous one, and, in such a case, it probably also indicates a

⁵See also G. L. Montet, S. P. Keller, and J. E. Mayer, J. Chem. Phys. **20**, 1057 (1952), and Keller's and Montet's Ph. D. Theses (The University of Chicago).

method of improving the convergence of the Ruedenberg procedure by using unsymmetrical multiplication factors.

In order to derive the Sklar formula, we observe that the quantities $\Delta_{ab}\psi_T^2$ and $\Delta_{cd}\psi_{T'}^2$ have the same total charge and the same total moment as the given distributions $\psi_a\psi_b$ and $\psi_c\psi_d$, respectively. Neglecting higher moments, we get therefore

$$\psi_a\psi_b \approx \Delta_{ab}\psi_T^2, \quad \psi_c\psi_d \approx \Delta_{cd}\psi_{T'}^2. \quad (7)$$

Here ψ_T and $\psi_{T'}$ are atomic orbitals associated with the centers of gravity T and T', respectively, which have to be chosen in a suitable way¹. Substitution of (6) into (1) gives then the approximate formula

$$(ab|cd) = \Delta_{ab}\Delta_{cd}(TT|T'T'), \quad (8)$$

which is essentially the Sklar formula. By combining the forms of (4) and (7), a still better result may sometimes be obtained by using a three-parameter formula and a third condition related to one of the higher moments.

The effect of the higher moments in general and the correction terms in (6) and (8) may be found by comparing these formulas with the exact expressions derived in another way⁶. However, a direct comparison with the numerical values of the integral (1) in special cases previously obtained by us⁷ for some alkali and alkali metals and with Lundqvist's⁸ material for LiH shows that formulas (6) and (8) in most cases have a surprisingly high accuracy, but also that there exist exceptional integrals of certain degenerate types which are better treated by more direct methods.

Formulas (6) and (8) are intended for use, e.g., in the MO-LCAO method based on ordinary atomic orbitals (AO). If the molecular orbitals instead are built up from orthonormalized AO⁹, the use of (4) and (5) for the ordinary AO will lead to results which are related to those recently intuitively given by Parr¹⁰.

⁶S. O. Lundqvist and P.-O. Löwdin, Arkiv Fysik **3**, 147 (1951).

⁷See P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950), **19**, 1579 (1951) and references in these papers.

⁸S. O. Lundqvist, private communication.

⁹P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

¹⁰R. G. Parr, J. Chem. Phys. **20**, 1499 (1952).

MANY-CENTER INTEGRALS

Finally, we wish to remark that the author's expressions¹¹ for the total and cohesive energies for the ground state of a molecule or crystal having its total wave function approximated by a single determinant may be essentially simplified by using formula (6) and by summing the contributions from all matrix elements constituting the coefficients of the remaining Coulomb integrals; in this process it is even possible to treat the degenerate integrals separately. More details will be given in a survey of the various methods of evaluating many-center integrals to be published elsewhere.

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¹¹P.-O. Lowdin, J. Chem. Phys. **19**, 1570 (1951), Eqs. (33) and (51).