

Approximate Formulas for Many-Center Integrals in the Theory of Molecules and Crystals

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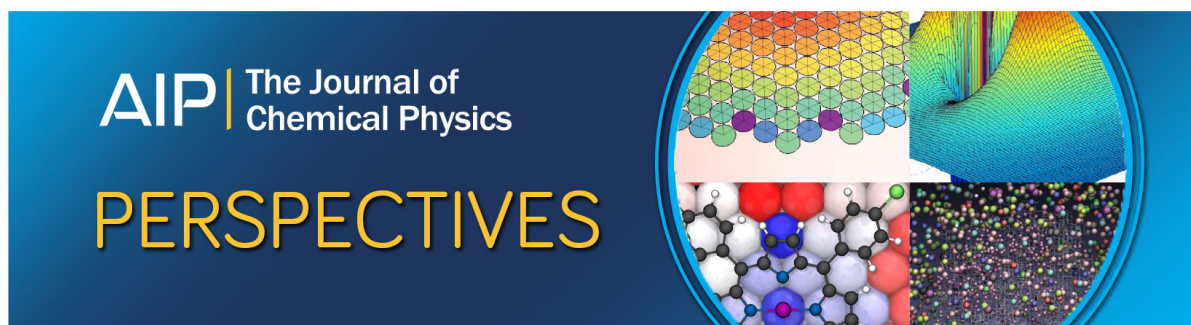
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During the course of our studies in flame spectroscopy we have independently obtained the following formula for the matrix element $\langle v'|u|v''\rangle$ using Morse wave functions:

$$\langle v'|u|v''\rangle = -[a(v'-v'')(k-v'-v''-1)]^{-1} \times \left\{ \frac{v'!(k-2v'-1)(k-2v''-1)}{v''! \prod_{t=0}^{v'-v''-1} (k-v'+t)} \right\}^{\frac{1}{2}} \quad (1)$$

where $ax_e = (\omega_e x_e/B_e)^{\frac{1}{2}}$ and $k=1/x_e$. By use of these expressions for a and k , one can rewrite Eq. (1) as

$$\langle v'|u|v''\rangle = -\frac{r_e(B_e/\omega_e)^{\frac{1}{2}} x_e^{(v'-v''-1)/2}}{(v'-v'')[1-(v'+v''+1)x_e]} \times \left\{ \frac{v'![1-(2v'+1)x_e][1-(2v''+1)x_e]}{v''! \prod_{t=0}^{v'-v''-1} [1-(v'-t)x_e]} \right\}^{\frac{1}{2}} \quad (2)$$

This somewhat more compact result is equivalent to that obtained by Heaps and Herzberg.⁴

In the approximation $(v'+v'')x_e \ll 1$, Eq. (2) yields for the square of the matrix element with $v'=v''+n$,

$$|\langle v''|u|v''+n\rangle|^2 \cong \frac{r_e^2 B_e x_e^{n-1} (v''+n)!}{\omega_e n^2 v''!} (1+v''x_e), \quad (3)$$

or

$$|\langle v''|u|v''+n\rangle|^2 \cong |0|u|n\rangle|^2 \frac{(v''+n)!}{n! v''!} (1+v''x_e). \quad (4)$$

The last equation generalizes the restricted result for $n=1, 2$, and 3 obtained by Crawford and Dinsmore³ using perturbation methods. It is interesting to note that within the above approximation both Morse and perturbed harmonic oscillator wave functions yield the same result.

As pointed out by Heaps and Herzberg, the use of Morse wave functions both with linear and higher terms in the dipole moment expansion does not give particularly accurate intensity formulas. The authors are therefore extending the perturbation treatments of Dunham and of Crawford and Dinsmore to include second-order corrections throughout.

* Supported by the U. S. Navy, Bureau of Ordnance.

¹ J. L. Dunham, Phys. Rev. **35**, 1347 (1930).

² J. E. Rosenthal, Proc. Natl. Acad. Sci. **21**, 281 (1935).

³ B. L. Crawford and H. L. Dinsmore, J. Chem. Phys. **18**, 983 (1950).

⁴ H. S. Heaps and G. Herzberg, Z. Physik **133**, 48 (1952).

Approximate Formulas for Many-Center Integrals in the Theory of Molecules and Crystals*

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(Received November 25, 1952)

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

$$\langle ab|cd\rangle = \int \int \psi_a(1)\psi_b(1)\{\epsilon^2|r_{12}\}\psi_c(2)\psi_d(2)d\tau_1d\tau_2, \quad (1)$$

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 Mulliken,² 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, Rüdberg⁴ 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 in 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 any contribution to the total charge and that these "quasi dipoles" may be used in the interpretation of the energy expression.⁵ 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 $\psi_{ab} - \lambda_a\psi_a^2 - \lambda_b\psi_b^2$, 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

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

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, Eq. (6) seems to be an essential improvement of the previous one, and, in such a case, it probably also indicates a method of improving the convergence of the Rüdberg 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 therefore get

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

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 way.¹ Substitution of (6) into (1) gives then the approximate formula

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

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 way.⁶ 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.

Equations (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 AO,⁹ the use of (4) and (5) for the ordinary AO will lead to results which are related to those recently intuitively given by Parr.¹⁰

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 Eq. (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.

I would like to express my sincere gratitude to Professor R. S. Mulliken for many valuable discussions and for his great hospitality during my stay in Chicago.

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

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

¶ Note 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 $S_{aa}=0$.

‡ K. Rüdénberg, *J. Chem. Phys.* **19**, 1433 (1951).

§ See also Montet, Keller, and Mayer, *J. Chem. Phys.* **20**, 1057 (1952), and Keller's and Montet's Ph.D. theses, University of Chicago.

¶ S. O. Löwdin and P. O. Löwdin, *Arkiv Fysik* **3**, 147 (1951).

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

§ S. O. Löwdin, private communication.

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

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

§ P. O. Löwdin, *J. Chem. Phys.* **19**, 1570 (1951), Eqs. (33) and (51).

Hydrogen Peroxide Formation by Cobalt Gamma-Radiation

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HYDROGEN peroxide formation in water irradiated with Co^{60} gamma-rays is shown in Fig. 1. The concentration in air-saturated pure water rises to a steady state measured after 16 hours of 143 $\mu\text{M}/\text{liter}$. The concentration in air-saturated 0.8*N* sulfuric acid, however, increases linearly with dose during the first hour and a concentration of 2840 $\mu\text{M}/\text{liter}$ was measured after 17 hours. This acid effect is in agreement with the experiments of

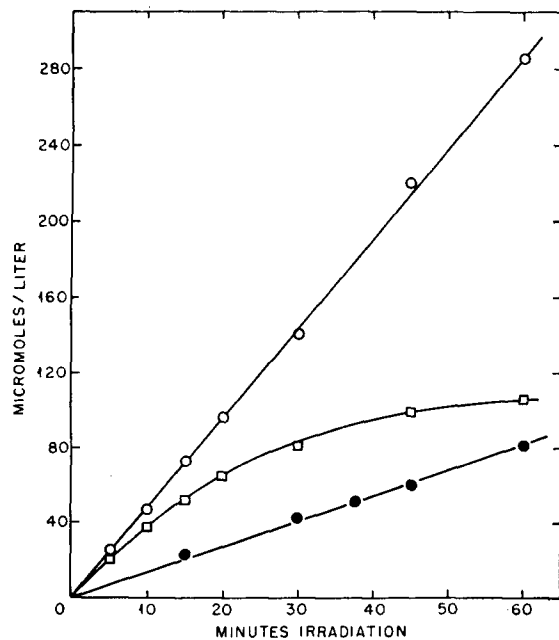


FIG. 1. Hydrogen peroxide formation by cobalt gamma-radiation: ○ air-saturated 0.8*N* H_2SO_4 ; □ air-saturated pure water; ● helium-saturated 0.8*N* H_2SO_4 .

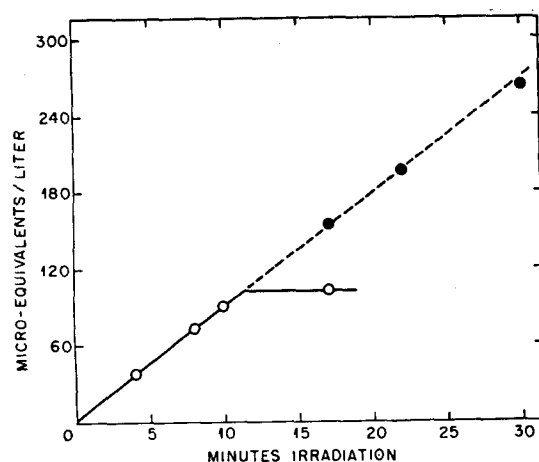


FIG. 2. Ceric sulfate reduction and hydrogen peroxide formation in air-saturated 0.8*N* H_2SO_4 by cobalt gamma-radiation: ○ cerous sulfate; ● hydrogen peroxide following complete ceric sulfate reduction.

Ebert and Boag.¹ Hydrogen peroxide formation in helium-saturated 0.8*N* sulfuric acid, interpreted as the molecular yield, indicates the solution contains a radical remover. Since no measurable amount of hydrogen peroxide is observed in helium-saturated pure water, the radical remover may be the acid or an impurity contained in the acid (Baker and Adamson reagent grade). The presence of a radical remover may explain the linearity of hydrogen peroxide formation in air-saturated 0.8*N* sulfuric acid.

The rate of hydrogen peroxide formation following complete ceric sulfate reduction is the same as that in air-saturated 0.8*N* sulfuric acid and is stoichiometrically equivalent to the rate of ceric sulfate reduction as shown in Fig. 2. This is in disagreement with the observations of Clark and Coe.² A similar stoichiometry has been reported between the reduction of chromate solutions and the formation of hydrogen peroxide in 0.8*N* sulfuric acid by x-rays.³ The stoichiometry indicates that ceric sulfate reduction in solutions containing oxygen may take place through the intermediate formation of hydrogen peroxide and not by reaction

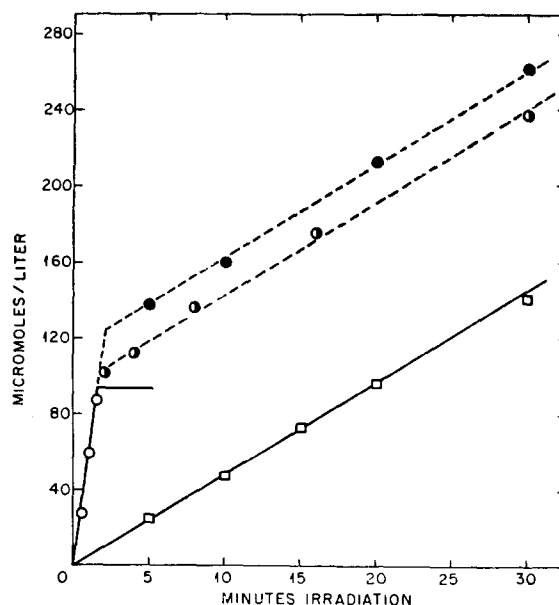


FIG. 3. Ferrous sulfate oxidation and hydrogen peroxide formation in air-saturated 0.8*N* H_2SO_4 by cobalt gamma-radiation: □ hydrogen peroxide formation in air-saturated 0.8*N* H_2SO_4 ; ○ ferric sulfate and ● hydrogen peroxide following complete ferrous sulfate oxidation, sample No. 1; ● hydrogen peroxide, sample No. 2.