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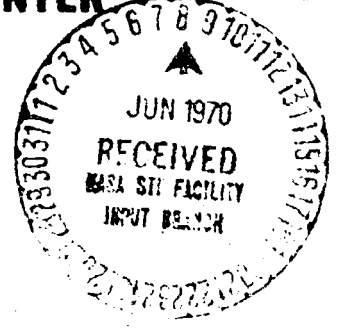

THE MARGENAU APPROXIMATIONS TO THREE- AND FOUR-CENTER MOLECULAR INTEGRALS

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THE MARGENAU APPROXIMATIONS TO THREE- AND FOUR-CENTER MOLECULAR INTEGRALS*†

by

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ABSTRACT

Because of the complexity of most three- and four-center integrals that arise in the variational treatment of molecular structure, approximations have been useful in their evaluation. The Margenau approximations are intended to have good accuracy when the distance, R, between the charge distributions involved in the integrals is large compared to the spatial size of the distributions. Comparisons of values given by these approximations with accurate values of some relatively simple three- and four-center integrals confirm this fact. Comparisons with the Sklar and Mulliken approximations indicate that Margenau's second approximation is more accurate than those latter approximations in nearly all cases similar to those considered here when R is at least about five times the radial size of the atomic orbitals upon which the molecular wave functions are based. The form of the multipole expansion for the integrals may be used to predict and interpret the relative accuracies of the approximations in terms of the inclusion or neglect of the effects of higher multipoles and overlaping of the charge distributions. A proposed combination of Margenau's two approximations is found to be superior to both in most cases.

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I. INTRODUCTION

In spite of the large amount of work that has been done on the evaluation of the three- and four-center integrals that occur in the variational treatment of molecular structure, many of these integrals remain a problem because of their great complexity. Except in a few cases the exact forms which have been found for some of the integrals involve infinite series and other expressions or procedures difficult to use.[1] Although computers have been successfully employed in the numerical evaluation of some of the integrals[2-4], the results often provide only limited insight into the nature of the integrals.

Several approximations for the three- and four-center molecular integrals have been proposed and have been used with apparent success.[5-17] Consideration is given here to two approximations proposed by Margenau[5] which are not specifically well known, but which have yielded good results for the H-H_2 and H_2-H_2 intermolecular potential energies.[5-7]

Direct determinations of the accuracy of these approximations by comparisons of accurate and approximate values are presented here for a number of relatively simple three- and four-center molecular integrals involving certain specific nuclear configurations. In addition, their accuracies are compared with the accuracies of the Sklar[8] and Mulliken[9] approximations. The results are capable of being predicted and interpreted in terms of the degree of neglect or overemphasis of the effects of overlap and higher multipoles of the charge distributions involved.

II. THE THREE- AND FOUR-CENTER MOLECULAR INTEGRALS EMPLOYED

The integrals for which comparisons between accurate and approximate values are given in Sec. VI are instances of the three- and four-center coulomb exchange integrals,

$$I(a\alpha, b\beta; c\delta, d\delta) = \iint \psi_{a\alpha}(\vec{r}_1)\psi_{b\beta}(\vec{r}_1)\frac{e^2}{r_{12}}\psi_{c\gamma}(\vec{r}_2)\psi_{d\delta}(\vec{r}_2)\, d\tau_1\, d\tau_2 \ , \qquad (1)$$

where $\psi_{a\alpha}$, $\psi_{b\beta}$, $\psi_{c\gamma}$, $\psi_{d\delta}$ are normalized real atomic wave functions whose forms are designated by α, β, γ, δ and which are centered on nuclei at positions a, b, c, d; $\vec{r}_1$ and $\vec{r}_2$ are general designations of the coordinates of electrons 1 and 2; and r_{12} is the interelectron distance.

Figure 1 shows the various nuclear centers, distances, angles, line segments, and points involved in the discussions of this and following sections.

Each integral given by Eq. (1) is equivalent to the electrostatic potential energy between two distributions of charge, $e\psi_{a\alpha}(\vec{r}_1)\,\psi_{b\beta}(\vec{r}_1)$ and $e\psi_{c\gamma}(\vec{r}_2)\,\psi_{d\gamma}(\vec{r}_2)$. The integrals are four-center integrals when the four nuclear centers a, b, c, d are distinct, three-center integrals when two of the centers coincide. In the latter case the resulting integrals are the absolute values of the negative nuclear attraction integrals if the charge distribution about the coinciding centers (taken here to be c and d) is a delta function of charge e. Hence, Eq. (1) may be considered to include the nuclear attraction integrals that are likewise considered in Sec. VI.

The integrals given by Eq. (1) are the only integrals involving more than two centers which arise in the variational treatment of molecular structure, provided the wave function for the molecular electrons is taken to be a linear combination of products of atomic electron wave functions (LCAO method).

The integrals considered here result from Eq. (1) when $\psi_{a\alpha}(\vec{r}_1)$ and $\psi_{b\beta}(\vec{r}_1)$ are each taken to be the ground state hydrogen wave functions for unit nuclear charge, $(\pi a_o^3)^{-\frac{1}{2}} e^{-r_{1a}/a_o}$ and $(\pi a_o^3)^{-\frac{1}{2}} e^{-r_{2b}/a_o}$, while $\psi_{c\gamma}(\vec{r}_2)$ and $\psi_{d\gamma}(\vec{r}_2)$ are either taken to be of the same form, or the charge distribution $e\,\psi_{d\gamma}(\vec{r}_2)\,\psi_{c\delta}(\vec{r}_2)$ is a delta function of charge e. Each of the resulting integrals then depends only on the positions of the centers a, b, c, d.

The approximations and accurate values are compared for two types of sequences of positions of the centers. In the first type, the distance, R, between $\overline{ab}$ and $\overline{cd}$, which are the midpoints of line segments ab and cd, is varied while the lengths, R_{ab} and R_{cd}, of line segments ab and cd are fixed. In the second type of sequence the ratios R_{ab}/R and R_{cd}/R are fixed while R varies. The sequences include the limits $R \to 0$ and $R \to \infty$.

In the first type of sequence and in the limit $R \to 0$ some three- and four-center integrals remain difficult to evaluate, whereas others, like those employed in Sec. VI, reduce to simpler forms which may be calculated. In the limit $R \to \infty$ all integrals represented by Eq. (1) approach $Q_1 Q_2/R$ in this sequence. The quantities Q_1 and Q_2 are the total charges of the distributions of electrons 1 and 2. In the second type of sequence and in the limit $R \to 0$ all integrals giver by Eq. (1) become single center integrals, the values of which are known or may be computed. For $R \to \infty$ in this sequence the limiting forms of the integrals are not always easy to evaluate. In this limit most, if not all, integrals for which lines ab and cd overlap for a portion of their lengths have a form, const. x $Q_1 Q_2 \ln R/R$, whereas most, if not all, of the other integrals reduce to const. x $Q_1 Q_2/R$.

III. A MEANS FOR INTERPRETING THE ACCURACIES

The bipolar multipole expansion of the integrals given by Eq. (1) may be used in the qualitative consideration of the nature and accuracies of the Margenau approximations as well as in comparing them with the Sklar and Mulliken approximations. The centers for the bipolar expansion are chosen to be $\bar{a}\bar{b}$ and $\bar{c}\bar{d}$, since these points are the geometric centers of the charge distributions involved in the integrals considered here. The bipolar multipole expansion may be obtained by expanding the integrals in spherical harmonics of the polar angles θ_1 and θ_2 between lines ab and cd and the line $\bar{a}\bar{b}\bar{c}\bar{d}$, and the azimuthal angles ϕ_1 and ϕ_2 of lines ab and cd around line $\bar{a}\bar{b}\bar{c}\bar{d}$. The result as applied to Eq. (1) may be written in the form,

$$I(a\alpha,b\beta;c\gamma,d\delta) = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m=>-l_1,-l_2}^{<l_1,l_2} f_{l_1,l_2|m|}^{(\alpha,\beta;\gamma,\delta)}(R, R_{ab}, R_{cd}) \cdot \cdot P_{l_1}^{|m|}(\cos\theta_1)\, P_{l_2}^{|m|}(\cos\theta_2)\, \cos m(\phi_1 - \phi_2) \,, \tag{2}$$

where the $P_l^{|m|}$ are associated Legendre polynomials, while the symbols > and < denote 'the greater of' and 'the lesser of' respectively. In the type of multipole expansion represented by Eq. (2) the implicit multipole moments are functions of R in addition to R_{ab} and R_{cd} and the expansion is exact for all values of R, R_{ab} and R_{cd}.

A term in the expansion, (2), when the sum over m has been carried out, is the contribution to I from the potential energy between the l_1^{th} multipole of the charge distribution of electron 1 and the l_2^{th} multipole of the charge distribution of electron 2. Because of the overlap of the charge distributions, which have non-zero extent, the f's have no simple dependence upon R, R_{ab}, and R_{cd}, except in the limits $R \to 0$ and $R \to \infty$. When I represents a nuclear attraction integral, only terms with $l_2 = 0$ occur in the expansion.

In the form given by Eq. (2) the evaluation of an integral consists of determining the $f^{(\alpha,\beta;\gamma,\delta)}_{\ell_1\ell_2\ |m|}$. Hence, the accuracy of an approximation for an integral may be evaluated in terms of the accuracy with which it approximates the $f^{(\alpha,\beta;\gamma,\delta)}_{\ell_1\ell_2\ |m|}$. Therefore, predictions and evaluations of the accuracies of the Margenau approximations and the accuracies of the Sklar and Mulliken approximations, to which they are compared, will be carried out by considering: (1) the degree and manner in which the approximations include each f (and hence the degree to which the various multipole interactions are included) and (2) the degree to which each f includes the effects of the overlap of the charge distributions.

IV. THE MARGENAU APPROXIMATIONS

The Margenau approximations[5] were employed on intuitive grounds in cases where the ratios R/a_o, R/R_{ab}, and R/R_{cd} are large. They were used to estimate and calculate values for the three- and four-center integrals which occurred in a determination of the $H\text{-}H_2$ and $H_2\text{-}H_2$ intermolecular potential energies at intermediate and long range distances.[5-7] The results are in good agreement with calculations by Mason and Hirschfelder for the same intermolecular potential energies at short and intermediate range distances.[10]

The Margenau approximations are apparently the original members of a class of approximations called the "point charge approximation."[11] These approximations involve the replacement of the charge distributions in the integrals by point charges. Different forms of the approximations involve differences in the number of point charges per charge distribution, differences in the positioning of the point charges, and whether one or both charge distributions are so replaced. In all cases a distribution is replaced by point charges with the same total charge. Under the condition that a distribution is replaced by a single charge, the Margenau approximations are probably the most accurate of the point charge approximations that could be generally applied to the types of integrals considered in Sec. IV.

In the first and extremely simple approximation, M_1, Margenau replaced both charge distributions in Eq. (1) by point charges at the geometric centers of the distributions. Each of the charges has a value equal to the total charge of the distribution replaced. For the integrals considered in Sec. VI the geometric centers are the points $\bar{ab}$ and $\bar{cd}$. In M_1, therefore,

$$I(a\alpha, b\beta; c\gamma, d\delta) = Q_1 Q_2 / R \quad , \tag{3}$$

where the total charges Q_1 and Q_2 of the two distributions of charge are equivalent to e times the overlap integrals, Δ_1 and Δ_2, given by

$$\Delta_1 = \int \psi_{a\alpha}(\vec{r}_1)\, \psi_{b\beta}(\vec{r}_1)\, d\tau_1 \quad \text{and} \quad \Delta_2 = \int \psi_{c\gamma}(\vec{r}_2)\, \psi_{d\delta}(\vec{r}_2)\, d\tau_2 \ . \tag{4}$$

Equation (3) results from Eq. (2) when only the $\ell_1 = \ell_2 = 0$ term is taken and f_{000} is approximated by its value in the limit R/a_0, R/R_{ab}, $R/R_{cd} \to \infty$. Thus, M_1 includes only the monopole-molopole term of an integral and neglects the effects of overlap entirely. M_1 will therefore be accurate when R/a_0, R/R_{ab}, and R/R_{cd} are simultaneously large but will be inaccurate when R/a_0 is small irrespective of the values of R_{ab} and R_{cd}. When $R/a_0 \to 0$ and either R_{ab} and R_{cd}, or R/R_{ab} and R/R_{cd} are fixed, the M_1 approximations to the integrals diverge, whereas the integrals themselves do not.

In the limit $R/a_0 \to \infty$ with R/R_{ab} and R/R_{cd} fixed, M_1 does not in general yield a value for an integral that approaches the exact value of that integral. In this limit an integral as approximated by M_1 will be proportional to the exact result in the case in which the integral is one whose exact value approaches const. x Q_1Q_2/R, but an integral as approximated by M_1 will tend to zero relative to the exact result in the other case in which the exact result approaches const. x $Q_1Q_2\, \ln R/R$.

In Margenau's second approximation, M_2, the charge distribution of electron 1 alone is replaced by an equal point charge at the geometric center of the charge distribution, and the integration over the coordinates of electron 2 in Eq. (1) is then carried out. This process is repeated with the charge distribution of electron 2 alone being similarly replaced, and the mean of the two results is taken. Thus, in M_2

$$I(a\alpha,b\beta;c\gamma,d\delta) = \tfrac{1}{2}\left(\Delta_1 \int \frac{e^2}{r_2'} \psi_{c\gamma}(\vec{r}_2)\,\psi_{d\delta}(\vec{r}_2)\,d\tau_2 + \Delta_2 \int \frac{e^2}{r_1'} \psi_{a\alpha}(\vec{r}_1)\,\psi_{b\beta}(\vec{r}_1)\,d\tau_1\right), \qquad (5)$$

where r_2' is the distance from electron 2 to the geometric center of the charge distribution of electron 1 and r_1' is analogously defined. Use of M_2 therefore reduces the determination of a three- or four-center integral involving two charge distributions of non-zero extent to the determination of two three-center integrals that are equivalent to nuclear attraction integrals. For the cases considered in Sec. VI these three-center integrals are known in relatively simple, closed form.

Equation (5) results from Eq. (2) in the following way. In Eq. (2) only $\ell_1 = 0$ terms are taken and each $f_{0\ell_2 0}$ is given the form it would have if the charge distribution of electron 1 were a point charge with a charge Q_1. This process is repeated, taking only the $\ell_2 = 0$ terms, and the mean of the two results is taken. If the terms in the final result are then put in the form of Eq. (2), the resulting f_{000} is exact in the limit R/a_0, R/R_{ab}, $R/R_{cd} \to \infty$, and the resulting $f_{\ell_1 00}$ and $f_{0\ell_2 0}$ for ℓ_1, $\ell_2 \geq 1$ possess one-half of their exact values in this limit. Since only one charge distribution at a time is replaced by a point charge in M_2, each of the f's includes the effects of overlap to a certain degree. Thus, M_2 takes account of the monopole-monopole term and a partial account of the monopole-higher multipole terms but neglects the higher multipole-higher multipole terms, and for each of the included terms, M_2 makes a partial allowance for the effects of overlap. M_2 is therefore expected to be accurate for simultaneously large values of R/a_0, R/R_{ab}, and R/R_{cd}, but inaccurate for small R/a_0, as was the case

with M_1. For most instances of the integrals, however, M_2 will give more accurate values than M_1 because M_2 includes part of the effects of higher multipoles and overlap whereas M_1 does not.

In general, M_2 like M_1 does not yield exact values for the integrals in the limit $R/a_o \to \infty$ with R/R_{ab} and R/R_{cd} fixed. However, in most, if not all cases in this limit M_2 gives expressions for the three- and four-center integrals that are proportional to the exact expressions, const. x $Q_1 Q_2/R$ or const. x $Q_1 Q_2$ ln R/R.

V. THE SKLAR AND MULLIKEN APPROXIMATIONS, COMPARISONS TO M_1 AND M_2

The accuracies of the Margenau approximations are compared in Sec. VI to the accuracies of the Sklar[8] and Mulliken[9] approximations. The latter are chosen for this purpose, in spite of the fact that more accurate approximations exist,[12] because they yield relatively simple formulae for the integrals and because they have been the most extensively employed.

In the Sklar approximation, S, as applied to the cases of Sec. VI, the charge distributions in Eq. (1), $e\,\psi_{a\alpha}(\vec{r}_1)\,\psi_{b\beta}(\vec{r}_1)$ and $e\,\psi_{c\gamma}(\vec{r}_2)\,\psi_{d\delta}(\vec{r}_2)$, are replaced by charge distributions of equal total charge, $e\,\Delta_{ab}\,\psi_{\overline{ab}\alpha}(\vec{r}_1)\cdot\psi_{\overline{ab}\beta}(\vec{r}_1)$ and $e\,\Delta_{cd}\,\psi_{\overline{cd}\gamma}(\vec{r}_2)\,\psi_{\overline{cd}\delta}(\vec{r}_2)$. The resulting charge distributions are centered at the points $\overline{ab}$ and $\overline{cd}$. Hence, S reduces three- and four-center integrals to two center integrals. In S,

$$I(a\alpha,b\beta;c\gamma,d\delta) = \Delta_{ab}\,\Delta_{cd}\iint \psi_{\overline{ab}\alpha}(\vec{r}_1)\,\psi_{\overline{ab}\beta}(\vec{r}_1)\,\frac{e^2}{r_{12}}\,\psi_{\overline{cd}\gamma}(\vec{r}_2)\,\psi_{\overline{cd}\delta}(\vec{r}_2)\,d\tau_1\,d\tau_2 . \quad (6)$$

The Sklar approximation results from Eq. (2) when only the $\ell_1 = \ell_2 = 0$ term is retained and a particular approximate form for f_{000} is employed. The approximate form of f_{000} is exact in the limit R/a_c, R/R_{ab}, $R/R_{cd} \to \infty$, and includes the effects of overlap. S is therefore similar to M_1 in that it includes only the monopole-monopole term of an integral but is superior to M_1, in particular for small R/a_c, in that it includes the effects of overlap. M_2 is superior to S in that it takes partial account of the higher multipole terms but is inferior in that it takes less account of overlap. It is therefore expected that S will be more accurate than M_2 for small R/a_c, but M_2 is expected to be more accurate than S for simultaneously large values of R/a_c, R/R_{ab}, and R/R_{cd}.

In the limit $R/a_o \to \infty$ with R/R_{ab} and R/R_{cd} fixed, values of integrals as approximated by S approach the values of corresponding integrals as approximated by M_1. Hence, S will also yield values for the integrals that are sometimes proportional to the exact values in this limit. It is therefore expected that the accuracy of S will usually be less than that of M_2 but greater than that of M_1 (since S includes the effect of overlap) for simultaneously large values of R/a_o, R_{ab}/a_o, and R_{cd}/a_o. In the limit $R/a_o \to 0$ with R/R_{ab} and R/R_{cd} fixed, the charge distributions of S approach the exact change distributions. Hence, the values of integrals given by S are exact in this limit, and S is expected to be more accurate than M_1 or M_2 for simultaneously small values of R/a_o, R_{ab}/a_o, and R_{cd}/a_o.

In the Mulliken approximation, M, the charge distributions, $e\,\psi_{a\alpha}(\vec{r}_1)\,\psi_{b\beta}(\vec{r}_1)$ and $e\,\psi_{c\gamma}(\vec{r}_2)\,\psi_{d\delta}(\vec{r}_2)$, in Eq. (1) are replaced by the charge distributions of equal total charges, $\frac{e}{2}\,\Delta_{ab}(\psi^2_{a\alpha}(\vec{r}_1)+\psi^2_{b\beta}(\vec{r}_1))$ and $\frac{e}{2}\,\Delta_{cd}(\psi^2_{c\gamma}(\vec{r}_2)+\psi^2_{d\delta}(\vec{r}_2))$.[9] The charge distribution of electron 1 thus becomes the sum of two charge distributions centered at nuclear centers a and b, and the charge distribution of electron 2 becomes the sum of two charge distributions centered at nuclear centers c and d. Hence, M reduces three- and four-center integrals to a finite sum of two center integrals. In M,

$$I(a\alpha,b\beta;c\gamma,d\delta) = \tfrac{1}{4}\Delta_{ab}\Delta_{cd}\Big(\iint \psi^2_{a\alpha}(\vec{r}_1)\frac{e^2}{r_{12}}\psi^2_{c\gamma}(\vec{r}_2)\,d\tau_1\,d\tau_2 + \iint \psi^2_{a\alpha}(\vec{r}_1)\frac{e^2}{r_{12}}\psi^2_{d\delta}(\vec{r}_2)\,d\tau_1\,d\tau_2 + \iint \psi^2_{b\beta}(\vec{r}_1)\frac{e^2}{r_{12}}\psi^2_{c\gamma}(\vec{r}_2)\,d\tau_1\,d\tau_2 + \iint \psi^2_{b\beta}(\vec{r}_1)\frac{e^2}{r_{12}}\psi^2_{d\delta}(\vec{r}_2)\,d\tau_1\,d\tau_2\Big). \qquad (7)$$

The Mulliken approximation results from Eq. (2) when all terms in the multipole expansion are retained and particular approximate forms for the $f_{\ell_1 \ell_2 m}$ are employed. Each of the approximate $f_{\ell_1 \ell_2 m}$ will include the effects of overlap, but each will in general be larger than the exact $f_{\ell_1 \ell_2 m}$ because M elongates the distributions along the internuclear axes. Since M includes the effects of overlap to a larger degree than M_1 or M_2, it is expected that M_1 and M_2 will be less accurate than M for small values of R/a_o. Without a more detailed consideration it is difficult to predict the accuracy of M_1 and M_2 relative to M for large values of R/a_o, R/R_{ab}, and R/R_{cd}.

In the limit $R/a_o \to \infty$ with R/R_{ab} and R/R_{cd} fixed, values of the integrals as approximated by M approach const. x $\Delta_{ab}\Delta_{cd}$ if either of the centers a and b are coincident with either of the centers c and d due to an overemphasis of overlap at the coincident centers, or the values approach const. x $\Delta_{ab}\Delta_{cd}/R$ otherwise. Hence, the accuracies of M may be inferior or superior to the accuracies of M_1 but will usually be inferior to the accuracies of M_2 for simultaneously large values of R/a_o, R_{ab}/a_o, and R_{cd}/a_o. As was true with S, the charge distributions of M approach the exact charge distributions in the limit $R/a_o \to 0$ with R/R_{ab} and R/R_{cd} fixed. Hence, M is expected to be more accurate than M_1 or M_2 for simultaneously small values of R/a_o, R_{ab}/a_o, and R_{cd}/a_o.

VI. DIRECT DETERMINATIONS OF M_1 AND M_2 ACCURACIES, COMPARISONS WITH M AND S ACCURACIES

The integrals for which comparisons between approximate and accurate values were made were chosen from the limited number of relatively simple three- and four-center integrals for which accurate values are readily available. The angular configurations of the nuclear centers for each basic type of integral were taken to be as different as possible, and for each configuration all values of R, R_{ab}, and/or R_{cd} for which accurate values could be obtained were included. The formulae for the specific integrals in the nine subsequent cases are given below. The nuclear configurations for each case are given in Fig. 2. In case 5 the nuclear centers lie in a single plane.

Cases 1, 2, 3, 4:

$$I(a,b;c) = \frac{e^2}{\pi a_0^5} \int e^{-r_{1a}/a_0} e^{-r_{1b}/a_0} \frac{1}{r_{1c}} d\tau_1 , \tag{8}$$

Case 5:

$$I(a,b;c,d) = \frac{e^2}{\pi^2 a_0^6} \iint e^{-r_{1a}/a_0} e^{-r_{1b}/a_0} \frac{1}{r_{12}} e^{-r_{2c}/a_0} e^{-r_{2d}/a_0} d\tau_1 d\tau_2 , \tag{9}$$

Cases 6, 7:

$$I(a,b;c,c) = \frac{e^2}{\pi^2 a_0^6} \iint e^{-r_{1a}/a_0} e^{-r_{1b}/a_0} \frac{1}{r_{12}} e^{-2r_{2c}/a_0} d\tau_1 d\tau_2 , \tag{10}$$

Cases 8, 9:

$$I(a,b;b,d) = \frac{e^2}{\pi^2 a_0^6} \iint e^{-r_{1a}/a_0} e^{-r_{1b}/a_0} \frac{1}{r_{12}} e^{-r_{2b}/a_0} e^{-r_{2d}/a_0} d\tau_1 d\tau_2 . \tag{11}$$

In cases 1-5 the sequences of configurations are of the first type in which R/a_o varies while R_{ab} and R_{cd} are fixed. In cases 6-9 the sequences are of the second type in which R/a_o varies while R/R_{ab} and R/R_{cd} are fixed. M_2 does not apply to the three-center nuclear attraction integrals of cases 1-4 whose evaluated form is known[18] because one of the two terms that are averaged in M_2 is the exact result in this case. Cases 6-9, and to a lesser degree the other cases, represent a severe test for M_1 and M_2 since these cases largely involve relatively small values of R/R_{ab} and/or R/R_{cd} whereas the intent of M_1 and M_2 is to be accurate for large values of R/R_{ab} and R/R_{cd}.

The M_1, M_2, S, and M formulae for the integrals of each case may be obtained from the equations and discussions of Sec. II-IV. For M_1, S, and M determination of the integrated formulae involve only simple, well known two-center integrations. In M_2, a three-center nuclear attraction integral occurs, the evaluated form of which is given in Ref. 18.

The results of the comparisons are given in Tables 1-9 for cases 1-9. The accurate values of the integrals are taken from the works of Hirschfelder and Weygant,[19] Boys and Shavitt,[3] and Magnasco and Musso.[4]

In considering the results it is important to bear in mind that neither M_1, M_2, S, nor M yield values for the integrals that are in general either upper or lower bounds to the exact values. Thus, the difference between accurate and approximate values for each case may pass through zero within the particular sequence of configurations of each case. In lieu of means by which these points of zero error can be predicted, the high accuracy in the vicinity of these points must be regarded as fortuitous and should not be considered to have any particular significance in assessing the accuracy of the approximations.

The exact $R = \infty$ limiting forms could not be determined for cases 8 and 9. The $R = \infty$ "accurate" value for case 8 was found by replacing the charge distributions by uniform line segments of charge extending from a to b and c to d. This process gives a result which is proportional to the exact value but gives only an approximate value for the constant of proportionality. For case 9 the above model fails and only an expression which is proportional to the exact result could be determined.

As expected, it is apparent from the tables that M_1 possesses poor accuracy in the majority of instances considered here and is usually inferior to M_2, S, and M. In most cases, therefore, M_1 is useful only in obtaining very rough estimates for the values of the integrals. Exceptions to this occur, as expected, for simultaneously large values of R/a_o, R/R_{ab}, and R/R_{cd} where M_1 is nearly as accurate as M_2 and S and more accurate than M, as illustrated by Tables 1-5. Tables 1-5 and to a lesser degree Tables 6-9 demonstrate the fact that as $R \to \infty$ values given by M_1 and S become equal. Since S includes the effects of overlap to a large degree while M_1 neglects overlap entirely, values of R for which M_1 and S give nearly equal results mark the points at which the effects of overlap become unimportant. Such values of R lie between $5\ a_o$ and $7\ a_o$ for Cases 1-5 and are estimated to be about the same for Cases 6-8. The value for Case 9 is uncertain. Due to the simplicity of M_1, it should be useful in determining which, if any, integrals may be neglected in a given molecular structure calculation.

The results given in all of the tables bear out to a large degree the expectations regarding the accuracy of M_2 relative to S and M expressed in Sec. V. A comparison of the accuracies of M_2, S, and M for sequences of values of R in which R_{ab} and R_{cd} remain fixed is illustrated only by Table 5. Here M_2 is less accurate than S and M for small values of R but more accurate than S for $R \gtrsim 5\ a_o$ and more accurate than M for $R \gtrsim 3.5\ a_o$. Comparisons of

accuracies for sequences in which R_{ab}/R and R_{cd}/R remain fixed occur in Tables 6-9. Here the maximum values of R included in the tables (except for $R \to \infty$) vary from about $4\ a_o$ for Table 6 down to about $1.5\ a_o$ for Table 9. It is therefore not unexpected that in these cases M_2 is inferior to both S and M in nearly all instances. It is clear, however, from the values and the tendencies of the values of the last rows of the tables and from the $R \to \infty$ limiting values that M_2 becomes more accurate than S and M for certain values of R, as was expected. For Table 7 these values of R are about $4\ a_o$ and $3\ a_o$ relative to S and M respectively, and for Table 8 the value relative to M is about $3\ a_o$. In the other cases these values of R lie off the tables but appear to be roughly the same. It may be concluded, therefore, that in nearly all cases M_2 is more accurate than S for values of $R \gtrsim 5\ a_o$ and more accurate than M for $R \gtrsim 3.5\ a_o$. An exception to this would probably occur for cases not included here in which R/R_{ab} and R/R_{cd} are considerably smaller than unity.

It is interesting to note that in all cases considered here S is more accurate than M_2 for $R \lesssim 4\ a_o$ and that S and M are more accurate than one another for the same values of R in about as many instances as not. Since S includes the effects of overlap but does not include the effects of higher multipoles, while M_2 and M include both effects, it may be concluded that the effects of overlap are more important than the effects of higher multipoles in most cases for $R \lesssim 4\ a_o$. Since M_2 is more accurate than S for $R \gtrsim 5\ a_o$, the opposite is true for these higher values of R. This is consistent with the conclusion previously reached by comparing M_1 and S that the effects of overlap are unimportant for $R \gtrsim 7\ a_o$.

The statement has been made[20] that the smallest of two approximate values for an integral is usually the more accurate. In comparing the Sklar and Mulliken approximations for the cases considered here it is found that there are 36 instances in which the smaller value is more accurate and 19 instances in which it is not.

VII. A COMBINATION OF THE MARGENAU APPROXIMATIONS

An approximation that is often superior to both M_1 and M_2 may be obtained by taking twice the value of an integral as given by M_2 and subtracting from that the value as given by M_1. There are two reasons why this should be an improved approximation. First, it may be seen from the discussion of Sec. IV that in the limit $R \to \infty$ with R_{ab} and R_{cd} fixed, $2M_2-M_1$ gives exactly the monopole monopole and monopole-higher multipole terms of the integral. This is in contrast to M_1 which includes only the monopole-monopole term and to M_2 which in addition includes only one half of each monopole-higher multipole term. Second, $2M_2-M_1$ will represent the effects of overlap to a better degree for values of R that are not very small. This is because the partial allowance of overlap in M_2 is improved upon by the subtraction of M_1 which includes no effects of overlap. In other words, the lack of complete allowance for the effects of overlap in M_2 is in some degree canceled by subtracting a quantity which has a greater lack of allowance for overlap. For very small values of R, $2M_2-M_1$ will be poor due to the divergence of M_1 for $R \to 0$.

Values of the integrals approximated by $2M_2-M_1$ fo. Cases 5-9 are given in Tables 5-9. Case 5 is the only case in this group which involves a sequence of configurations in which R varies while R_{ab} and R_{cd} remain fixed. In Case 5 $2M_2-M_1$ is more accurate than M_1 and M_2 for $R \gtrsim a_o$, is more accurate than S and M for $R \gtrsim 3a_o$, is at least nearly as accurate as S and M for $R \gtrsim a_o$, and is less accurate than M_2, S, and M for $R \lesssim a_o$.

For Cases 6 and 7, where R_{ab}/R remains fixed as R is varied, $2M_2-M_1$ is exact in the limit $R \to \infty$. This is due to the fact that one of the charge distributions is spherically symmetric, and the integrals therefore do not contain any of the higher multipole-higher multipole terms which are neglected

by $2M_2-M_1$. In spite of the fact that R_{ab} increases in proportion to R as $R \to \infty$, $2M_2-M_1$ gives exactly each monopole-multipole term (each approaching $e\Delta \times R^{-1}$ as $R \to \infty$) in this limit. In Case 6, $2M_2-M_1$ is superior to the other approximations for $R \gtrsim 2a_o$. In Case 7, where the effects of overlap are greater due to the different nuclear configuration, $2M_2-M_1$ is superior to M for $R \gtrsim 3a_o$, superior to S for $R \gtrsim 4a_o$, and comparable or superior to M_2 for $R \gtrsim 2a_o$.

In Case 8, where R_{ab}/R and R_{bd}/R are fixed as R varies, the integral includes higher multipole-higher multipole terms and hence $2M_2-M_1$ is not exact in the limit $R \to \infty$. The limiting value is nevertheless better than that given by the other approximations. Here $2M_2-M_1$ is superior to M for $R \gtrsim 3a_o$, superior to S for $R \gtrsim$ a value of (probably) about $4a_o$, and comparable or superior to M_2 for $R \gtrsim a_o$. In Case 9, where R_{ab}/R and R_{bd}/R are fixed and where lines ab and bd partially overlap, $2M_2-M_1$ like M_2 has the proper form is the limit $R \to \infty$ whereas the other approximations do not. Here $2M_2-M_1$ is apparently roughly comparable or superior to M_2, S, and M for $R \gtrsim 1.5\ a_o$.

It may be concluded, therefore, that in most cases $2M_2-M_1$ is more accurate than S for $R \gtrsim 4a_o$, is more accurate than M for $R \gtrsim 3a_o$, and has about the same or better accuracy than M_2 for $R \gtrsim 2a_o$. Exceptions to these conclusions might be cases involving values of R comparable to those considered here but involving much larger values of R_{ab}, R_{cd}, and R_{bd} than considered.

VIII. SUMMARY AND COMMENTS

The Margenau approximations to three- and four-center molecular integrals have been tested for accuracy and compared with the Sklar and Mulliken approximations for many cases involving atomic orbitals of the form e^{-r/a_o}. The former approximations were designed to be accurate for cases involving large distances between charge centers. It was found that Margenau's first very simple approximation is accurate for cases in which the distance between the centers of charge is at least about five times as large as a_o and at the same time the internuclear distances of each charge distribution are less than or about equal to a_o. In such cases this approximation is nearly as accurate as the Sklar approximation and is more accurate than the Mulliken approximation. Margenau's second, more complicated approximation was found to be accurate in the same cases and for these cases is more accurate than the other approximations considered. This approximation was also found to be more accurate than the other approximations when the intercharge separation is again at least about $5\ a_o$ but where the internuclear distances have any value except values that are very large relative to the intercharge distance.

An approximation was proposed in which an integral is taken equal to twice the value given by Margenau's second approximation minus the value given by Margenau's first approximation. This approximation was found to have an accuracy about equal to or better than Margenau's second approximation in all instances except those in which the intercharge separation is small. Furthermore, the approximation was found to be superior to the Sklar and Mulliken approximations for somewhat smaller values of intercharge separation than was true of Margenau's second approximation.

The results obtained here may be generalized to cases where the basic atomic orbital is e^{-ar/a_o} by an appropriate change of distance scale.

In addition, a means was presented for predicting and understanding the accuracies of molecular integral approximations, in which consideration is given to the effects of overlap and higher multipoles of the charge distributions. It was found that predictions of the relative accuracies of the approximations considered here were borne out. This means of considering the approximations led to the combined form of the Margenau approximations.

For small values of R/a_o the accuracy of any of the approximations considered here is probably insufficient for all molecular structure calculations, although they may be adequate for determining the configuration of the molecule.[16] Approximations which are sometimes more accurate than those considered here have been proposed and employed. There have been many suggested generalizations of the Sklar and Mulliken approximations which improve their accuracy to some degree.[17] The Cizek approximations[12] offer a more substantial improvement. In the latter each charge distribution is replaced by a sum of spherically symmetric charge distributions placed along the internuclear axis in such a fashion that the first few ℓ_1, ℓ_2 terms of Eq. (2) are exact in the limit $R/a_o \to \infty$ with R_{ab} and R_{cd} fixed. In this process the effects of overlap are apparently well accounted for. The accuracies for configuration sequences in which R varies while R/R_{ab} and R/R_{cd} remain fixed (the only case considered by Cizek) are quite good, and the accuracies for simultaneously large values of R/a_o, R/R_{ab}, and R/R_{cd} must be good. However, the approximations would be expected to be less accurate for simultaneously small values of R/a_o, R/R_{ab}, and R/R_{cd}. In the latter case improved accuracy might result if the placement of the approximate charge distributions were such as to yield the first few ℓ_1, ℓ_2 terms of Eq. (2) exactly in the limit $R/a_o \to 0$ with R_{ab}/a_o and R_{cd}/a_o fixed.

Hirschfelder[17] has made direct use of Eq. (2) with approximations to the first few $f_{\ell_1 \ell_2 |m|}$. Silverstone[1] and Rudenberg [1,2] have used Eq. (2) but with the bipolar expansion centers placed on the nuclei, to obtain exact, highly complicated expressions for some of the three- and four-center integrals. This author has given consideration to obtaining exact expressions for each of the $f_{\ell_1 \ell_2 |m|}$ in Eq. (2) for the case in which the expansion points are chosen to be the geometric charge centers $\overline{ab}$ and $\overline{cd}$ in order to obtain more rapid convergence of the expansion. At the present time an exact multipole expansion for the charge distribution $e(\pi a_o^3)^{-1} e^{-(r_{1a}+r_{1b})/a_o}$ about the point $\overline{ab}$ has been obtained.

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FIGURE CAPTIONS

Fig. 1. The various line segments, distances, angles and particles involved in the discussions of the text. The nuclei are particles a, b, c, and d and the electrons are particles 1 and 2. Points $\bar{ab}$ and $\bar{cd}$ bisect line segments ab and cd respectively, and particles and points a, b, $\bar{cd}$, P, and a' lie in a single plane, as do c, d, $\bar{ab}$, P, and c'. The self-descriptive distances r_{1c}, r_{1d}, r_{2a}, and r_{2b} are not shown.

Fig. 2. The nuclear configurations involved in the integrals of cases 1-9. All nuclei may be considered to lie in the plane of this page. Dots mark the midpoints of the line segments on which they are placed.

ρ	$\mathcal{R}/a_o$	accurate (ref.)	M_1	S	M
1	0	0.782455 (19)	∞ ($+\infty$%)	0.858385 (+9.70%)	0.769424 (-1.66%)
3	1.4142	0.509687 (19)	0.606970 (+19.1%)	0.520359 (+2.09%)	0.501029 (-1.70%)
5	2.4495	0.339261 (19)	0.350434 (+3.29%)	0.341424 (+0.638%)	0.335257 (-1.18%)
7	3.4641	0.246089 (19)	0.247794 (+0.693%)	0.246711 (+0.253%)	0.244247 (-0.743%)
9	4.4721	0.191549 (19)	0.191941 (+0.205%)	0.191804 (+0.133%)	0.190623 (-0.483%)
13	6.4807	0.132370 (19)	0.132452 (+0.062%)	0.132450 (+0.060%)	0.132057 (-0.236%)
∞	∞	$0.858385/\mathcal{R}'$	$0.858385/\mathcal{R}'$ (0%)	$0.858385/\mathcal{R}'$ (0%)	$0.858385/\mathcal{R}'$ (0%)

Table 1. Comparison of accurate and approximate values for the integral of case 1. Values of the integral have been divided by e^2/a_o. $R = a_o$. $\rho = \sqrt{1 + (2\mathcal{R}/R)^2}$. $\mathcal{R} = \mathcal{R}/a_o$.

ρ	$\mathcal{R}/a_o$	accurate (ref.)	M_1	S	M
1	0	0.464605 (19)	∞ ($+\infty$%)	0.586453 (+26.2%)	0.427717 (-7.94%)
3	2.8284	0.201223 (19)	0.207342 (+3.04%)	0.204569 (+1.66%)	0.193546 (-3.82%)
5	4.8990	0.119160 (19)	0.119709 (+0.461%)	0.119670 (+0.430%)	0.117259 (-1.60%)
7	6.9282	0.084471 (19)	0.084647 (+0.208%)	0.084647 (+0.208%)	0.083778 (-.820%)
9	8.9443	0.065486 (19)	0.065567 (+0.124%)	0.065567 (+0.124%)	0.065161 (-0.496%)
∞	∞	$0.858385/\mathcal{R}'$	$0.858385/\mathcal{R}'$ (0%)	$0.858385/\mathcal{R}'$ (0%)	$0.858385/\mathcal{R}'$ (0%)

Table 2. Comparison of accurate and approximate values for the integral of case 2. Values of the integral have been divided by e^2/a_o. $R = 2a_o$. $\rho = \sqrt{1 + (2\mathcal{R}/R)^2}$. $\mathcal{R}' = \mathcal{R}/a_o$.

ρ	$\mathcal{R}/a_o$	accurate (ref.)	M_1	S	M
0	0	0.782455 (19)	∞ ($+\infty$%)	0.858385 (+9.70%)	0.769424 (-1.66%)
1	0.5	0.735758 (19)	1.716771 (+133.3%)	0.769424 (+4.58%)	0.742216 (+0.878%)
3	1.5	0.500574 (19)	0.572257 (+14.3%)	0.501029 (+0.091%)	0.515828 (+1.05%)
5	2.5	0.336648 (19)	0.343354 (+1.99%)	0.335257 (-0.413%)	0.344451 (+2.32%)
7	3.5	0.245086 (19)	0.245253 (+0.068%)	0.244247 (-0.342%)	0.248764 (+1.50%)
9	4.5	0.191074 (19)	0.190752 (-0.168%)	0.190623 (-0.236%)	0.192933 (+0.973%)
13	6.5	0.132212 (19)	0.132059 (-0.116%)	0.132057 (-0.117%)	0.132842 (+0.476%)
∞	∞	$0.858385/\mathcal{R}'$	$0.858385/\mathcal{R}'$ (0%)	$0.858385/\mathcal{R}'$ (0%)	$0.858385/\mathcal{R}'$ (0%)

Table 3. Comparison of accurate and approximate values for the integral of case 3. Values of the integral have been divided by e^2/a_o. $R = a_o$. $\rho = 2\mathcal{R}/a_o$. $\mathcal{R}' = \mathcal{R}/a_o$.

ρ	$\mathcal{R}/a_o$	accurate (ref.)	M_1	S	M
0	0	0.464605 (19)	∞ ($+\infty$%)	0.586433 (+26.2%)	0.427717 (-7.94%)
1	1	0.406005 (19)	0.586453 (+44.4%)	0.427717 (+5.35%)	0.431784 (+6.35%)
3	3	0.196678 (19)	0.195484 (-0.607%)	0.193546 (-1.59%)	0.211741 (+7.66%)
5	5	0.118191 (19)	0.117291 (-0.761%)	0.117259 (-0.788%)	0.122053 (+3.27%)
7	7	0.084130 (19)	0.083779 (-0.417%)	0.083778 (-0.418%)	0.085522 (+1.65%)
9	9	0.065324 (19)	0.065161 (-0.250%)	0.065161 (-0.250%)	0.065876 (+0.998%)
∞	∞	$0.858385/\mathcal{R}'$	$0.858385/\mathcal{R}'$ (0%)	$0.858385/\mathcal{R}'$ (0%)	$0.858385/\mathcal{R}'$ (0%)

Table 4. Comparison of accurate and approximate values for the integral of case 4. Values of the integral have been divided by e^2/a_o. $R = 2a_o$. $\rho = 2\mathcal{R}/R$. $\mathcal{R}' = \mathcal{R}/a_o$.

$\mathcal{R}/R$	$\mathcal{R}/a_o$	accurate (ref.)	M_1	M_2	S	M	$2M_2 - M_1$
0	0	0.2499	∞ (+∞%)	0.4064 (+62.6%)	0.2823 (+12.9%)	0.2462 (-1.48%)	$-\infty$ (-∞%)
1	1.69	0.1973 (4)	0.2672 (+35.4%)	0.2335 (+18.3%)	0.2102 (+6.53%)	0.1910 (-3.21%)	0.1998 (+1.3%)
1.5	2.535	0.1591 (4)	0.1782 (+12.0%)	0.1715 (+7.80%)	0.1647 (+3.34%)	0.1536 (-3.41%)	0.1648 (+3.6%)
2	3.38	0.1280 (4)	0.1336 (+4.36%)	0.1319 (+3.04%)	0.1304 (+1.86%)	0.1242 (-3.03%)	0.1302 (+1.7%)
2.5	4.225	0.1051 (4)	0.1069 (+1.72%)	0.1063 (+1.18%)	0.1061 (+1.01%)	0.1025 (-2.47%)	0.1057 (+0.6%)
3	5.07	0.08834 (4)	0.08908 (+0.83%)	0.08881 (+0.53%)	0.08890 (+0.64%)	0.08665 (-1.91%)	0.08854 (+0.2%)
3.5	5.915	0.07596 (4)	0.07635 (+0.52%)	0.07619 (+0.31%)	0.07631 (+0.47%)	0.07485 (-1.45%)	0.07603 (+0.1%)
4	6.76	0.06654 (4)	0.06681 (+0.41%)	0.06671 (+0.26%)	0.06680 (+0.40%)	0.06580 (-1.10%)	0.06661 (+0.1%)
∞	∞	0.4516/$\mathcal{R}'$	0.4516/$\mathcal{R}'$ (0%)	0.4516/$\mathcal{R}'$ (0%)	0.4516/$\mathcal{R}'$ (0%)	0.4516/$\mathcal{R}'$ (0%)	0.4516/$\mathcal{R}'$ (0%)

Table 5. Comparison of accurate and approximate values for the integral of case 5. Values of the integral have been divided by e^2/a_o. $R = 1.69\ a_o$. $\mathcal{R}' = \mathcal{R}/a_o$.

R/a_o	$\mathcal{R}/a_o$	accurate (ref.)	M_1	M_2	S	M	$2M_2 - M_1$
0	0	0.6250	∞ ($+\infty$%)	1.0000 (+60%)	0.6250 (0%)	0.6250 (0%)	$-\infty$ ($-\infty$%)
1.6	1.386	0.3394 (3)	0.5032 (+48.2%)	0.4143 (+22.1%)	0.3524 (+3.82%)	0.3327 (-1.98%)	0.3254 (-4.0%)
2	1.732	0.2584 (19)	0.3386 (+31.0%)	0.3007 (+16.4%)	0.2697 (+4.38%)	0.2498 (-3.32%)	0.2628 (+1.8%)
2.4	2.078	0.1926 (3)	0.2322 (+20.6%)	0.2153 (+11.8%)	0.2010 (+4.34%)	0.1830 (-4.98%)	0.1984 (+3.0%)
2.5	2.165	0.1777 (19)	0.2117 (+19.1%)	0.1978 (+11.3%)	0.1864 (+4.88%)	0.1688 (-4.98%)	0.1839 (+3.5%)
3	2.598	0.1192 (19)	0.1341 (+12.5%)	0.1286 (+7.85%)	0.1248 (+4.71%)	0.1115 (-6.49%)	0.1231 (+3.2%)
∞	∞	$0.9698\Delta/\mathcal{R}'$	$\Delta/\mathcal{R}'$ (+3.12%)	$0.9849\Delta/\mathcal{R}'$ (+1.56%)	$\Delta/\mathcal{R}'$ (+3.12%)	$0.8660\Delta/\mathcal{R}'$ (-10.7%)	$0.9698\Delta/\mathcal{R}'$ (0%)

Table 6. Comparison of accurate and approximate values for the integral of case 6. Values of the integral have been divided by e^2/a_o. $\mathcal{R}' = \sqrt{3}\ R'/2$. $\Delta = (R'^2/3 + R' + 1)\exp(-R')$, $R' = R/a_o$.

R/a_o	$\mathcal{R}/a_o$	accurate (ref.)	M_1	M_2	S	M	$2M_2 - M_1$
0	0	0.6250	∞ (+∞%)	1.0000 (+60%)	0.6250 (0%)	0.6250 (0%)	$-\infty$ ($-\infty$%)
1.2	1.8	0.3610 (3)	0.4484 (+24.2%)	0.4208 (+16.6%)	0.3642 (+0.88%)	0.3668 (+1.60%)	0.3932 (+8.9%)
1.4	2.1	0.3096 (3)	0.3585 (+15.8%)	0.3453 (+11.5%)	0.3116 (+0.63%)	0.3169 (+2.34%)	0.3321 (+7.3%)
1.6	2.4	0.2636 (3)	0.2905 (+10.2%)	0.2859 (+8.44%)	0.2644 (+0.30%)	0.2719 (3.16%)	0.2813 (+6.7%)
1.8	2.7	0.2232 (3)	0.2375 (+6.42%)	0.2356 (+5.57%)	0.2231 (-0.04%)	0.2322 (+4.03%)	0.2337 (+4.7%)
2.1	3.15	0.1733 (3)	0.1777 (+2.52%)	0.1780 (+2.72%)	0.1718 (-0.87%)	0.1819 (+4.97%)	0.178[illegible] (+2.9%)
2.4	3.6	0.1335 (3)	0.1341 (+0.42%)	0.1350 (+1.12%)	0.1317 (-1.34%)	0.1416 (+6.09%)	0.1359 (+1.8%)
2.7	4.05	0.1025 (3)	0.1017 (-0.76%)	0.1027 (+0.18%)	0.1008 (-1.66%)	0.1098 (+7.07%)	0.1037 (+1.2%)
∞	∞	$1.0233\,\Delta/\mathcal{R}'$	$\Delta/\mathcal{R}'$ (-2.28%)	$1.0116\Delta/\mathcal{R}'$ (-1.14%)	$\Delta/\mathcal{R}'$ (-2.28%)	$1.1250\Delta/\mathcal{R}'$ (+9.94%)	$1.0233\Delta/\mathcal{R}'$ (0%)

Table 7. Comparison of accurate and approximate values for the integral of case 7. Values of the integral have been divided by e^2/a_o. $\mathcal{R}' = 3R'/2$. $\Delta = (R'^2/3 + R' + 1)\exp(-R')$, $R' = R/a_o$.

R/	$\mathcal{R}/a_o$	accurate (ref.)	M_1	M_2	S	M	$2M_2 - M_1$
0	0	0.6250	∞ ($+\infty$%)	1.0000 (+60%)	0.6250 (0%)	0.6250 (0%)	$-\infty$ ($-\infty$%)
1.2	1.2	0.3317 (3)	0.5430 (+63.7%)	0.4306 (+29.8%)	0.3451 (+4.03%)	0.3361 (+1.33%)	0.3182 (-4.1%)
1.4	1.4	0.2739 (3)	0.4049 (+47.8%)	0.3443 (+25.7%)	0.2855 (+4.22%)	0.2792 (+1.95%)	0.2837 (+3.6%)
1.6	1.6	0.2227 (3)	0.3038 (+36.4%)	0.2719 (+22.1%)	0.2320 (+4.16%)	0.2287 (+2.71%)	0.2400 (+7.8%)
1.8	1.8	0.1786 (3)	0.2285 (+28.0%)	0.2125 (+19.0%)	0.1856 (+3.91%)	0.1851 (3.66%)	0.1965 (+10.0%)
2.1	2.1	0.1265 (3)	0.1491 (+17.9%)	0.1444 (+14.2%)	0.1296 (+2.44%)	0.1322 (+4.54%)	0.1397 (+10.4%)
2.4	2.4	0.08707 (3)	0.09705 (+11.5%)	0.09658 (+10.9%)	0.08833 (+1.44%)	0.09265 (+6.41%)	0.09611 (+10.4%)
2.7	2.7	0.05891 (3)	0.06286 (+6.70%)	0.06371 (+8.15%)	0.05904 (+0.22%)	0.06388 (+8.44%)	0.06456 (+9.6%)
∞	∞	$\simeq 1.3863\Delta^2/\mathcal{R}'$	$\Delta^2/\mathcal{R}'$ ($\simeq$ -27.9%)	$1.0563\Delta^2/\mathcal{R}'$ ($\simeq$ -23.8%)	$\Delta^2/\mathcal{R}'$ ($\simeq$ -27.9%)	$0.15625\Delta^2$ ($+\infty$%)	$1.1136\Delta^2/\mathcal{R}'$ ($\simeq$ -19.7%)

Table 8. Comparison of accurate and approximate values for the integral of case 8. Values of the integral have been divided by e^2/a_o. $\mathcal{R} = R$. $\Delta = (R'^2/3 + R' + 1)\exp(-R')$, $R' = R/a_o$. $\mathcal{R}' = \mathcal{R}/a_o$.

R/a_o	$\mathcal{R}/a_o$	accurate (ref.)	M_1	M_2	S	M	$2M_2 - M_1$
0	0	0.6250	∞ (+∞%)	1.0000 (+60%)	0.6250 (0%)	0.6250 (0%)	$-\infty$ (-∞%)
1.2	0.6	0.2058 (3)	0.6493 (+216%)	0.2975 (+44.6%)	0.2325 (+13.0%)	0.2010 (-2.40%)	-0.0543 (-126%)
1.4	0.7	0.1495 (3)	0.4195 (+181%)	0.2133 (+42.7%)	0.1725 (+15.4%)	0.1446 (-3.37%)	0.0071 (-95.3%)
1.6	0.8	0.1061 (3)	0.2705 (+155%)	0.1497 (+41.1%)	0.1249 (+17.7%)	0.1018 (-4.04%)	0.0289 (-72.7%)
1.8	0.9	0.07397 (3)	0.1737 (+135%)	0.1032 (+39.6%)	0.08852 (+19.7%)	0.07035 (-1.89%)	0.0327 (-55.8%)
2.1	1.05	0.04186 (3)	0.08855 (+112%)	0.05746 (+37.3%)	0.05100 (+21.8%)	0.03926 (-6.21%)	0.02637 (-37.0%)
2.4	1.2	0.02286 (3)	0.04461 (+95.2%)	0.03108 (+35.9%)	0.02820 (+23.4%)	0.02130 (-6.84%)	0.01755 (-23.2%)
2.7	1.35	0.01220 (3)	0.02222 (+82.1%)	0.01641 (+34.5%)	0.01530 (+25.4%)	0.01129 (-7.46%)	0.01060 (-13.1%)
∞	∞	$\approx \frac{\Delta_1\Delta_2}{\mathcal{R}'} \ln \frac{\mathcal{R}'}{a_o}$	$\Delta_1\Delta_2/\mathcal{R}'$ (-100%)	$\frac{3}{4}\frac{\Delta_1\Delta_2}{\mathcal{R}'} \ln \frac{\mathcal{R}'}{a_o}$ (-X%, 100 > X > 0)	$\Delta_1\Delta_2/\mathcal{R}'$ (-100%)	0.15625 (+∞%)	$\frac{3}{2}\frac{\Delta_1\Delta_2}{\mathcal{R}'} \ln \frac{\mathcal{R}'}{a_o}$ (±X%, 100 > X > 0)

Table 9. Comparison of accurate and approximate values for the integral of case 9. Values of the integral have been divided by e^2/a_o. $\mathcal{R}' = R'/2$. $\Delta_1 = (R'^2/3 + R' + 1) \exp(-R')$, $\Delta_2 = (4R'^2/3 + 2R' + 1) \exp(-2R')$, $R' = \frac{R}{a_o}$.

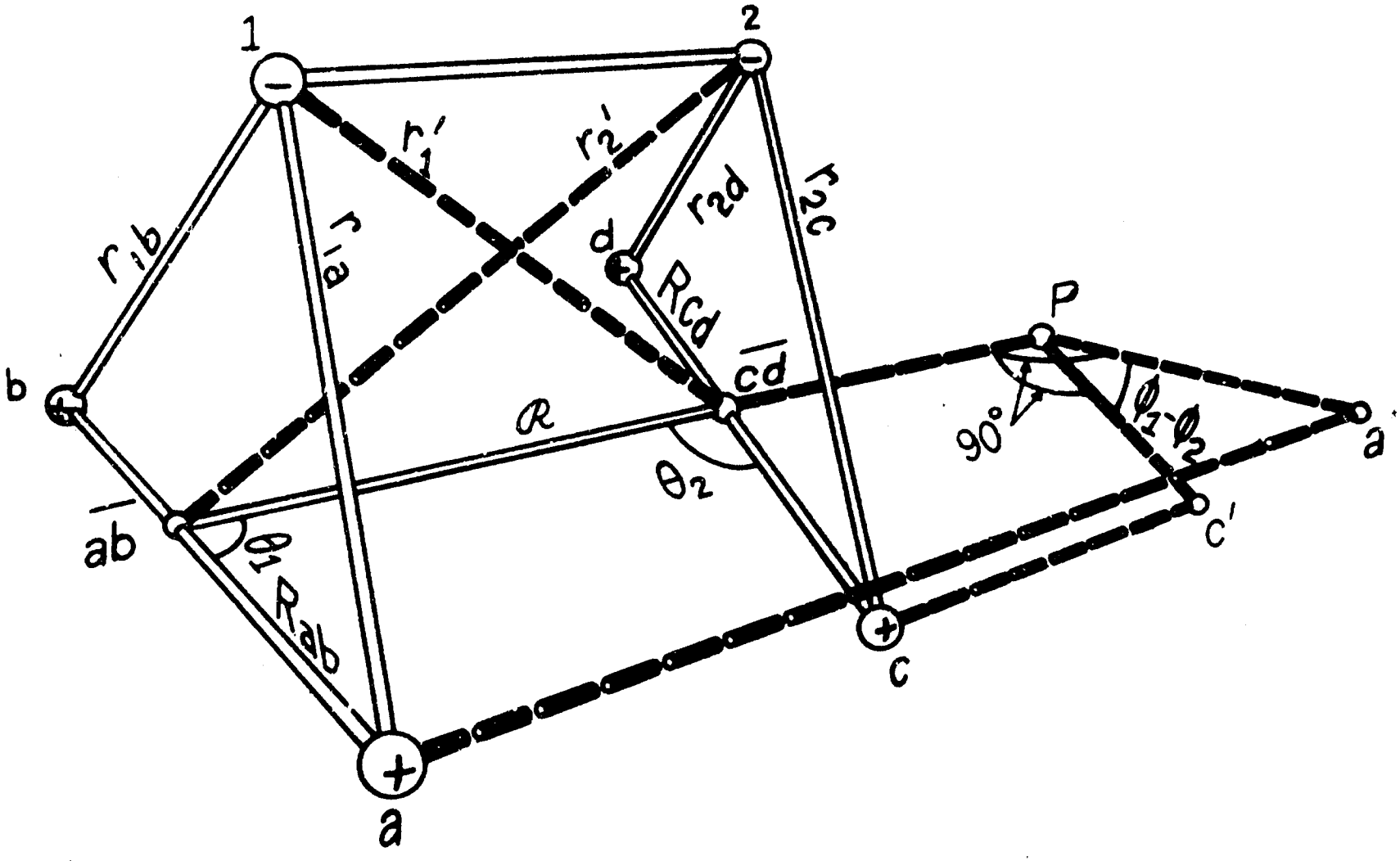
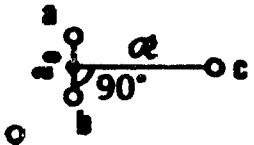
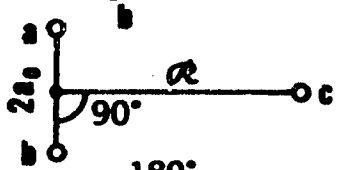

1
2
r_1'
r_2'
r_{1b}
r_{1a}
d
r_{2d}
r_{2c}
R_{cd}
P
b
$\overline{cd}$
$\mathcal{R}$
90°
$\phi_1 - \phi_2$
a
θ_2
$\overline{ab}$
θ_1
R_{ab}
c'
c
a

Figure 1

CASE	NUCLEAR CONFIGURATION
1	
2	
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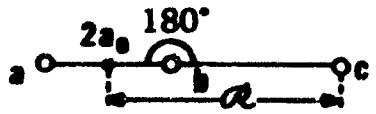
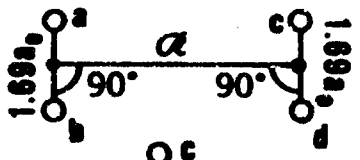
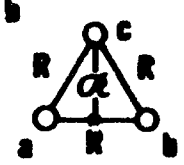
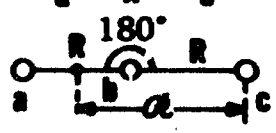
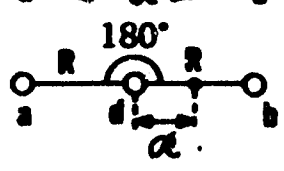
4	
5	
6	
7	
8	
9	

Figure 2