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A Study of Two-Center Integrals Useful in Calculations on Molecular Structure. I

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Convenient formulas have been obtained for the overlap integrals $\int \chi_a\chi_b dv$, kinetic energy integrals $-\frac{1}{2}\int \chi_a\Delta\chi_b dv$, nuclear attraction integrals $Z\int \chi_a(1/r_a)\chi_b dv$ and $Z\int \chi_b(1/r_a)\chi_b' dv$, and coulomb repulsion integrals $\int\int \chi_a(1)\chi_b(2)(1/r_{12})\chi_a'(1)\chi_b'(2)dv_1dv_2$, where χ_a, χ_a', χ_b, χ_b' are Slater-type AO's on the centers a and b. Explicit formulas are given for all the integrals arising from the principal quantum numbers 1 and 2, for arbitrary values of the effective nuclear charges and the interatomic distance.

INTRODUCTION

In calculations on molecular structure by either the VB (valence bond) or the MO (molecular orbital) method in LCAO (linear combinations of atomic orbitals) approximation, the molecular wave functions are built from AO's (atomic orbitals). The calculation of energies, transition moments, bond strengths, and other physical and chemical quantities then finally reduces to the evaluation of a great many integrals over these AO's. If we use Slater-type AO's, then all the integrals involving only two centers can be obtained in closed analytical form (except for one type, which is treated in Paper II in this series). These two-center integrals are the only ones occurring in diatomic molecules, and also the most important ones occurring in polyatomic molecules. Whereas formulas and tables for many of the two-center integrals can be found in the literature,[1] others are lacking; and it was considered worth while to undertake the systematic study of which this paper forms the first part. We shall give formulas which are convenient for numerical calculations for the overlap integrals, kinetic energy integrals, nuclear attraction integrals, and electronic repulsion integrals of the coulomb type. We shall consider all the possibilities arising from the principal quantum numbers 1 and 2, using Slater-type AO's with arbitrary values for the effective nuclear charges.

CHOICE OF UNITS AND COORDINATES

We shall use the following atomic units: lengths in units of the Bohr radius $a_H=0.5293$A; energies in units of $e^2/a_H=27.204$ ev. (This is twice the ionization energy of the hydrogen atom.)

In these units, the kinetic energy operator for an electron is $-\frac{1}{2}\Delta$, the potential energy of an electron at a distance r from a nucleus of charge Z is $-Z/r$, and the repulsion energy of two electrons 1 and 2 at a distance r_{12} apart is $1/r_{12}$.

The two centers we shall designate by subscripts a and b; their mutual distance by R.

To describe an electron with reference to the two centers, we shall use the following coordinate systems:

(i) Cartesian coordinates at the centers a and b. The Z axes we choose along the internuclear axis, pointing toward each other; the X axes we take parallel, and also the Y axes. Hence, on one of the two centers, say a, we have a right-handed coordinate system, and on the other center a left-handed one.

(ii) Spherical coordinates at the centers a and b; these are given in terms of the cartesian coordinates by

$$\left.\begin{aligned} r_a&=(x_a^2+y_a^2+z_a^2)^{\frac{1}{2}}, \quad \tan\theta_a=z_a/(x_a^2+y_a^2)^{\frac{1}{2}}, \quad \tan\phi_a=y_a/x_a,\\ r_b&=(x_b^2+y_b^2+z_b^2)^{\frac{1}{2}}, \quad \tan\theta_b=z_b/(x_b^2+y_b^2)^{\frac{1}{2}}, \quad \tan\phi_b=y_b/x_b.\end{aligned}\right\} \quad (1)$$

Note that if the same electron is described with reference to either atom a or atom b, then $x_a=x_b$, $y_a=y_b$, $\phi_a=\phi_b$.

(iii) Prolate spheroidal coordinates, defined by

$$\xi=(r_a+r_b)/R, \quad \eta=(r_a-r_b)/R, \quad \phi=\phi_a=\phi_b; \quad (2)$$

and conversely

$$\left.\begin{aligned} &r_a=\tfrac{1}{2}(\xi+\eta)R, \quad r_b=\tfrac{1}{2}(\xi-\eta)R,\\ &\cos\theta_a=(1+\xi\eta)/(\xi+\eta), \quad \cos\theta_b=(1-\xi\eta)/(\xi-\eta),\\ &\sin\theta_a=[(\xi^2-1)(1-\eta^2)]^{\frac{1}{2}}/(\xi+\eta),\\ &\sin\theta_b=[(\xi^2-1)(1-\eta^2)]^{\frac{1}{2}}/(\xi-\eta).\end{aligned}\right\} \quad (3)$$

For volume integration in these coordinates the volume element is $(R^3/8)(\xi^2-\eta^2)d\xi d\eta d\phi$; the integration limits are for ϕ from 0 to 2π, for η from -1 to 1, and for ξ from 1 to ∞.

TYPES OF INTEGRALS

We list below the types of integrals which we shall treat in this paper. We write for the general AO's on atom a, χ_a, χ_a', χ_a'', $\cdots$, and similarly with subscripts b for the AO's on atom b.

Overlap integrals:

$$(\chi_a|\chi_b)=\int \chi_a\chi_b dv; \quad (4)$$

Kinetic energy integrals:

$$(\chi_a|-\tfrac{1}{2}\Delta|\chi_b)=-\tfrac{1}{2}\int \chi_a\Delta\chi_b dv; \quad (5)$$

Nuclear attraction integrals:

$$(\chi_a|Z/r_a|\chi_b)=Z\int (\chi_a\chi_b/r_a)dv; \quad (6)$$

$$(\chi_b|Z/r_a|\chi_b')=Z\int (\chi_b\chi_b'/r_a)dv; \quad (7)$$

[1] See the bibliography.

TABLE I.

O_3	E	∞C_ϕ	i	∞iC_ϕ
$D_g^{(0)}$ S	1	1	1	1
$D_u^{(0)}$ S'	1	1	-1	-1
$D_g^{(1)}$ P'	3	$1+2\cos\phi$	3	$1+2\cos\phi$
$D_u^{(1)}$ P	3	$1+2\cos\phi$	-3	$-1-2\cos\phi$
$D_g^{(2)}$ D	5	$1+2\cos\phi+2\cos2\phi$	5	$1+2\cos\phi+2\cos2\phi$
$D_u^{(2)}$ D'	5	$1+2\cos\phi+2\cos2\phi$	-5	$-1-2\cos\phi-2\cos2\phi$
. . .	. . .	. . .	. . .	. . .
$D_g^{(l)}$ $\cdots$	$2l+1$	$1+2\sum_{k=1}^{l}\cos k\phi$	$2l+1$	$1+2\sum_{k=1}^{l}\cos k\phi$
$D_u^{(l)}$ $\cdots$	$2l+1$	$1+2\sum_{k=1}^{l}\cos k\phi$	$-2l-1$	$-1-2\sum_{k=1}^{l}\cos k\phi$

Coulomb repulsion integrals:

$$(\chi_a\chi_b|1/r|\chi_a'\chi_b') = \int\int[\chi_a(1)\chi_b(2)\chi_a'(1)\chi_b'(2)/r_{12}]dv_1dv_2. \quad (8)$$

CHOICE OF AO'S

For free atoms, the best AO's are SCF (self-consistent field) AO's obtained by solving Fock's equations for the atoms. These are available for a number of atoms in numerical tables, but are unsuitable in this form for our present purpose. A reasonable compromise is offered by Slater's AO's which are given in a simple analytical form. Moreover, it has been pointed out by Slater[2] that SCF AO's can be very closely approximated by a two- or three-term sum of Slater-type AO's.

For molecules, the best AO's are certainly not the Slater-type free-atom AO's, nor even the free-atom SCF AO's; but it should be possible to express the best AO's in this case also as a sum of Slater-type AO's. This justifies the evaluation of all our integrals with Slater-type AO's in which the effective nuclear charges are regarded as free parameters, and which contain only integral powers of r.

We shall use the Slater-type AO's in real form and normalized, namely,

$$(n,l,m)=(2\zeta)^{n+\frac{1}{2}}[(2n)!]^{-\frac{1}{2}}r^{n-1}e^{-\zeta r}S_{l,m}(\theta,\phi), \quad (9)$$

where the functions $S_{l,m}(\theta,\phi)$ are the normalized real spherical harmonics, defined by

$$\begin{aligned} S_{l,0}(\theta,\phi)&=Y_{l,0}(\theta,\phi)=[(2l+1)/4\pi]^{\frac{1}{2}}P_l(\cos\theta),\\ S_{l,|m|}(\theta,\phi)&=(1/\sqrt{2})\{Y_{l,-|m|}(\theta,\phi)+Y_{l,|m|}(\theta,\phi)\}\\ &=\left[\frac{2l+1}{2\pi}\cdot\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}}P_l^{|m|}(\cos\theta)\cos|m|\phi,\\ S_{l,-|m|}(\theta,\phi)&=(1/\sqrt{2})\{Y_{l,-|m|}(\theta,\phi)-Y_{l,|m|}(\theta,\phi)\}\\ &=\left[\frac{2l+1}{2\pi}\cdot\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}}P_l^{|m|}(\cos\theta)\sin|m|\phi. \end{aligned} \quad (10)$$

[2] Reference 10 in the bibliography.

The quantum number m is, of course, restricted by $-l\leqslant m\leqslant l$. The parameter ζ is connected with Slater's effective nuclear charge by $\zeta=Z/n$. The principal quantum number n is restricted by $n\geqslant l+1$, in order that (n,l,m) has no singularity at $r=0$. However, in the following we shall use for purely mathematical purposes also the AO's defined by Eq. (9) for $n=l$.

The quantum numbers l and m have a group-theoretical meaning with reference to the three-dimensional rotation-reflection group O_3, which is the symmetry group of a free atom. In Table I are given the characters of the irreducible representations of this group. The representation symbols $S, P, D, \cdots, S', P', D', \cdots$ are the standard spectroscopic symbols; the notation $D_{g,u}^{(l)}$ is more suitable for purely mathematical purposes.

The AO's (n,l,m) belong to $D_g^{(l)}$ or $D_u^{(l)}$ for l even or odd, respectively; m labels the $2l+1$ different AO's which transform together like $D_g^{(l)}$ or $D_u^{(l)}$ under symmetry operations. It is said that l indicates the *species*, and m the *subspecies* of the AO's *with respect to* O_3.

If two unlike atoms form a heteronuclear diatomic molecule, then the symmetry is reduced to $C_{\infty v}$. The character table of this group is given in Table II. The representation symbols $\Sigma^+, \Sigma^-, \Pi, \Delta, \cdots$ are the standard spectroscopic symbols; A_1, A_2, and E_λ are more suitable for purely mathematical purposes.

The AO's (n,l,m) were defined with reference to a particular choice of the polar axis; we let this polar axis coincide with the diatomic axis. Then all AO's of the type $(n,l,0)$ belong to the representation A_1; and every pair (n,l,λ) and $(n,l,-\lambda)$, $\lambda>0$, belongs to the representation E_λ of $C_{\infty v}$.

The customary notation for the AO's in diatomic molecules with reference to the groups O_3 and $C_{\infty v}$ is ns, $np\sigma$, $np\pi$, $nd\sigma$, $nd\pi$, $nd\delta$, $\cdots$; since this notation does not distinguish between $m=\pm\lambda$, we introduce a completely explicit notation by using π, δ, $\cdots$ for $m>0$ and $\bar{\pi}$, $\bar{\delta}$, $\cdots$ for $m<0$.

CHARGE DISTRIBUTIONS ON ATOMS

The integrals (7) and (8) can be interpreted as electrostatic interactions between charge distributions on the atoms a and b. Namely, Eq. (7) represents the interaction energy of a point charge Z on atom a with the charge distribution $\chi_b\chi_b'$ on atom b; and Eq. (8) represents the interaction energy of the two charge distributions $\chi_a\chi_a'$ and $\chi_b\chi_b'$. Omitting for the moment the subscript a or b, such a charge distribution $\chi\chi'$ has, apart from a numerical factor, the form

$$r^{n+n'-2}e^{-2\bar{\zeta}r}S_{l,m}(\theta,\phi)S_{l',m'}(\theta,\phi),\ \text{with}\ \bar{\zeta}=\tfrac{1}{2}(\zeta+\zeta').$$

Now the product $S_{l,m}(\theta,\phi)S_{l',m'}(\theta,\phi)$ can always be expressed as a finite linear combination of spherical harmonics:

$$S_{l,m}(\theta,\phi)S_{l',m'}(\theta,\phi)=\textstyle\sum_{L,M}a_{L,M}S_{L,M}(\theta,\phi).$$

Hence, it is obvious that the charge distribution $\chi\chi'$ can be written as a linear combination of the following *basic charge distributions*:

$$[N,L,M]=\left(\frac{2L+1}{4\pi}\right)^{\frac{1}{2}}\frac{2^L(2\bar{\zeta})^{N+2}}{(N+L+1)!}\times r^{N-1}e^{-2\bar{\zeta}r}S_{L,M}(\theta,\phi).\quad(11)$$

At a large distance $[N,L,M]$ acts like a multipole of order 2^L and magnitude $\bar{\zeta}^{-L}$. In analogy to the AO's, we shall denote these basic charge distributions by NS, $NP\Sigma$, $NP\Pi$, $NP\bar{\Pi}$, $ND\Sigma$, $ND\Pi$, $ND\bar{\Pi}$, $ND\Delta$, $ND\bar{\Delta}$, $\cdots$.

We give below the explicit expansions in terms of basic charge distributions for all the cases involving s and p electrons:

$$
\left.
\begin{array}{l}
(ns)(n's)=(1+\tau)^{n+\frac{1}{2}}(1-\tau)^{n'+\frac{1}{2}}(n+n')![(2n)!(2n')!]^{-\frac{1}{2}}[n+n'-1,S],\\[2ex]
\left.\begin{array}{r}(ns)(n'p\sigma)\\(ns)(n'p\pi)\\(ns)(n'p\bar{\pi})\end{array}\right\}=\dfrac{1}{2\sqrt{3}}(1+\tau)^{n+\frac{1}{2}}(1-\tau)^{n'+\frac{1}{2}}\dfrac{(n+n'+1)!}{[(2n)!(2n')!]^{\frac{1}{2}}}\left\{\begin{array}{l}[n+n'-1,P\Sigma]\\{}[n+n'-1,P\Pi],\\{}[n+n'-1,P\bar{\Pi}]\end{array}\right.\\[6ex]
\left.\begin{array}{r}(np\sigma)(n'p\sigma)\\(np\sigma)(n'p\pi)\\(np\sigma)(n'p\bar{\pi})\\(np\pi)(n'p\pi)\\(np\pi)(n'p\bar{\pi})\\(np\bar{\pi})(n'p\bar{\pi})\end{array}\right\}=(1+\tau)^{n+\frac{1}{2}}(1-\tau)^{n'+\frac{1}{2}}\dfrac{(n+n'+2)!}{[(2n)!(2n')!]^{\frac{1}{2}}}\left\{\begin{array}{l}
\dfrac{(n+n')!}{(n+n'+2)!}[n+n'-1,S]+\dfrac{1}{10}[n+n'-1,D\Sigma]\\
(\sqrt{3}/20)[n+n'-1,D\Pi]\\
(\sqrt{3}/20)[n+n'-1,D\bar{\Pi}]\\
\dfrac{(n+n')!}{(n+n'+2)!}[n+n'-1,S]\\
\quad-(1/20)[n+n'-1,D\Sigma]+(\sqrt{3}/20)[n+n'-1,D\Delta]\\
(\sqrt{3}/20)[n+n'-1,D\bar{\Delta}]\\
\dfrac{(n+n')!}{(n+n'+2)!}[n+n'-1,S]\\
\quad-(1/20)[n+n'-1,D\Sigma]-(\sqrt{3}/20)[n+n'-1,D\Delta]
\end{array}\right.
\end{array}
\right\}\quad(12)
$$

where

$$\bar{\zeta}=\tfrac{1}{2}(\zeta+\zeta'),\quad \tau=(\zeta-\zeta')/(\zeta+\zeta').\quad(13)$$

In Eqs. (12) the left-hand sides contain ζ and ζ' in the AO's; the right-hand sides contain $\bar{\zeta}$ in the charge distributions.

REDUCTION OF THE NUMBER OF INTEGRALS ON ACCOUNT OF THE MOLECULAR SYMMETRY

The AO's we classified according to the species and subspecies of $C_{\infty v}$, the symmetry group of our two-center problem: σ, π, $\bar{\pi}$, δ, $\bar{\delta}$, $\cdots$.

The one-electron integrals (4), (5), and (6) all have the form $(\chi_a|M|\chi_b)$, where M is a totally symmetrical operator. Group theory provides the following useful theorem concerning such integrals:

Theorem I.—The integral $(\chi_a|M|\chi_b)$ vanishes if χ_a and χ_b belong to (i) different species, (ii) the same species, but different subspecies. Furthermore, the integral is independent of the subspecies.

TABLE II.

$C_{\infty v}$		E	$2C_\phi$	$\infty\sigma_v$
A_1	Σ^+	1	1	1
A_2	Σ^-	1	1	-1
E_1	Π	2	$2\cos\phi$	0
E_2	Δ	2	$2\cos2\phi$	0
$\cdot$		$\cdot$	$\cdot$	$\cdot$
E_λ	$\cdots$	2	$2\cos\lambda\phi$	0

So, for instance, we have

$$(2p\sigma_a|M|3d\pi_b)=0,\quad (2p\pi_a|M|3d\bar{\pi}_b)=0,$$
$$(2p\pi_a|M|3d\pi_b)=(2p\bar{\pi}_a|M|3d\pi_b).$$

If we consider s and p AO's only, the integrals $(\chi_a|M|\chi_b)$ to be evaluated are

$$(ns_a|M|n's_b),\ (ns_a|M|n'p\sigma_b),$$
$$(np\sigma_a|M|n'p\sigma_b),\text{ and }(np\pi_a|M|n'p\pi_b).$$

The basic charge distributions on an atom we also classified according to the species and subspecies of $C_{\infty v}$: Σ, Π, $\bar{\Pi}$, Δ, $\bar{\Delta}$, $\cdots$. If we designate the basic charge distributions in general by Ω_a and Ω_b, then for a coulomb integral

$$[\Omega_a|\Omega_b]=\int\int[\Omega_a(1)\Omega_b(2)/r_{12}]dv_1dv_2 \tag{14}$$

a theorem analogous to that for the one-electron integrals $(\chi_a|M|\chi_b)$ holds:

Theorem II.—The integral $[\Omega_a|\Omega_b]$ vanishes if Ω_a and Ω_b belong to (i) different species, (ii) the same species, but different subspecies. Furthermore, the integral is independent of the subspecies.

The nuclear attraction integrals (7) are similar to the coulomb integrals; instead of the charge distribution Ω_a there occurs a point charge, which we symbolize by a; so we write $Z\int\Omega_b dv/r_a=[a|\Omega_b]$. The point charge a can be considered as a limiting case of a charge distribution Ω_a of S type. Obviously then, $[a|\Omega_b]$ vanishes unless Ω_b is of species Σ.

If we consider again s and p AO's only, we obtain S, P, and D charge distributions. This leads to the following types of basic integrals: $[a|NS_b]$, $[a|NP\Sigma_b]$, $[a|ND\Sigma_b]$; $[NS_a|N'S_b]$, $[NS_a|N'P\Sigma_b]$, $[NS_a|N'D\Sigma_b]$, $[NP\Sigma_a|N'P\Sigma_b]$, $[NP\Sigma_a|N'D\Sigma_b]$, $[ND\Sigma_a|N'D\Sigma_b]$; $[NP\Pi_a|N'P\Pi_b]$, $[NP\Pi_a|N'D\Pi_b]$, $[ND\Pi_a|N'D\Pi_b]$; $[ND\Delta_a|N'D\Delta_b]$.

THE ONE-ELECTRON INTEGRALS $(\chi_a|M|\chi_b)$

The one-electron integrals $(\chi_a|M|\chi_b)$ are obviously functions of the three parameters ζ_a, ζ_b, and R. The final results are most conveniently written down in terms of the parameters ζ, τ, ρ, κ, ρ_a, and ρ_b, defined by

$$\left.\begin{aligned}\zeta&=\tfrac{1}{2}(\zeta_a+\zeta_b),\\ \tau&=(\zeta_a-\zeta_b)/(\zeta_a+\zeta_b),\\ \rho&=\tfrac{1}{2}(\zeta_a+\zeta_b)R;\end{aligned}\right\} \tag{15}$$

$$\left.\begin{aligned}\kappa&=\tfrac{1}{2}(\tau+1/\tau)=(\zeta_a^2+\zeta_b^2)/(\zeta_a^2-\zeta_b^2),\\ \rho_a&=(1+\tau)\rho=\zeta_aR,\\ \rho_b&=(1-\tau)\rho=\zeta_bR.\end{aligned}\right\} \tag{16}$$

We shall consider ζ, τ, ρ as the independent parameters. The original parameters ζ_a, ζ_b, and R are defined in terms of ζ, τ, and ρ by

$$\zeta_a=(1+\tau)\zeta,\quad \zeta_b=(1-\tau)\zeta,\quad R=\rho/\zeta. \tag{17}$$

We proceed now to show how the kinetic energy integrals $(M=-\frac{1}{2}\Delta)$ and the nuclear attraction integrals (6) $(M=Z/r_a)$ can be expressed in terms of the overlap integrals $(M=1)$. Namely, from the definition of the AO's (9) it is easily established that

$$\begin{aligned}-\tfrac{1}{2}\Delta(n,l,m)&\\ =-\tfrac{1}{2}\zeta^2\Big\{&(n,l,m)-2(2n/2n-1)^{\frac{1}{2}}(n-1,l,m)\\ &+\frac{4(n+l)(n-l-1)}{[2n(2n-1)(2n-2)(2n-3)]^{\frac{1}{2}}}(n-2,l,m)\Big\}\end{aligned} \tag{18}$$

and

$$(Z/r)(n,l,m)=2Z\zeta(2n)^{\frac{1}{2}}(2n-1)^{-\frac{1}{2}}(n-1,l,m). \tag{19}$$

Applying Eqs. (18) and (19) for $(n,l,m)\rightarrow(n,l,m)_a$, $\zeta\rightarrow\zeta_a$, $r\rightarrow r_a$, and using Eqs. (17), we find

$$\begin{aligned}\{(n,l,m)_a|&-\tfrac{1}{2}\Delta|(n',l',m)_b\}\\ &=\{-\tfrac{1}{2}\Delta(n,l,m)_a|(n',l',m)_b\}\\ &=-\tfrac{1}{2}\zeta^2(1+\tau)^2\Big[\{(n,l,m)_a|(n',l',m)_b\}\\ &\quad-2(2n)^{\frac{1}{2}}(2n-1)^{-\frac{1}{2}}\{(n-1,l,m)_a|(n',l',m)_b\}\\ &\quad+\frac{4(n+l)(n-l-1)}{[2n(2n-1)(2n-2)(2n-3)]^{\frac{1}{2}}}\\ &\qquad\times\{(n-2,l,m)_a|(n',l',m)_b\}\Big],\end{aligned} \tag{20}$$

$$\begin{aligned}\{(n,l,m)_a|&Z/r_a|(n',l',m)_b\}\\ &=2Z\zeta(1+\tau)[2n(2n-1)]^{-\frac{1}{2}}\\ &\qquad\times\{(n-1,l,m)_a|(n',l',m)_b\}.\end{aligned} \tag{21}$$

Applying Eqs. (20) and (21) for 1s, 2s, and 2p AO's, we obtain the explicit formulas

$$\left.\begin{aligned}&(1s_a|-\tfrac{1}{2}\Delta|1s_b)\\ &\quad=-\tfrac{1}{2}\zeta^2(1+\tau)^2\{(1s_a|1s_b)-2\sqrt{2}(0s_a|1s_b)\},\\ &(1s_a|-\tfrac{1}{2}\Delta|2s_b)\\ &\quad=-\tfrac{1}{2}\zeta^2(1+\tau)^2\{(1s_a|2s_b)-2\sqrt{2}(0s_a|2s_b)\},\\ &(2s_a|-\tfrac{1}{2}\Delta|2s_b)\\ &\quad=-\tfrac{1}{2}\zeta^2(1+\tau)^2\{(2s_a|2s_b)\\ &\qquad-(4/\sqrt{3})(1s_a|2s_b)+(2\sqrt{2}/\sqrt{3})(0s_a|2s_b)\},\\ &(1s_a|-\tfrac{1}{2}\Delta|2p\sigma_b)\\ &\quad=-\tfrac{1}{2}\zeta^2(1+\tau)^2\{(1s_a|2p\sigma_b)-2\sqrt{2}(0s_a|2p\sigma_b)\},\\ &(2s_a|-\tfrac{1}{2}\Delta|2p\sigma_b)\\ &\quad=-\tfrac{1}{2}\zeta^2(1+\tau)^2\{(2s_a|2p\sigma_b)\\ &\qquad-(4/\sqrt{3})(1s_a|2p\sigma_b)+(2\sqrt{2}/\sqrt{3})(0s_a|2p\sigma_b)\},\\ &(2p\sigma_a|-\tfrac{1}{2}\Delta|2p\sigma_b)\\ &\quad=-\tfrac{1}{2}\zeta^2(1+\tau)^2\{(2p\sigma_a|2p\sigma_b)\\ &\qquad-(4/\sqrt{3})(1p\sigma_a|2p\sigma_b)\},\\ &(2p\pi_a|-\tfrac{1}{2}\Delta|2p\pi_b)=-\tfrac{1}{2}\zeta^2(1+\tau)^2\{(2p\pi_a|2p\pi_b)\\ &\qquad-(4/\sqrt{3})(1p\pi_a|2p\pi_b)\},\end{aligned}\right\} \tag{22}$$

and

$$\left.\begin{aligned}
(1s_a|Z/r_a|1s_b)&=\sqrt{2}Z\zeta(1+\tau)(0s_a|1s_b),\\
(1s_a|Z/r_a|2s_b)&=\sqrt{2}Z\zeta(1+\tau)(0s_a|2s_b),\\
(2s_a|Z/r_a|1s_b)&=(1/\sqrt{3})Z\zeta(1+\tau)(1s_a|1s_b),\\
(2s_a|Z/r_a|2s_b)&=(1/\sqrt{3})Z\zeta(1+\tau)(1s_a|2s_b),\\
(1s_a|Z/r_a|2p\sigma_b)&=\sqrt{2}Z\zeta(1+\tau)(0s_a|2p\sigma_b),\\
(2s_a|Z/r_a|2p\sigma_b)&=(1/\sqrt{3})Z\zeta(1+\tau)(1s_a|2p\sigma_b),\\
(2p\sigma_a|Z/r_a|1s_b)&=(1/\sqrt{3})Z\zeta(1+\tau)(1p\sigma_a|1s_b),\\
(2p\sigma_a|Z/r_a|2s_b)&=(1/\sqrt{3})Z\zeta(1+\tau)(1p\sigma_a|2s_b),\\
(2p\sigma_a|Z/r_a|2p\sigma_b)&=(1/\sqrt{3})Z\zeta(1+\tau)(1p\sigma_a|2p\sigma_b),\\
(2p\pi_a|Z/r_a|2p\pi_b)&=(1/\sqrt{3})Z\zeta(1+\tau)(1p\pi_a|2p\pi_b).
\end{aligned}\right\}\quad(23)$$

In view of Eqs. (22) and (23) we now need explicit expressions for the overlap integrals only. Our overlap integrals, except those which involve the $0s$ and $1p$ AO's, have been evaluated by Mulliken, Rieke, Orloff, and Orloff.[2] Their formulas are given in terms of the functions

$$\left.\begin{aligned}
A_n(\rho)&=\int_1^\infty \xi^n e^{-\rho\xi}d\xi=n!\rho^{-n-1}e^{-\rho}\sum_{k=0}^{n}\rho^k/k!,\\
B_n(\tau\rho)&=\int_{-1}^{1}\eta^n e^{-\tau\rho\eta}d\eta\\
&=-A_n(\tau\rho)-(-1)^nA_n(-\tau\rho).
\end{aligned}\right\}\quad(24)$$

Note that in Eqs. (24) the definition of $A_n(\rho)$ by means of the integral only applies for $\rho>0$, since otherwise the integral diverges.

The cases $\tau=0$ and $\rho=0$ had to be dealt with separately, since if one puts $\tau=0$ or $\rho=0$ in the general formulas, one obtains the difference of two infinite terms, and the limits for $\tau\to0$ and $\rho\to0$ have to be calculated.

For those overlap integrals which were given by Mulliken *et al.* we derived our final formulas in terms of the six parameters (15) and (16) by substituting for $A_n(\rho)$ and $B_n(\tau\rho)$ the explicit expressions given by Eqs. (24); the remaining integrals involving the $0s$ and $1p$ AO's we evaluated in the same manner. The results are

$$\left.\begin{aligned}
(0s_a|1s_b)&=[(1-\tau^2)^{\frac12}/\sqrt{2}\tau\rho][-(1-\kappa)e^{-\rho_a}+\{(1-\kappa)+\rho_b\}e^{-\rho_b}],\\
(1s_a|1s_b)&=[(1-\tau^2)^{\frac12}/\tau\rho][-(1-\kappa)\{2(1+\kappa)+\rho_a\}e^{-\rho_a}+(1+\kappa)\{2(1-\kappa)+\rho_b\}e^{-\rho_b}],\\
(0s_a|2s_b)&=[(1-\tau^2)^{\frac12}/6^{\frac12}\tau\rho][-(1-\kappa)(1-2\kappa)e^{-\rho_a}+\{(1-\kappa)(1-2\kappa)+2(1-\kappa)\rho_b+\rho_b^2\}e^{-\rho_b}],\\
(1s_a|2s_b)&=[(1-\tau^2)^{\frac12}/\sqrt{3}\tau\rho][-(1-\kappa)\{2(1+\kappa)(2-3\kappa)+(1-2\kappa)\rho_a\}e^{-\rho_a}\\
&\qquad+(1+\kappa)\{2(1-\kappa)(2-3\kappa)+4(1-\kappa)\rho_b+\rho_b^2\}e^{-\rho_b}],\\
(2s_a|2s_b)&=[(1-\tau^2)^{\frac12}/3\tau\rho][-(1-\kappa)\{2(1+\kappa)(7-12\kappa^2)+4(1+\kappa)(2-3\kappa)\rho_a+(1-2\kappa)\rho_a^2\}e^{-\rho_a}\\
&\qquad+(1+\kappa)\{2(1-\kappa)(7-12\kappa^2)+4(1-\kappa)(2+3\kappa)\rho_b+(1+2\kappa)\rho_b^2\}e^{-\rho_b}],\\
(0s_a|2p\sigma_b)&=[(1+\tau)/(1-\tau)]^{\frac12}(1/\sqrt{2}\tau\rho^2)[-2(1-\kappa)^2(1+\rho_a)e^{-\rho_a}+\{2(1-\kappa)^2(1+\rho_b)+2(1-\kappa)\rho_b^2+\rho_b^3\}e^{-\rho_b}],\\
(1s_a|2p\sigma_b)&=[(1+\tau)/(1-\tau)]^{\frac12}(1/\tau\rho^2)[-(1-\kappa)^2\{6(1+\kappa)(1+\rho_a)+2\rho_a^2\}e^{-\rho_a}\\
&\qquad+(1+\kappa)\{6(1-\kappa)^2(1+\rho_b)+4(1-\kappa)\rho_b^2+\rho_b^3\}e^{-\rho_b}],\\
(2s_a|2p\sigma_b)&=[(1+\tau)/(1-\tau)]^{\frac12}(1/\sqrt{3}\tau\rho^2)[-(1-\kappa)^2\{6(1+\kappa)(3+4\kappa)(1+\rho_a)+2(5+6\kappa)\rho_a^2+2\rho_a^3\}e^{-\rho_a}\\
&\qquad+(1+\kappa)\{6(1-\kappa)^2(3+4\kappa)(1+\rho_b)+4(1-\kappa)(2+3\kappa)\rho_b^2+(1+2\kappa)\rho_b^3\}e^{-\rho_b}],\\
(1p\sigma_a|1s_b)&=[(1-\tau)/(1+\tau)]^{\frac12}(\sqrt{3}/\tau\rho^2)[-(1-\kappa)\{2(1+\kappa)(1+\rho_a)+\rho_a^2\}e^{-\rho_a}\\
&\qquad+(1+\kappa)\{2(1-\kappa)(1+\rho_b)+\rho_b^2\}e^{-\rho_b}],\\
(1p\sigma_a|2s_b)&=[(1-\tau)/(1+\tau)]^{\frac12}(1/\tau\rho^2)[-(1-\kappa)\{2(1+\kappa)(2-3\kappa)(1+\rho_a)+(1-2\kappa)\rho_a^2\}e^{-\rho_a}\\
&\qquad+(1+\kappa)\{2(1-\kappa)(2-3\kappa)(1+\rho_b)+(3-4\kappa)\rho_b^2+\rho_b^3\}e^{-\rho_b}],\\
(1p\sigma_a|2p\sigma_b)&=[\sqrt{3}/(1-\tau^2)^{\frac12}\tau\rho^3][-(1-\kappa)^2\{12(1+\kappa)(1+\rho_a+\tfrac12\rho_a^2)+2\rho_a^3\}e^{-\rho_a}\\
&\qquad+(1+\kappa)\{12(1-\kappa)^2(1+\rho_b+\tfrac12\rho_b^2)+(3-4\kappa)\rho_b^3+\rho_b^4\}e^{-\rho_b}],\\
(2p\sigma_a|2p\sigma_b)&=[1/(1-\tau^2)^{\frac12}\tau\rho^3][-(1-\kappa)^2\{48(1+\kappa)^2(1+\rho_a+\tfrac12\rho_a^2)+2(5+6\kappa)\rho_a^3+2\rho_a^4\}e^{-\rho_a}\\
&\qquad+(1+\kappa)^2\{48(1-\kappa)^2(1+\rho_b+\tfrac12\rho_b^2)+2(5-6\kappa)\rho_b^3+2\rho_b^4\}e^{-\rho_b}],\\
(1p\pi_a|2p\pi_b)&=[\sqrt{3}/(1-\tau^2)^{\frac12}\tau\rho^3][-(1-\kappa)^2\{6(1+\kappa)(1+\rho_a)+2\rho_a^2\}e^{-\rho_a}\\
&\qquad+(1+\kappa)\{6(1-\kappa)^2(1+\rho_b)+4(1-\kappa)\rho_b^2+\rho_b^3\}e^{-\rho_b}],\\
(2p\pi_a|2p\pi_b)&=[1/(1-\tau^2)^{\frac12}\tau\rho^3][-(1-\kappa)^2\{24(1+\kappa)^2(1+\rho_a)+12(1+\kappa)\rho_a^2+2\rho_a^3\}e^{-\rho_a}\\
&\qquad+(1+\kappa)^2\{24(1-\kappa)^2(1+\rho_b)+12(1-\kappa)\rho_b^2+2\rho_b^3\}e^{-\rho_b}];
\end{aligned}\right\}\quad(25)$$

$$
\left.\begin{aligned}
&\tau=0,\\
&(0s_a|1s_b)=(1/\sqrt{2})(1+\rho)e^{-\rho},\\
&(1s_a|1s_b)=(1+\rho+\tfrac{1}{3}\rho^2)e^{-\rho},\\
&(0s_a|2s_b)=6^{-\frac{1}{2}}(1+\rho+\tfrac{2}{3}\rho^2)e^{-\rho},\\
&(1s_a|2s_b)=\tfrac{1}{2}\sqrt{3}[1+\rho+(4/9)\rho^2+(1/9)\rho^3]e^{-\rho},\\
&(2s_a|2s_b)=[1+\rho+(4/9)\rho^2+(1/9)\rho^3+(1/45)\rho^4]e^{-\rho},\\
&(0s_a|2p\sigma_b)=\tfrac{1}{3}\sqrt{2}\rho(1+\rho)e^{-\rho},\\
&(1s_a|2p\sigma_b)=\tfrac{1}{2}\rho(1+\rho+\tfrac{1}{3}\rho^2)e^{-\rho},\\
&(2s_a|2p\sigma_b)=(1/2\sqrt{3})\rho[1+\rho+(7/15)\rho^2+(2/15)\rho^3]e^{-\rho},\\
&(1p\sigma_a|1s_b)=(1/\sqrt{3})\rho(1+\rho)e^{-\rho},\\
&(1p\sigma_a|2s_b)=\tfrac{1}{6}\rho(1+\rho+\rho^2)e^{-\rho},\\
&(1p\sigma_a|2p\sigma_b)=\tfrac{1}{2}\sqrt{3}(-1-\rho+\tfrac{1}{3}\rho^3)e^{-\rho},\\
&(2p\sigma_a|2p\sigma_b)=[-1-\rho-\tfrac{1}{5}\rho^2+(2/15)\rho^3+(1/15)\rho^4]e^{-\rho},\\
&(1p\pi_a|2p\pi_b)=\tfrac{1}{2}\sqrt{3}(1+\rho+\tfrac{1}{3}\rho^2)e^{-\rho},\\
&(2p\pi_a|2p\pi_b)=[1+\rho+\tfrac{2}{5}\rho^2+(1/15)\rho^3]e^{-\rho};
\end{aligned}\right\}\quad(25\text{a})
$$

$$
\left.\begin{aligned}
&\rho=0,\\
&(0s_a|1s_b)=(1/\sqrt{2})(1+\tau)^{\frac{1}{2}}(1-\tau)^{\frac{3}{2}},\\
&(1s_a|1s_b)=(1+\tau)^{\frac{3}{2}}(1-\tau)^{\frac{3}{2}},\\
&(0s_a|2s_b)=6^{-\frac{1}{2}}(1+\tau)^{\frac{1}{2}}(1-\tau)^{5/2},\\
&(1s_a|2s_b)=\tfrac{1}{2}\sqrt{3}(1+\tau)^{\frac{3}{2}}(1-\tau)^{5/2},\\
&(2s_a|2s_b)=(1+\tau)^{5/2}(1-\tau)^{5/2},\\
&(0s_a|2p\sigma_b)=(1s_a|2p\sigma_b)=(2s_a|2p\sigma_b)\\
&\qquad=(1p\sigma_a|1s_b)=(1p\sigma_a|2s_b)=0,\\
&-(1p\sigma_a|2p\sigma_b)=(1p\pi_a|2p\pi_b)\\
&\qquad=\tfrac{1}{2}\sqrt{3}(1+\tau)^{\frac{3}{2}}(1-\tau)^{5/2},\\
&-(2p\sigma_a|2p\sigma_b)=(2p\pi_a|2p\pi_b)\\
&\qquad=(1+\tau)^{5/2}(1-\tau)^{5/2}.
\end{aligned}\right\}\quad(25\text{b})
$$

THE NUCLEAR ATTRACTION INTEGRALS $(\chi_b|Z/r_a|\chi_b')$ AND THE COULOMB INTEGRALS $(\chi_a\chi_b|1/r|\chi_a'\chi_b')$

The nuclear attraction integrals (7) and the coulomb integrals (8) we shall evaluate making use of the charge distributions (12). We shall use the following notation which refers directly to the charge distributions:

$$
\left.\begin{aligned}
(\chi_b|Z/r_a|\chi_b')&=[a|\chi_b\chi_b']Z,\\
(\chi_a\chi_b|1/r|\chi_a'\chi_b')&=[\chi_a\chi_a'|\chi_b\chi_b'].
\end{aligned}\right\}\quad(26)
$$

From Eqs. (12) we find for all the possible charge distributions arising from $1s$, $2s$, and $2p$ AO's the following expansions in terms of the basic charge distributions (11):

$$
\left.\begin{aligned}
&(1s)(1s')=(1+\tau)^{\frac{3}{2}}(1-\tau)^{\frac{3}{2}}[1S],\\
&(1s)(2s)=\tfrac{1}{2}\sqrt{3}(1+\tau)^{\frac{3}{2}}(1-\tau)^{5/2}[2S],\\
&(2s)(2s')=(1+\tau)^{5/2}(1-\tau)^{5/2}[3S],\\
&\left.\begin{matrix}(1s)(2p\sigma)\\(1s)(2p\pi)\\(1s)(2p\bar{\pi})\end{matrix}\right\}=(1+\tau)^{\frac{3}{2}}(1-\tau)^{5/2}\left\{\begin{matrix}[2P\Sigma]\\ [2P\Pi],\\ [2P\bar{\Pi}]\end{matrix}\right.\\
&\left.\begin{matrix}(2s)(2p\sigma)\\(2s)(2p\pi)\\(2s)(2p\bar{\pi})\end{matrix}\right\}=(5/2\sqrt{3})(1+\tau)^{5/2}(1-\tau)^{5/2}\left\{\begin{matrix}[3P\Sigma]\\ [3P\Pi],\\ [3P\bar{\Pi}]\end{matrix}\right.\\
&\left.\begin{matrix}(2p\sigma)(2p\sigma')\\(2p\sigma)(2p\pi')\\(2p\sigma)(2p\bar{\pi}')\\(2p\pi)(2p\pi')\\(2p\pi)(2p\bar{\pi}')\\(2p\bar{\pi})(2p\bar{\pi}')\end{matrix}\right\}=(1+\tau)^{5/2}(1-\tau)^{5/2}\left\{\begin{matrix}[3S]+3[3D\Sigma]\\ \tfrac{3}{2}\sqrt{3}[3D\Pi]\\ \tfrac{3}{2}\sqrt{3}[3D\bar{\Pi}]\\ [3S]-\tfrac{3}{2}[3D\Sigma]+\tfrac{3}{2}\sqrt{3}[3D\Delta]\\ \tfrac{3}{2}\sqrt{3}[3D\bar{\Delta}]\\ [3S]-\tfrac{3}{2}[3D\Sigma]-\tfrac{3}{2}\sqrt{3}[3D\Delta]\end{matrix}\right.
\end{aligned}\right\}\quad(27)
$$

Considering Theorem II and using Eqs. (27), we find for the nonvanishing nuclear attraction integrals the following expansions in terms of basic integrals:

$$
\left.\begin{aligned}
&[a|1s_b1s_b']=(\tfrac{3}{2},\tfrac{3}{2})[a|1S_b],\\
&[a|1s_b2s_b]=\tfrac{1}{2}\sqrt{3}(\tfrac{3}{2},5/2)[a|2S_b],\\
&[a|2s_b2s_b']=(5/2,5/2)[a|3S_b],\\
&[a|1s_b2p\sigma_b]=(\tfrac{3}{2},5/2)[a|2P\Sigma_b],\\
&[a|2s_b2p\sigma_b]=(5/2\sqrt{3})(5/2,5/2)[a|3P\Sigma_b],\\
&[a|2p\sigma_b2p\sigma_b']=(5/2,5/2)\{[a|3S_b]+3[a|3D\Sigma_b]\},\\
&[a|2p\pi_b2p\pi_b']=[a|2p\bar{\pi}_b2p\bar{\pi}_b']\\
&\qquad=(5/2,5/2)\{[a|3S_b]-\tfrac{3}{2}[a|3D\Sigma_b]\},
\end{aligned}\right\}\quad(28)
$$

where (β,β') is an abbreviation for $(1+\tau)^{\beta}(1-\tau)^{\beta'}$.

In Eqs. (28) the left-hand sides contain the parameters ζ and ζ' in the AO's; the right-hand sides contain the parameter $\bar{\zeta}$ defined by Eq. (13).

In the coulomb integrals we have to deal with two charge distributions $\chi_a\chi_a'$ and $\chi_b\chi_b'$. We define accordingly

$$
\left.\begin{aligned}
\bar{\zeta}_a&=\tfrac{1}{2}(\zeta_a+\zeta_a'), & \tau_a&=(\zeta_a-\zeta_a')/(\zeta_a+\zeta_a'),\\
\bar{\zeta}_b&=\tfrac{1}{2}(\zeta_b+\zeta_b'), & \tau_b&=(\zeta_b-\zeta_b')/(\zeta_b+\zeta_b').
\end{aligned}\right\}\quad(29)
$$

Considering Theorem II and using Eqs. (26), we find for the nonvanishing coulomb integrals the following expansions in terms of basic integrals:

$$
\begin{aligned}
&[1s_a1s_a'|1s_b1s_b']=(\tfrac{3}{2},\tfrac{3}{2},\tfrac{3}{2},\tfrac{3}{2})[1S_a|1S_b],\\
&[1s_a1s_a'|1s_b2s_b]=\tfrac{1}{2}\sqrt{3}(\tfrac{3}{2},\tfrac{3}{2},\tfrac{3}{2},5/2)[1S_a|2S_b],\\
&[1s_a1s_a'|2s_b2s_b']=(\tfrac{3}{2},\tfrac{3}{2},5/2,5/2)[1S_a|3S_b],\\
&[1s_a2s_a|1s_b2s_b]=\tfrac{3}{4}(\tfrac{3}{2},5/2,\tfrac{3}{2},5/2)[2S_a|2S_b],\\
&[1s_a2s_a|2s_b2s_b']=\tfrac{1}{2}\sqrt{3}(\tfrac{3}{2},5/2,5/2,5/2)[2S_a|3S_b],\\
&[2s_a2s_a'|2s_b2s_b']=(5/2,5/2,5/2,5/2)[3S_a|3S_b],\\
&[1s_a1s_a'|1s_b2p\sigma_b]=(\tfrac{3}{2},\tfrac{3}{2},\tfrac{3}{2},5/2)[1S_a|2P\Sigma_b],\\
&[1s_a1s_a'|2s_b2p\sigma_b]=(5/2\sqrt{3})(\tfrac{3}{2},\tfrac{3}{2},5/2,5/2)[1S_a|3P\Sigma_b],\\
&[1s_a2s_a|1s_b2p\sigma_b]=\tfrac{1}{2}\sqrt{3}(\tfrac{3}{2},5/2,\tfrac{3}{2},5/2)[2S_a|2P\Sigma_b],\\
&[1s_a2s_a|2s_b2p\sigma_b]=(5/4)(\tfrac{3}{2},5/2,5/2,5/2)[2S_a|3P\Sigma_b],\\
&[2s_a2s_a'|1s_b2p\sigma_b]=(5/2,5/2,\tfrac{3}{2},5/2)[3S_a|2P\Sigma_b],\\
&[2s_a2s_a'|2s_b2p\sigma_b]=(5/2\sqrt{3})(5/2,5/2,5/2,5/2)[3S_a|3P\Sigma_b],\\
&[1s_a1s_a'|2p\sigma_b2p\sigma_b']=(\tfrac{3}{2},\tfrac{3}{2},5/2,5/2)\{[1S_a|3S_b]+3[1S_a|3D\Sigma_b]\},\\
&[1s_a1s_a'|2p\pi_b2p\pi_b']=[1s_a1s_a'|2p\bar{\pi}_b2p\bar{\pi}_b']=(\tfrac{3}{2},\tfrac{3}{2},5/2,5/2)\{[1S_a|3S_b]-\tfrac{3}{2}[1S_a|3D\Sigma_b]\},\\
&[1s_a2s_a|2p\sigma_b2p\sigma_b']=\tfrac{1}{2}\sqrt{3}(\tfrac{3}{2},5/2,5/2,5/2)\{[2S_a|3S_b]+3[2S_a|3D\Sigma_b]\},\\
&[1s_a2s_a|2p\pi_b2p\pi_b']=[1s_a2s_a|2p\bar{\pi}_b2p\bar{\pi}_b']=\tfrac{1}{2}\sqrt{3}(\tfrac{3}{2},5/2,5/2,5/2)\{[2S_a|3S_b]-\tfrac{3}{2}[2S_a|3D\Sigma_b]\},\\
&[2s_a2s_a'|2p\sigma_b2p\sigma_b']=(5/2,5/2,5/2,5/2)\{[3S_a|3S_b]+3[3S_a|3D\Sigma_b]\},\\
&[2s_a2s_a'|2p\pi_b2p\pi_b']=[2s_a2s_a|2p\bar{\pi}_b2p\bar{\pi}_b']=(5/2,5/2,5/2,5/2)\{[3S_a|3S_b]-\tfrac{3}{2}[3S_a|3D\Sigma_b]\},\\
&[1s_a2p\sigma_a|1s_b2p\sigma_b]=(\tfrac{3}{2},5/2,\tfrac{3}{2},5/2)[2P\Sigma_a|2P\Sigma_b],\\
&[1s_a2p\sigma_a|2s_b2p\sigma_b]=(5/2\sqrt{3})(\tfrac{3}{2},5/2,5/2,5/2)[2P\Sigma_a|3P\Sigma_b],\\
&[2s_a2p\sigma_a|2s_b2p\sigma_b]=(25/12)(5/2,5/2,5/2,5/2)[3P\Sigma_a|3P\Sigma_b],\\
&[1s_a2p\pi_a|1s_b2p\pi_b]=[1s_a2p\bar{\pi}_a|1s_b2p\bar{\pi}_b]=(\tfrac{3}{2},5/2,\tfrac{3}{2},5/2)[2P\Pi_a|2P\Pi_b],\\
&[1s_a2p\pi_a|2s_b2p\pi_b]=[1s_a2p\bar{\pi}_a|2s_b2p\bar{\pi}_b]=(5/2\sqrt{3})(\tfrac{3}{2},5/2,5/2,5/2)[2P\Pi_a|3P\Pi_b],\\
&[2s_a2p\pi_a|2s_b2p\pi_b]=[2s_a2p\bar{\pi}_a|2s_b2p\bar{\pi}_b]=(25/12)(5/2,5/2,5/2,5/2)[3P\Pi_a|3P\Pi_b],\\
&[1s_a2p\sigma_a|2p\sigma_b2p\sigma_b']=(\tfrac{3}{2},5/2,5/2,5/2)\{[2P\Sigma_a|3S_b]+3[2P\Sigma_a|3D\Sigma_b]\},\\
&[1s_a2p\sigma_a|2p\pi_b2p\pi_b']=[1s_a2p\sigma_a|2p\bar{\pi}_b2p\bar{\pi}_b']=(\tfrac{3}{2},5/2,5/2,5/2)\{[2P\Sigma_a|3S_b]-\tfrac{3}{2}[2P\Sigma_a|3D\Sigma_b]\},\\
&[2s_a2p\sigma_a|2p\sigma_b2p\sigma_b']=(5/2\sqrt{3})(5/2,5/2,5/2,5/2)\{[3P\Sigma_a|3S_b]+3[3P\Sigma_a|3D\Sigma_b]\},\\
&[2s_a2p\sigma_a|2p\pi_b2p\pi_b']=[2s_a2p\sigma_a|2p\bar{\pi}_b2p\bar{\pi}_b']=(5/2\sqrt{3})(5/2,5/2,5/2,5/2)\{[3P\Sigma_a|3S_b]-\tfrac{3}{2}[3P\Sigma_a|3D\Sigma_b]\},\\
&[1s_a2p\pi_a|2p\sigma_b2p\pi_b']=[1s_a2p\bar{\pi}_a|2p\sigma_b2p\bar{\pi}_b']=\tfrac{3}{2}\sqrt{3}(\tfrac{3}{2},5/2,5/2,5/2)[2P\Pi_a|3D\Pi_b],\\
&[2s_a2p\pi_a|2p\sigma_b2p\pi_b']=[2s_a2p\bar{\pi}_a|2p\sigma_b2p\bar{\pi}_b']=(15/4)(5/2,5/2,5/2,5/2)[3P\Pi_a|3D\Pi_b],\\
&[2p\sigma_a2p\sigma_a'|2p\sigma_b2p\sigma_b']=(5/2,5/2,5/2,5/2)\{[3S_a|3S_b]+3[3S_a|3D\Sigma_b]+3[3D\Sigma_a|3S_b]+9[3D\Sigma_a|3D\Sigma_b]\},\\
&[2p\sigma_a2p\sigma_a'|2p\pi_b2p\pi_b']=[2p\sigma_a2p\sigma_a'|2p\bar{\pi}_b2p\bar{\pi}_b']\\
&\qquad=(5/2,5/2,5/2,5/2)\{[3S_a|3S_b]-\tfrac{3}{2}[3S_a|3D\Sigma_b]+3[3D\Sigma_a|3S_b]-(9/2)[3D\Sigma_a|3D\Sigma_b]\},\\
&[2p\pi_a2p\pi_a'|2p\pi_b2p\pi_b']=[2p\bar{\pi}_a2p\bar{\pi}_a'|2p\bar{\pi}_b2p\bar{\pi}_b']=(5/2,5/2,5/2,5/2)\{[3S_a|3S_b]-\tfrac{3}{2}[3S_a|3D\Sigma_b]\\
&\qquad-\tfrac{3}{2}[3D\Sigma_a|3S_b]+(9/4)[3D\Sigma_a|3D\Sigma_b]+(27/4)[3D\Delta_a|3D\Delta_b]\},\\
&[2p\pi_a2p\pi_a'|2p\bar{\pi}_b2p\bar{\pi}_b']=(5/2,5/2,5/2,5/2)\{[3S_a|3S_b]-\tfrac{3}{2}[3S_a|3D\Sigma_b]-\tfrac{3}{2}[3D\Sigma_a|3S_b]\\
&\qquad+(9/4)[3D\Sigma_a|3D\Sigma_b]-(27/4)[3D\Delta_a|3D\Delta_b]\},\\
&[2p\pi_a2p\bar{\pi}_a'|2p\pi_b2p\bar{\pi}_b']=(27/4)(5/2,5/2,5/2,5/2)[3D\Delta_a|3D\Delta_b],\\
&[2p\sigma_a2p\pi_a'|2p\sigma_b2p\pi_b']=(27/4)(5/2,5/2,5/2,5/2)[3D\Pi_a|3D\Pi_b],
\end{aligned}
\tag{30}
$$

where $(\alpha, \alpha', \beta, \beta')$ is an abbreviation for $(1+\tau_a)^\alpha(1-\tau_a)^{\alpha'}(1+\tau_b)^\beta(1-\tau_b)^{\beta'}$.

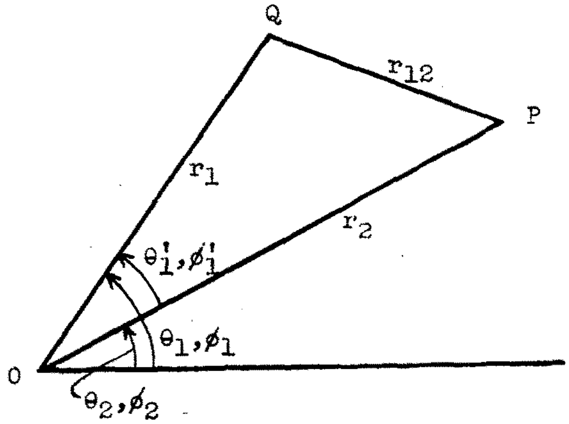

FIG. 1. Diagram of notation.

We turn now to the evaluation of the basic integrals. The integrals $[a|\Omega_b]$ are functions of $\bar{\zeta}$ and R; we replace this set of parameters by $\bar{\zeta}$ and $\rho=\bar{\zeta}R$. The integrals are easily evaluated by introducing the spheroidal coordinates (2); they appear then in terms of $A_n(\rho)$ and $B_n(-\rho)$, the latter of which we convert to $B_n(\rho)$ by means of $B_n(-\rho)=(-1)^n B_n(\rho)$. Writing out $A_n(\rho)$ and $B_n(\rho)$, we obtain the final formulas:

$$\left.\begin{aligned}
[a|1S_b]&=(\bar{\zeta}/\rho)\{1-(1+\rho)e^{-2\rho}\},\\
[a|2S_b]&=(\bar{\zeta}/\rho)\{1-[1+(4/3)\rho+\tfrac{2}{3}\rho^2]e^{-2\rho}\},\\
[a|3S_b]&=(\bar{\zeta}/\rho)\{1-(1+\tfrac{3}{2}\rho+\rho^2+\tfrac{1}{3}\rho^3)e^{-2\rho}\},\\
[a|2P\Sigma_b]&=(\bar{\zeta}/\rho^2)\{1-(1+2\rho+2\rho^2+\rho^3)e^{-2\rho}\},\\
[a|3P\Sigma_b]&=(\bar{\zeta}/\rho^2)\{1-[1+2\rho+2\rho^2+(6/5)\rho^3\\
&\qquad+\tfrac{2}{5}\rho^4]e^{-2\rho}\},\\
[a|3D\Sigma_b]&=(\bar{\zeta}/\rho^3)\{1-[1+2\rho+2\rho^2+(4/3)\rho^3\\
&\qquad+\tfrac{2}{3}\rho^4+(2/9)\rho^5]e^{-2\rho}\}.
\end{aligned}\right\}\quad(31)$$

The integrals

$$[\Omega_a|\Omega_b]=\int\int[\Omega_a(1)\Omega_b(2)/r_{12}]dv_1dv_2$$

involve two volume integrations. The integration over the coordinates of one electron, say 1, amounts to calculating the potential of the corresponding charge distribution. These potentials can be found from the integrals (31) in the following manner.

Let the charge distribution of which we wish to know the potential be (see Eq. (11))

$$[N, L, M]=F(r)S_{L,M}(\theta,\phi).$$

Then the potential for electron 2 at the point P due to the charge distribution $[N, L, M]$ of electron 1 is given by (see Fig. 1)

$$U_{NLM}(r_2,\theta_2,\phi_2)=\int\int[F(r_1)S_{L,M}(\theta_1,\phi_1)/r_{12}]r_1^2dr_1d\omega_1,$$

where $d\omega_1$ is the infinitesimal solid angle. The angles θ_1, ϕ_1, and θ_2, ϕ_2 are defined with reference to the same polar axis and zero meridian. We now carry out a transformation of the integration variables $\theta_1,\phi_1\rightarrow\theta_1',\phi_1'$, so that the new polar axis coincides with OP. Since the spherical harmonics $S_{L,M}$ are the basis of an irreducible representation of the rotation-reflection group O_3, we have

$$S_{L,M}(\theta_1,\phi_1)=\sum_{M'}c_{M'}S_{L,M'}(\theta_1',\phi_1'),$$

where the $c_{M'}$ are constants as far as the integration is concerned, but may depend on θ_2, ϕ_2, L, M. Because of the orthonormality of the spherical harmonics these $c_{M'}$ are given by

$$c_{M'}=\int S_{L,M}(\theta_1,\phi_1)S_{L,M'}(\theta_1',\phi_1')d\omega_1'.$$

It is further easily seen that

$$d\omega_1=d\omega_1'.$$

Carrying out the transformation, we find

$$U_{NLM}(r_2,\theta_2,\phi_2)$$
$$=\sum_{M'}c_{M'}\int[F(r_1)S_{L,M'}(\theta_1',\phi_1')/r_{12}]r_1^2dr_1d\omega_1'.$$

Now the integrals involving $S_{L,M'}(\theta_1',\phi_1')$ are just the nuclear attraction integrals $[a|\Omega_b]$ if we identify a with P, b with O, and R with r_2. We have seen that these integrals vanish unless Ω_b is of species Σ, that is, $M'=0$. Hence, we have

$$U_{NLM}(r_2,\theta_2,\phi_2)=c_0[a|NL0_b]_{\rho=\bar{\zeta}r_2}.$$

The constant c_0 we find from

$$c_0=\int S_{L,M}(\theta_1,\phi_1)S_{L,0}(\theta_1',\phi_1')d\omega_1'.$$

This integral we evaluate by transforming θ_1', ϕ_1' back to θ_1, ϕ_1. Now

$$S_{L,0}(\theta_1',\phi_1')=[(2L+1)/4\pi]^{\frac{1}{2}}P_L(\cos\theta_1').$$

Since θ_1' is the angle POQ, we can make use of the addition theorem for the Legendre polynomials:

$$P_L(\cos\theta_1')$$
$$=[4\pi/(2L+1)]\sum_{M'}S_{L,M'}(\theta_2,\phi_2)S_{L,M'}(\theta_1,\phi_1),$$

so that

$$c_0=\sum_{M'}[4\pi/(2L+1)]^{\frac{1}{2}}S_{L,M'}(\theta_2,\phi_2)$$
$$\times\int S_{L,M}(\theta_1,\phi_1)S_{L,M'}(\theta_1,\phi_1)d\omega_1$$
$$=[4\pi/(2L+1)]^{\frac{1}{2}}S_{L,M}(\theta_2,\phi_2);$$

hence, we have

$$U_{NLM}(r,\theta,\phi)=[4\pi/(2L+1)]^{\frac{1}{2}}S_{L,M}(\theta,\phi)[a|NLO_b]_{\rho=\sigma},\quad(32)$$

where $\sigma=\bar{\zeta}r$.

Explicitly, we find for the potentials of the charge distributions arising from $1s$, $2s$, and $2p$ AO's

$$\left.\begin{array}{l}
U_{1S}=(\bar{\zeta}/\sigma)\{1-(1+\sigma)e^{-2\sigma}\},\\
U_{2S}=(\bar{\zeta}/\sigma)\{1-[1+(4/3)\sigma+\frac{2}{3}\sigma^2]e^{-2\sigma}\},\\
U_{3S}=(\bar{\zeta}/\sigma)\{1-(1+\frac{3}{2}\sigma+\sigma^2+\frac{1}{3}\sigma^3)e^{-2\sigma}\},\\
U_{\left\{\begin{smallmatrix}2P\Sigma\\2P\Pi\\2P\bar{\Pi}\end{smallmatrix}\right\}}=(\bar{\zeta}/\sigma^2)\{1-(1+2\sigma+2\sigma^2+\sigma^3)e^{-2\sigma}\}\left\{\begin{array}{l}\cos\theta\\ \sin\theta\,\cos\phi,\\ \sin\theta\,\sin\phi\end{array}\right.\\
U_{\left\{\begin{smallmatrix}3P\Sigma\\3P\Pi\\3P\bar{\Pi}\end{smallmatrix}\right\}}=(\bar{\zeta}/\sigma^2)\{1-[(1+2\sigma+2\sigma^2+(6/5)\sigma^3+\frac{2}{5}\sigma^4]e^{-2\sigma}\}\left\{\begin{array}{l}\cos\theta\\ \sin\theta\,\cos\phi,\\ \sin\theta\,\sin\phi\end{array}\right.\\
U_{\left\{\begin{smallmatrix}3D\Sigma\\3D\Pi\\3D\bar{\Pi}\\3D\Delta\\3D\bar{\Delta}\end{smallmatrix}\right\}}=(\bar{\zeta}/\sigma^3)\{1-[1+2\sigma+2\sigma^2+(4/3)\sigma^3+\frac{2}{3}\sigma^4+(2/9)\sigma^5]e^{-2\sigma}\}\left\{\begin{array}{l}\frac{3}{2}\cos^2\theta-\frac{1}{2}\\ \sqrt{3}\,\cos\theta\,\sin\theta\,\cos\phi\\ \sqrt{3}\,\cos\theta\,\sin\theta\,\sin\phi\\ (\sqrt{3}/2)\,\sin^2\theta(\cos^2\phi-\sin^2\phi)\\ \sqrt{3}\,\sin^2\theta\,\cos\phi\,\sin\phi\end{array}\right.
\end{array}\right\}\tag{33}$$

The basic coulomb integrals $[\Omega_a|\Omega_b]$ can now be calculated as one-electron integrals using the potentials (33). The integrations were carried out in the spheroidal coordinates (2). For those integrals which involve the potentials U_{NS} (pole potentials), the evaluation is easy and straightforward. However, the integrals involving the potentials U_{NP} and U_{ND} (dipole and quadrupole potentials) require elaborate partial integrations.

The integrals are obviously functions of $\bar{\zeta}_a$, $\bar{\zeta}_b$, and R; the final formulas are most easily written down in terms of the parameters ζ, τ, ρ, κ, ρ_a, ρ_b, which are defined in the same way as previously in Eqs. (15) and (16), except that ζ_a and ζ_b have to be replaced by $\bar{\zeta}_a$ and $\bar{\zeta}_b$. The results are

$$\begin{aligned}
[1S_a|1S_b]={}&(\zeta/\rho)[1-(1-\kappa)^2\{\tfrac{1}{4}(2+\kappa)+\tfrac{1}{4}\rho_a\}e^{-2\rho_a}-(1+\kappa)^2\{\tfrac{1}{4}(2-\kappa)+\tfrac{1}{4}\rho_b\}e^{-2\rho_b}],\\
[1S_a|2S_b]={}&(\zeta/\rho)[1-(1-\kappa)^2\{\tfrac{1}{4}(1-\kappa-\kappa^2)+(1/12)(1-2\kappa)\rho_a\}e^{-2\rho_a}\\
&-(1+\kappa)^2\{\tfrac{1}{4}(3-3\kappa+\kappa^2)+\tfrac{1}{3}(2-\kappa)\rho_b+\tfrac{1}{6}\rho_b^2\}e^{-2\rho_b}],\\
[1S_a|3S_b]={}&(\zeta/\rho)[1-(1-\kappa)^3\{\tfrac{1}{16}(1-5\kappa-4\kappa^2)-\tfrac{1}{8}\kappa\rho_a\}e^{-2\rho_a}-(1+\kappa)^2\{\tfrac{1}{16}(15-22\kappa+15\kappa^2-4\kappa^3)\\
&+\tfrac{3}{8}(3-3\kappa+\kappa^2)\rho_b+\tfrac{1}{4}(2-\kappa)\rho_b^2+(1/12)\rho_b^3\}e^{-2\rho_b}],\\
[2S_a|2S_b]={}&(\zeta/\rho)[1-(1-\kappa)^2\{(1/12)(6-\kappa-8\kappa^2-4\kappa^3)+\tfrac{1}{3}(1-\kappa+\kappa^2)\rho_a+(1/18)(1-2\kappa)\rho_a^2\}e^{-2\rho_a}\\
&-(1+\kappa)^2\{(1/12)(6+\kappa-8\kappa^2+4\kappa^3)+\tfrac{1}{3}(1+\kappa+\kappa^2)\rho_b+(1/18)(1+2\kappa)\rho_b^2\}e^{-2\rho_b}],\\
[2S_a|3S_b]={}&(\zeta/\rho)[1-(1-\kappa)^3\{(1/48)(11-19\kappa-44\kappa^2-20\kappa^3)+(1/12)(1-5\kappa-4\kappa^2)\rho_a-(1/12)\kappa\rho_a^2\}e^{-2\rho_a}\\
&-(1+\kappa)^2\{(1/48)(37-22\kappa-39\kappa^2+56\kappa^3-20\kappa^4)+\tfrac{1}{8}(6+\kappa-8\kappa^2+4\kappa^3)\rho_b\\
&+\tfrac{1}{4}(1+\kappa-\kappa^2)\rho_b^2+(1/36)(1+2\kappa)\rho_b^3\}e^{-2\rho_b}],\\
[3S_a|3S_b]={}&(\zeta/\rho)[1-(1-\kappa)^3\{\tfrac{1}{16}(8-\kappa-27\kappa^2-30\kappa^3-10\kappa^4)+\tfrac{1}{32}(11-19\kappa-44\kappa^2-20\kappa^3)\rho_a\\
&+\tfrac{1}{16}(1-5\kappa-4\kappa^2)\rho_a^2-(1/24)\kappa\rho_a^3\}e^{-2\rho_a}-(1+\kappa)^3\{\tfrac{1}{16}(8+\kappa-27\kappa^2+30\kappa^3-10\kappa^4)\\
&+\tfrac{1}{32}(11+19\kappa-44\kappa^2+20\kappa^3)\rho_b+\tfrac{1}{16}(1+5\kappa-4\kappa^2)\rho_b^2+(1/24)\kappa\rho_b^3\}e^{-2\rho_b}],\\
[1S_a|2P\Sigma_b]={}&[\zeta/(1-\tau)\rho^2][1-(1-\kappa)^3\{\tfrac{1}{16}(5+3\kappa)(1+2\rho_a)+\tfrac{1}{4}\rho_a^2\}e^{-2\rho_a}\\
&-(1+\kappa)^2\{\tfrac{1}{16}(11-10\kappa+3\kappa^2)(1+2\rho_b)+\tfrac{1}{2}(2-\kappa)\rho_b^2+\tfrac{1}{4}\rho_b^3\}e^{-2\rho_b}],\\
[1S_a|3P\Sigma_b]={}&[\zeta/(1-\tau)\rho^2][1-(1-\kappa)^3\{(1/80)(13-9\kappa-12\kappa^2)(1+2\rho_a)+(1/20)(2-3\kappa)\rho_a^2\}e^{-2\rho_a}\\
&-(1+\kappa)^2\{(1/80)(67-86\kappa+51\kappa^2-12\kappa^3)(1+2\rho_b)\\
&+(1/20)(29-28\kappa+9\kappa^2)\rho_b^2+(3/10)(2-\kappa)\rho_b^3+(1/10)\rho_b^4\}e^{-2\rho_b}],\\
[2S_a|2P\Sigma_b]={}&[\zeta/(1-\tau)\rho^2][1-(1-\kappa)^3\{\tfrac{1}{16}(9+11\kappa+4\kappa^2)(1+2\rho_a)+\tfrac{1}{4}(3+2\kappa)\rho_a^2+\tfrac{1}{6}\rho_a^3\}e^{-2\rho_a}\\
&-(1+\kappa)^2\{\tfrac{1}{16}(7+2\kappa-9\kappa^2+4\kappa^3)(1+2\rho_b)+\tfrac{1}{2}(1+\kappa-\kappa^2)\rho_b^2+(1/12)(1+2\kappa)\rho_b^3\}e^{-2\rho_b}],\\
[2S_a|3P\Sigma_b]={}&[\zeta/(1-\tau)\rho^2][1-(1-\kappa)^3\{(1/80)(29+3\kappa-36\kappa^2-20\kappa^3)(1+2\rho_a)+(1/20)(8-5\kappa-8\kappa^2)\rho_a^2\\
&+(1/30)(2-3\kappa)\rho_a^3\}e^{-2\rho_a}-(1+\kappa)^2\{(1/80)(51-18\kappa-57\kappa^2+64\kappa^3-20\kappa^4)(1+2\rho_b)\\
&+(1/20)(19+4\kappa-25\kappa^2+12\kappa^3)\rho_b^2+(3/10)(1+\kappa-\kappa^2)\rho_b^3+(1/30)(1+2\kappa)\rho_b^4\}e^{-2\rho_b}],
\end{aligned}$$

$$
\begin{aligned}
[3S_a|2P\Sigma_b]=&[\zeta/(1-\tau)\rho^2][1-(1-\kappa)^3\{\tfrac{1}{16}(13+24\kappa+18\kappa^2+5\kappa^3)(1+2\rho_a)+\tfrac{1}{8}(11+15\kappa+6\kappa^2)\rho_a^2\\
&+(1/24)(13+9\kappa)\rho_a^3+(1/12)\rho_a^4\}e^{-2\rho_a}-(1+\kappa)^3\{\tfrac{1}{16}(3+6\kappa-12\kappa^2+5\kappa^3)(1+2\rho_b)\\
&+\tfrac{1}{8}(1+5\kappa-4\kappa^2)\rho_b^2+\tfrac{1}{8}\kappa\rho_b^3\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[3S_a|3P\Sigma_b]=&[\zeta/(1-\tau)\rho^2][1-(1-\kappa)^3\{\tfrac{1}{16}(10+9\kappa-9\kappa^2-16\kappa^3-6\kappa^4)(1+2\rho_a)\\
&+(1/40)(37+9\kappa-48\kappa^2-30\kappa^3)\rho_a^2+(1/120)(35-21\kappa-36\kappa^2)\rho_a^3+(1/60)(2-3\kappa)\rho_a^4\}e^{-2\rho_a}\\
&-(1+\kappa)^3\{\tfrac{1}{16}(6+3\kappa-21\kappa^2+20\kappa^3-6\kappa^4)(1+2\rho_b)+(1/40)(17+31\kappa-68\kappa^2+30\kappa^3)\rho_b^2\\
&+(3/40)(1+5\kappa-4\kappa^2)\rho_b^3+(1/20)\kappa\rho_b^4\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[1S_a|3D\Sigma_b]=&[\zeta/(1-\tau)^2\rho^3][1-(1-\kappa)^4\{\tfrac{1}{16}(3+2\kappa)(1+2\rho_a)+(1/24)(7+4\kappa)\rho_a^2+(1/12)\rho_a^3\}e^{-2\rho_a}\\
&-(1+\kappa)^2\{\tfrac{1}{16}(13-16\kappa+9\kappa^2-2\kappa^3)(1+2\rho_b)+(1/24)(37-42\kappa+21\kappa^2-4\kappa^3)\rho_b^2\\
&+(1/12)(11-10\kappa+3\kappa^2)\rho_b^3+\tfrac{1}{6}(2-\kappa)\rho_b^4+(1/18)\rho_b^5\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[2S_a|3D\Sigma_b]=&[\zeta/(1-\tau)^2\rho^3][1-(1-\kappa)^4\{(1/48)(19+26\kappa+10\kappa^2)(1+2\rho_a)+(1/72)(49+60\kappa+20\kappa^2)\rho_a^2\\
&+(1/36)(11+8\kappa)\rho_a^3+(1/18)\rho_a^4\}e^{-2\rho_a}-(1+\kappa)^2\{(1/48)(29-8\kappa-33\kappa^2\\
&+34\kappa^3-10\kappa^4)(1+2\rho_b)+(1/72)(79-10\kappa-93\kappa^2+80\kappa^3-20\kappa^4)\rho_b^2+(1/12)(7\\
&+2\kappa-9\kappa^2+4\kappa^3)\rho_b^3+\tfrac{1}{6}(1+\kappa-\kappa^2)\rho_b^4+(1/54)(1+2\kappa)\rho_b^5\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[3S_a|3D\Sigma_b]=&[\zeta/(1-\tau)^2\rho^3][1-(1-\kappa)^4\{\tfrac{1}{32}(21+44\kappa+35\kappa^2+10\kappa^3)(1+2\rho_a)\\
&+(1/24)(29+56\kappa+40\kappa^2+10\kappa^3)\rho_a^2+(1/12)(8+12\kappa+5\kappa^2)\rho_a^3\\
&+(1/24)(5+4\kappa)\rho_a^4+(1/36)\rho_a^5\}e^{-2\rho_a}-(1+\kappa)^3\{\tfrac{1}{32}(11+7\kappa-39\kappa^2+35\kappa^3-10\kappa^4)(1+2\rho_b)\\
&+(1/24)(14+13\kappa-51\kappa^2+40\kappa^3-10\kappa^4)\rho_b^2+(1/12)(3+6\kappa-12\kappa^2+5\kappa^3)\rho_b^3\\
&+(1/24)(1+5\kappa-4\kappa^2)\rho_b^4+(1/36)\kappa\rho_b^5\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[2P\Sigma_a|2P\Sigma_b]=&[2\zeta/(1+\tau)(1-\tau)\rho^3][1-(1-\kappa)^3\{\tfrac{1}{16}(8+9\kappa+3\kappa^2)(1+2\rho_a+2\rho_a^2)+\tfrac{3}{16}(3+2\kappa)\rho_a^3+\tfrac{1}{8}\rho_a^4\}e^{-2\rho_a}\\
&-(1+\kappa)^3\{\tfrac{1}{16}(8-9\kappa+3\kappa^2)(1+2\rho_b+2\rho_b^2)+\tfrac{3}{16}(3-2\kappa)\rho_b^3+\tfrac{1}{8}\rho_b^4\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[2P\Sigma_a|3P\Sigma_b]=&[2\zeta/(1+\tau)(1-\tau)\rho^3][1-(1-\kappa)^3\{\tfrac{1}{16}(5-6\kappa^2-3\kappa^3)(1+2\rho_a+2\rho_a^2)+(3/80)(8-5\kappa-8\kappa^2)\rho_a^3\\
&+(1/40)(2-3\kappa)\rho_a^4\}e^{-2\rho_a}-(1+\kappa)^3\{\tfrac{1}{16}(11-18\kappa+12\kappa^2-3\kappa^3)(1+2\rho_b+2\rho_b^2)\\
&+(1/80)(71-93\kappa+36\kappa^2)\rho_b^3+(1/40)(13-9\kappa)\rho_b^4+(1/20)\rho_b^5\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[3P\Sigma_a|3P\Sigma_b]=&[2\zeta/(1+\tau)(1-\tau)\rho^3][1-(1-\kappa)^3\{(1/80)(40+27\kappa-39\kappa^2-54\kappa^3-18\kappa^4)(1+2\rho_a+2\rho_a^2)\\
&+(1/80)(47+9\kappa-60\kappa^2-36\kappa^3)\rho_a^3+(1/200)(35-21\kappa-36\kappa^2)\rho_a^4+(1/100)(2-3\kappa)\rho_a^5\}e^{-2\rho_a}\\
&-(1+\kappa)^3\{(1/80)(40-27\kappa-39\kappa^2+54\kappa^3-18\kappa^4)(1+2\rho_b+2\rho_b^2)\\
&+(1/80)(47-9\kappa-60\kappa^2+36\kappa^3)\rho_b^3+(1/200)(35+21\kappa-36\kappa^2)\rho_b^4+(1/100)(2+3\kappa)\rho_b^5\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[2P\Pi_a|2P\Pi_b]=&[\zeta/(1+\tau)(1-\tau)\rho^3][1-(1-\kappa)^3\{\tfrac{1}{16}(8+9\kappa+3\kappa^2)(1+2\rho_a)+\tfrac{1}{8}(5+3\kappa)\rho_a^2+\tfrac{1}{8}\rho_a^3\}e^{-2\rho_a}\\
&-(1+\kappa)^3\{\tfrac{1}{16}(8-9\kappa+3\kappa^2)(1+2\rho_b)+\tfrac{1}{8}(5-3\kappa)\rho_b^2+\tfrac{1}{8}\rho_b^3\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[2P\Pi_a|3P\Pi_b]=&[\zeta/(1+\tau)(1-\tau)\rho^3][1-(1-\kappa)^3\{\tfrac{1}{16}(5-6\kappa^2-3\kappa^3)(1+2\rho_a)+(1/40)(13-9\kappa-12\kappa^2)\rho_a^2\\
&+(1/40)(2-3\kappa)\rho_a^3\}e^{-2\rho_a}-(1+\kappa)^3\{\tfrac{1}{16}(11-18\kappa+12\kappa^2-3\kappa^3)(1+2\rho_b)\\
&+(1/40)(43-51\kappa+18\kappa^2)\rho_b^2+(3/40)(5-3\kappa)\rho_b^3+(1/20)\rho_b^4\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[3P\Pi_a|3P\Pi_b]=&[\zeta/(1+\tau)(1-\tau)\rho^3][1-(1-\kappa)^3\{(1/80)(40+27\kappa-39\kappa^2-54\kappa^3-18\kappa^4)(1+2\rho_a)\\
&+(1/200)(137+9\kappa-168\kappa^2-90\kappa^3)\rho_a^2+(3/200)(13-9\kappa-12\kappa^2)\rho_a^3+(1/100)(2-3\kappa)\rho_a^4\}e^{-2\rho_a}\\
&-(1+\kappa)^3\{(1/80)(40-27\kappa-39\kappa^2+54\kappa^3-18\kappa^4)(1+2\rho_b)+(1/200)(137-9\kappa-168\kappa^2+90\kappa^3)\rho_b^2\\
&+(3/200)(13+9\kappa-12\kappa^2)\rho_b^3+(1/100)(2+3\kappa)\rho_b^4\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[2P\Sigma_a|3D\Sigma_b]=&[[3\zeta/(1+\tau)(1-\tau)^2\rho^4][1-(1-\kappa)^4\{\tfrac{1}{32}(11+14\kappa+5\kappa^2)(1+2\rho_a)+(1/72)(47+58\kappa+20\kappa^2)\rho_a^2\\
&+(1/36)(14+16\kappa+5\kappa^2)\rho_a^3+(1/72)(11+8\kappa)\rho_a^4+(1/36)\rho_a^5\}e^{-2\rho_a}\\
&-(1+\kappa)^3\{\tfrac{1}{32}(21-33\kappa+21\kappa^2-5\kappa^3)(1+2\rho_b)+(1/72)(92-141\kappa+87\kappa^2-20\kappa^3)\rho_b^2\\
&+(1/36)(29-42\kappa+24\kappa^2-5\kappa^3)\rho_b^3+(1/24)(9-11\kappa+4\kappa^2)\rho_b^4\\
&+(1/108)(13-9\kappa)\rho_b^5+(1/54)\rho_b^6\}e^{-2\rho_b}],
\end{aligned}
$$

$$
\begin{aligned}
[3P\Sigma_a|3D\Sigma_b]=&[3\zeta/(1+\tau)(1-\tau)^2\rho^4][1-(1-\kappa)^4\{\tfrac{1}{32}(17+32\kappa+23\kappa^2+6\kappa^3)(1+2\rho_a)\\
&+(1/72)(74+136\kappa+95\kappa^2+24\kappa^3)\rho_a^2+(1/36)(23+40\kappa+26\kappa^2+6\kappa^3)\rho_a^3\\
&+(1/360)(103+148\kappa+60\kappa^2)\rho_a^4+(1/60)(5+4\kappa)\rho_a^5+(1/90)\rho_a^6\}e^{-2\rho_a}\\
&-(1+\kappa)^3\{\tfrac{1}{32}(15-9\kappa-15\kappa^2+19\kappa^3-6\kappa^4)(1+2\rho_b)+(1/72)(65-36\kappa-66\kappa^2+79\kappa^3-24\kappa^4)\rho_b^2\\
&+(1/36)(20-9\kappa-21\kappa^2+22\kappa^3-6\kappa^4)\rho_b^3+(1/120)(29-3\kappa-36\kappa^2+20\kappa^3)\rho_b^4\\
&+(1/540)(35+21\kappa-36\kappa^2)\rho_b^5+(1/270)(2+3\kappa)\rho_b^6\}e^{-2\rho_b}],
\end{aligned}
$$

$$[2P\Pi_a|3D\Pi_b]=[\sqrt{3}\zeta/(1+\tau)(1-\tau)^2\rho^4][1-(1-\kappa)^4\{\tfrac{1}{32}(11+14\kappa+5\kappa^2)(1+2\rho_a)+(1/24)(14+16\kappa+5\kappa^2)\rho_a^2$$
$$+(1/12)(3+2\kappa)\rho_a^3+(1/24)\rho_a^4\}e^{-2\rho_a}-(1+\kappa)^3\{\tfrac{1}{32}(21-33\kappa+21\kappa^2-5\kappa^3)(1+2\rho_b)$$
$$+(1/24)(29-42\kappa+24\kappa^2-5\kappa^3)\rho_b^2+(1/12)(8-9\kappa+3\kappa^2)\rho_b^3$$
$$+(1/24)(5-3\kappa)\rho_b^4+(1/36)\rho_b^5\}e^{-2\rho_b}],$$

$$[3P\Pi_a|3D\Pi_b]=[\sqrt{3}\zeta/(1+\tau)(1-\tau)^2\rho^4][1-(1-\kappa)^4\{\tfrac{1}{32}(17+32\kappa+23\kappa^2+6\kappa^3)(1+2\rho_a)$$
$$+(1/24)(23+40\kappa+26\kappa^2+6\kappa^3)\rho_a^2+(1/12)(6+8\kappa+3\kappa^2)\rho_a^3+(1/120)(17+12\kappa)\rho_a^4$$
$$+(1/60)\rho_a^5\}e^{-2\rho_a}-(1+\kappa)^3\{\tfrac{1}{32}(15-9\kappa-15\kappa^2+19\kappa^3-6\kappa^4)(1+2\rho_b)$$
$$+(1/24)(20-9\kappa-21\kappa^2+22\kappa^3-6\kappa^4)\rho_b^2+(1/12)(5-6\kappa^2+3\kappa^3)\rho_b^3$$
$$+(1/120)(13+9\kappa-12\kappa^2)\rho_b^4+(1/180)(2+3\kappa)\rho_b^5\}e^{-2\rho_b}],$$

$$[3D\Sigma_a|3D\Sigma_b]=[6\zeta/(1+\tau)^2(1-\tau)^2\rho^5][1-(1-\kappa)^4\{\tfrac{1}{32}(16+29\kappa+20\kappa^2+5\kappa^3)(1+2\rho_a)$$
$$+(1/144)(139+246\kappa+165\kappa^2+40\kappa^3)\rho_a^2+(1/72)(43+72\kappa+45\kappa^2+10\kappa^3)\rho_a^3$$
$$+(1/216)(57+88\kappa+50\kappa^2+10\kappa^3)\rho_a^4+(1/432)(39+52\kappa+20\kappa^2)\rho_a^5+(1/216)(5+4\kappa)\rho_a^6$$
$$+(1/324)\rho_a^7\}e^{-2\rho_a}-(1+\kappa)^4\{\tfrac{1}{32}(16-29\kappa+20\kappa^2-5\kappa^3)(1+2\rho_b)$$
$$+(1/144)(139-246\kappa+165\kappa^2-40\kappa^3)\rho_b^2+(1/72)(43-72\kappa+45\kappa^2-10\kappa^3)\rho_b^3$$
$$+(1/216)(57-88\kappa+50\kappa^2-10\kappa^3)\rho_b^4+(1/432)(39-52\kappa+20\kappa^2)\rho_b^5$$
$$+(1/216)(5-4\kappa)\rho_b^6+(1/324)\rho_b^7\}e^{-2\rho_b}\},$$

$$[3D\Pi_a|3D\Pi_b]=[4\zeta/(1+\tau)^2(1-\tau)^2\rho^5][1-(1-\kappa)^4\{\tfrac{1}{32}(16+29\kappa+20\kappa^2+5\kappa^3)(1+2\rho_a)$$
$$+(1/96)(91+159\kappa+105\kappa^2+25\kappa^3)\rho_a^2+(1/48)(27+43\kappa+25\kappa^2+5\kappa^3)\rho_a^3$$
$$+(1/48)(11+14\kappa+5\kappa^2)\rho_a^4+(1/288)(17+12\kappa)\rho_a^5+(1/144)\rho_a^6\}e^{-2\rho_a}$$
$$-(1+\kappa)^4\{\tfrac{1}{32}(16-29\kappa+20\kappa^2-5\kappa^3)(1+2\rho_b)+(1/96)(91-159\kappa+105\kappa^2-25\kappa^3)\rho_b^2$$
$$+(1/48)(27-43\kappa+25\kappa^2-5\kappa^3)\rho_b^3+(1/48)(11-14\kappa+5\kappa^2)\rho_b^4$$
$$+(1/288)(17-12\kappa)\rho_b^5+(1/144)\rho_b^6\}e^{-2\rho_b}],$$

$$[3D\Delta_a|3D\Delta_b]=[\zeta/(1+\tau)^2(1-\tau)^2\rho^5][1-(1-\kappa)^4\{\tfrac{1}{32}(16+29\kappa+20\kappa^2+5\kappa^3)(1+2\rho_a)$$
$$+(1/48)(43+72\kappa+45\kappa^2+10\kappa^3)\rho_a^2+(1/24)(11+14\kappa+5\kappa^2)\rho_a^3+(1/24)(3+2\kappa)\rho_a^4$$
$$+(1/72)\rho_a^5\}e^{-2\rho_a}-(1+\kappa)^4\{\tfrac{1}{32}(16-29\kappa+20\kappa^2-5\kappa^3)(1+2\rho_b)$$
$$+(1/48)(43-72\kappa+45\kappa^2-10\kappa^3)\rho_b^2+(1/24)(11-14\kappa+5\kappa^2)\rho_b^3$$
$$+(1/24)(3-2\kappa)\rho_b^4+(1/72)\rho_b^5\}e^{-2\rho_b}]; \quad (34)$$

$\tau=0$,

$$[1S_a|1S_b]=\frac{\zeta}{\rho}\left\{1-\left(1+\frac{11}{8}\rho+\frac{3}{4}\rho^2+\frac{1}{6}\rho^3\right)e^{-2\rho}\right\},$$

$$[1S_a|2S_b]=\frac{\zeta}{\rho}\left\{1-\left(1+\frac{71}{48}\rho+\frac{23}{24}\rho^2+\frac{1}{3}\rho^3+\frac{1}{18}\rho^4\right)e^{-2\rho}\right\},$$

$$[2S_a|2S_b]=\frac{\zeta}{\rho}\left\{1-\left(1+\frac{37}{24}\rho+\frac{13}{12}\rho^2+\frac{4}{9}\rho^3+\frac{1}{9}\rho^4+\frac{2}{135}\rho^5\right)e^{-2\rho}\right\},$$

$$[1S_a|3S_b]=\frac{\zeta}{\rho}\left\{1-\left(1+\frac{25}{16}\rho+\frac{9}{8}\rho^2+\frac{23}{48}\rho^3+\frac{1}{8}\rho^4+\frac{1}{60}\rho^5\right)e^{-2\rho}\right\},$$

$$[2S_a|3S_b]=\frac{\zeta}{\rho}\left\{1-\left(1+\frac{307}{192}\rho+\frac{115}{96}\rho^2+\frac{79}{144}\rho^3+\frac{1}{6}\rho^4+\frac{1}{30}\rho^5+\frac{1}{270}\rho^6\right)e^{-2\rho}\right\},$$

$$[3S_a|3S_b]=\frac{\zeta}{\rho}\left\{1-\left(1+\frac{419}{256}\rho+\frac{163}{128}\rho^2+\frac{119}{192}\rho^3+\frac{5}{24}\rho^4+\frac{1}{20}\rho^5+\frac{1}{120}\rho^6+\frac{1}{1260}\rho^7\right)e^{-2\rho}\right\},$$

$$[1S_a|2P\Sigma_b]=\frac{\zeta}{\rho^2}\left\{1-\left(1+2\rho+2\rho^2+\frac{59}{48}\rho^3+\frac{11}{24}\rho^4+\frac{1}{12}\rho^5\right)e^{-2\rho}\right\},$$

$$[1S_a|3P\Sigma_b]=\frac{\zeta}{\rho^2}\left\{1-\left(1+2\rho+2\rho^2+\frac{19}{15}\rho^3+\frac{8}{15}\rho^4+\frac{43}{300}\rho^5+\frac{1}{50}\rho^6\right)e^{-2\rho}\right\},$$

$$[2S_a|2P\Sigma_b]=\frac{\zeta}{\rho^2}\left\{1-\left(1+2\rho+2\rho^2+\frac{61}{48}\rho^3+\frac{13}{24}\rho^4+\frac{3}{20}\rho^5+\frac{1}{45}\rho^6\right)e^{-2\rho}\right\},$$

$$[2S_a|3P\Sigma_b]=\frac{\zeta}{\rho^2}\left\{1-\left(1+2\rho+2\rho^2+\frac{103}{80}\rho^3+\frac{23}{40}\rho^4+\frac{9}{50}\rho^5+\frac{17}{450}\rho^6+\frac{1}{225}\rho^7\right)e^{-2\rho}\right\},$$

$$[3S_a|2P\Sigma_b]=\frac{\zeta}{\rho^2}\left\{1-\left(1+2\rho+2\rho^2+\frac{83}{64}\rho^3+\frac{19}{32}\rho^4+\frac{23}{120}\rho^5+\frac{13}{360}\rho^6+\frac{1}{180}\rho^7\right)e^{-2\rho}\right\},$$

$$[3S_a|3P\Sigma_b]=\frac{\zeta}{\rho^2}\left\{1-\left(1+2\rho+2\rho^2+\frac{417}{320}\rho^3+\frac{97}{160}\rho^4+\frac{5}{24}\rho^5+\frac{19}{360}\rho^6+\frac{59}{6300}\rho^7+\frac{1}{1050}\rho^8\right)e^{-2\rho}\right\},$$

$$[1S_a|3D\Sigma_b]=\frac{\zeta}{\rho^3}\left\{1-\left(1+2\rho+2\rho^2+\frac{4}{3}\rho^3+\frac{2}{3}\rho^4+\frac{31}{120}\rho^5+\frac{13}{180}\rho^6+\frac{1}{90}\rho^7\right)e^{-2\rho}\right\},$$

$$[2S_a|3D\Sigma_b]=\frac{\zeta}{\rho^3}\left\{1-\left(1+2\rho+2\rho^2+\frac{4}{3}\rho^3+\frac{2}{3}\rho^4+\frac{71}{270}\rho^5+\frac{11}{135}\rho^6+\frac{1}{54}\rho^7+\frac{1}{405}\rho^8\right)e^{-2\rho}\right\},$$

$$[3S_a|3D\Sigma_b]=\frac{\zeta}{\rho^3}\left\{1-\left(1+2\rho+2\rho^2+\frac{4}{3}\rho^3+\frac{2}{3}\rho^4+\frac{191}{720}\rho^5+\frac{31}{360}\rho^6+\frac{19}{840}\rho^7+\frac{17}{3780}\rho^8+\frac{1}{1890}\rho^9\right)e^{-2\rho}\right\},$$

$$[2P\Sigma_a|2P\Sigma_b]=\frac{2\zeta}{\rho^3}\left\{1-\left(1+2\rho+2\rho^2+\frac{263}{192}\rho^3+\frac{71}{96}\rho^4+\frac{77}{240}\rho^5+\frac{1}{10}\rho^6+\frac{1}{60}\rho^7\right)e^{-2\rho}\right\},$$

$$[2P\Sigma_a|3P\Sigma_b]=\frac{2\zeta}{\rho^3}\left\{1-\left(1+2\rho+2\rho^2+\frac{2609}{1920}\rho^3+\frac{689}{960}\rho^4+\frac{37}{120}\rho^5+\frac{5}{48}\rho^6+\frac{1}{40}\rho^7+\frac{1}{300}\rho^8\right)e^{-2\rho}\right\},$$

$$[3P\Sigma_a|3P\Sigma_b]=\frac{2\zeta}{\rho^3}\left\{1-\left(1+2\rho+2\rho^2+\frac{2597}{1920}\rho^3+\frac{677}{960}\rho^4+\frac{719}{2400}\rho^5+\frac{31}{300}\rho^6+\frac{29}{1050}\rho^7+\frac{11}{2100}\rho^8+\frac{1}{1750}\rho^9\right)e^{-2\rho}\right\},$$

$$[2P\Pi_a|2P\Pi_b]=\frac{\zeta}{\rho^3}\left\{1-\left(1+2\rho+2\rho^2+\frac{121}{96}\rho^3+\frac{25}{48}\rho^4+\frac{2}{15}\rho^5+\frac{1}{60}\rho^6\right)e^{-2\rho}\right\},$$

$$[2P\Pi_a|3P\Pi_b]=\frac{\zeta}{\rho^3}\left\{1-\left(1+2\rho+2\rho^2+\frac{1231}{960}\rho^3+\frac{271}{480}\rho^4+\frac{41}{240}\rho^5+\frac{1}{30}\rho^6+\frac{1}{300}\rho^7\right)e^{-2\rho}\right\},$$

$$[3P\Pi_a|3P\Pi_b]=\frac{\zeta}{\rho^3}\left\{1-\left(1+2\rho+2\rho^2+\frac{1243}{960}\rho^3+\frac{283}{480}\rho^4+\frac{29}{150}\rho^5+\frac{9}{200}\rho^6+\frac{73}{10500}\rho^7+\frac{1}{1750}\rho^8\right)e^{-2\rho}\right\},$$

$$[2P\Sigma_a|3D\Sigma_b]=\frac{3\zeta}{\rho^4}\left\{1-\left(1+2\rho+2\rho^2+\frac{4}{3}\rho^3+\frac{2}{3}\rho^4+\frac{583}{2160}\rho^5+\frac{103}{1080}\rho^6+\frac{11}{360}\rho^7+\frac{13}{1620}\rho^8+\frac{1}{810}\rho^9\right)e^{-2\rho}\right\},$$

$$[3P\Sigma_a|3D\Sigma_b]=\frac{3\zeta}{\rho^4}\left\{1-\left(1+2\rho+2\rho^2+\frac{4}{3}\rho^3+\frac{2}{3}\rho^4+\frac{29}{108}\rho^5+\frac{5}{54}\rho^6+\frac{1}{35}\rho^7+\frac{22}{2835}\rho^8+\frac{47}{28350}\rho^9+\frac{1}{4725}\rho^{10}\right)e^{-2\rho}\right\},$$

$$[2P\Pi_a|3D\Pi_b]=\frac{\sqrt{3}\zeta}{\rho^4}\left\{1-\left(1+2\rho+2\rho^2+\frac{4}{3}\rho^3+\frac{2}{3}\rho^4+\frac{377}{1440}\rho^5+\frac{19}{240}\rho^6+\frac{1}{60}\rho^7+\frac{1}{540}\rho^8\right)e^{-2\rho}\right\},$$

$$[3P\Pi_a|3D\Pi_b]=\frac{\sqrt{3}\zeta}{\rho^4}\left\{1-\left(1+2\rho+2\rho^2+\frac{4}{3}\rho^3+\frac{2}{3}\rho^4+\frac{19}{72}\rho^5+\frac{1}{12}\rho^6+\frac{17}{840}\rho^7+\frac{13}{3780}\rho^8+\frac{1}{3150}\rho^9\right)e^{-2\rho}\right\},$$

$$[3D\Sigma_a|3D\Sigma_b]=\frac{6\zeta}{\rho^5}\left\{1-\left(1+2\rho+2\rho^2+\frac{4}{3}\rho^3+\frac{2}{3}\rho^4+\frac{511}{1920}\rho^5+\frac{253}{2880}\rho^6+\frac{2237}{90720}\rho^7+\frac{71}{11340}\rho^8+\frac{1}{630}\rho^9+\frac{13}{34020}\rho^{10}+\frac{1}{17010}\rho^{11}\right)e^{-2\rho}\right\},$$

$$[3D\Pi_a|3D\Pi_b]=\frac{4\zeta}{\rho^5}\left\{1-\left(1+2\rho+2\rho^2+\frac{4}{3}\rho^3+\frac{2}{3}\rho^4+\frac{1027}{3840}\rho^5+\frac{521}{5760}\rho^6+\frac{67}{2520}\rho^7+\frac{67}{10080}\rho^8+\frac{19}{15120}\rho^9+\frac{1}{7560}\rho^{10}\right)e^{-2\rho}\right\},$$

$$[3D\Delta_a|3D\Delta_b]=\frac{\zeta}{\rho^5}\left\{1-\left(1+2\rho+2\rho^2+\frac{4}{3}\rho^3+\frac{2}{3}\rho^4+\frac{253}{960}\rho^5+\frac{119}{1440}\rho^6+\frac{11}{560}\rho^7+\frac{1}{315}\rho^8+\frac{1}{3780}\rho^9\right)e^{-2\rho}\right\}; \quad (34a)$$

$$\left.\begin{aligned}
&\rho=0,\\
&[1S_a|1S_b]=\tfrac{1}{8}(1-\tau^2)(5-\tau^2)\zeta,\\
&[1S_a|2S_b]=(1/48)(1-\tau^2)(25-7\tau-5\tau^2+3\tau^3)\zeta,\\
&[2S_a|2S_b]=(1/24)(1-\tau^2)(11-4\tau^2+\tau^4)\zeta,\\
&[1S_a|3S_b]=\tfrac{1}{32}(1-\tau^2)(14-7\tau-\tau^2+3\tau^3-\tau^4)\zeta,\\
&[2S_a|3S_b]=(1/192)(1-\tau^2)(77-19\tau-28\tau^2+16\tau^3+7\tau^4-5\tau^5)\zeta,\\
&[3S_a|3S_b]=(1/256)(1-\tau^2)(93-47\tau^2+23\tau^4-5\tau^6)\zeta,\\
&[NS_a|N'P\Sigma_b]=0,\\
&[NS_a|N'D\Sigma_b]=0,\\
&-[2P\Sigma_a|2P\Sigma_b]=[2P\Pi_a|2P\Pi_b]=(1/96)(1-\tau^2)^2(7-3\tau^2)\zeta,\\
&-[2P\Sigma_a|3P\Sigma_b]=[2P\Pi_a|3P\Pi_b]=(1/960)(1-\tau^2)^2(49-27\tau-21\tau^2+15\tau^3)\zeta,\\
&-[3P\Sigma_a|3P\Sigma_b]=[3P\Pi_a|3P\Pi_b]=(1/960)(1-\tau^2)^2(37-30\tau^2+9\tau^4)\zeta,\\
&[NP\Sigma_a|N'D\Sigma_b]=[NP\Pi_a|N'D\Pi_b]=0,\\
&[3D\Sigma_a|3D\Sigma_b]=-[3D\Pi_a|3D\Pi_b]=[3D\Delta_a|3D\Delta_b]=(1/2880)(1-\tau^2)^3(9-5\tau^2)\zeta.
\end{aligned}\right\} \quad (34b)$$

The formulas (30), (34), (34a), and (34b) enable us to obtain any desired coulomb integral $[\chi_a\chi_a'|\chi_b\chi_b']$. It is to be noted that in Eqs. (30) there occur the basic integrals $[2P\Sigma_a|3S_b]$, $[3P\Sigma_a|3S_b]$, and $[3D\Sigma_a|3S_b]$, which are not listed explicitly in Eqs. (34), (34a), and (34b). However, these integrals follow directly from $[3S_a|2P\Sigma_b]$, $[3S_a|3P\Sigma_b]$, and $[3S_b|3D\Sigma_b]$, respectively, when the following change is made in the latter: $\rho_a\leftrightarrow\rho_b$, $\kappa\to-\kappa$, $\tau\to-\tau$.

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The wave functions employed in the formulas are real Slater (nodeless) wave functions, unless explicitly stated otherwise.

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$[2p\sigma_a2p\pi_a|2p\sigma_b2p\pi_b]$, $[2p\sigma_a2p\sigma_a|2p\sigma_b2p\sigma_b]$,
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$(2p\sigma_a|1/r_a|1s_b)$, $(2p\sigma_a|1/r_a|2p\sigma_b)$,
$[a|1s_a1s_a]$, $[a|1s_b1s_b]$, $[a|1s_b2p\sigma_b]$,

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$[1s_a 1s_a|2p\sigma_b 2p\sigma_b]$, $[1s_a 2p\sigma_a|2p\sigma_b 2p\sigma_b]$,
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$(2s_a|1/r_a|2s_b)$, $(2p\sigma_a|1/r_a|2p\sigma_b)$, $(2p\pi_a|1/r_a|2p\pi_b)$,
$(2s_a|1/r_a|2p\sigma_b)$, $(2p\sigma_a|1/r_a|2s_b)$
in terms of A_n for $\tau=0$;
$[a|1s_b 1s_b]$, $[a|2s_b 2s_b]$, $[a|2p\sigma_b 2p\sigma_b]$,
$[a|2p\pi_b 2p\pi_b]$, $[a|2s_b 2p\sigma_b)$ in terms of A_n;
$[2s_a 2s_a|2s_b 2s_b]$, $[2p\sigma_a 2s_a|2s_b 2s_b]$,
$[2p\sigma_a 2s_a|2p\sigma_b 2s_b]$, $[2p\sigma_a 2p\sigma_a|2p\sigma_b 2s_b]$,
$[2s_a 2s_a|2p\pi_b 2p\pi_b]$, $[2s_a 2p\pi_a|2s_b 2p\pi_b]$,
$[2p\sigma_a 2p\pi_a|2p\sigma_b 2p\pi_b]$, $[2p\sigma_a 2p\pi_a|2s_b 2p\pi_b]$,
in terms of ρ for $\tau=0$;
$(1s_a|2s_b)$, $(1s_a|2p\sigma_b)$,
$(2s_a|1/r_a|1s_b)$, $(2p\sigma_a|1/r_a|1s_b)$,
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expressed in terms of ρ for $\tau=0$. Also, certain linear combinations of overlap and nuclear attraction integrals are evaluated, and a compilation of integrals evaluated by other authors is made.

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