APPENDIX

A

INTEGRAL EVALUATION WITH 1s PRIMITIVE GAUSSIANS

In most molecular calculations one uses a fixed molecular coordinate system such that the basis functions are centered at position vectors $\mathbf{R}_A$ in this coordinate system, as shown in Fig. A.1. The value at a position vector **r,** of a function centered at $\mathbf{R}_A$, will depend on $\mathbf{r} - \mathbf{R}_A$ and we hence write a general basis function as $\phi_\mu(\mathbf{r} - \mathbf{R}_A)$ to denote that it is centered at $\mathbf{R}_A$. In a
molecular calculation we will need to evaluate a number of one- and two-electron integrals involving functions $\phi_\mu(\mathbf{r} - \mathbf{R}_A)$ at different centers. If we have basis functions at four or more centers, then the two-electron integrals will involve 1-, 2-, 3-, and 4-center integrals. Nuclear attraction integrals can involve at most 3 centers. These multicenter (more than 2) integrations are difficult for Slater-type functions but are relatively simple for Gaussian-type functions. Thus most polyatomic calculations use Gaussian functions.

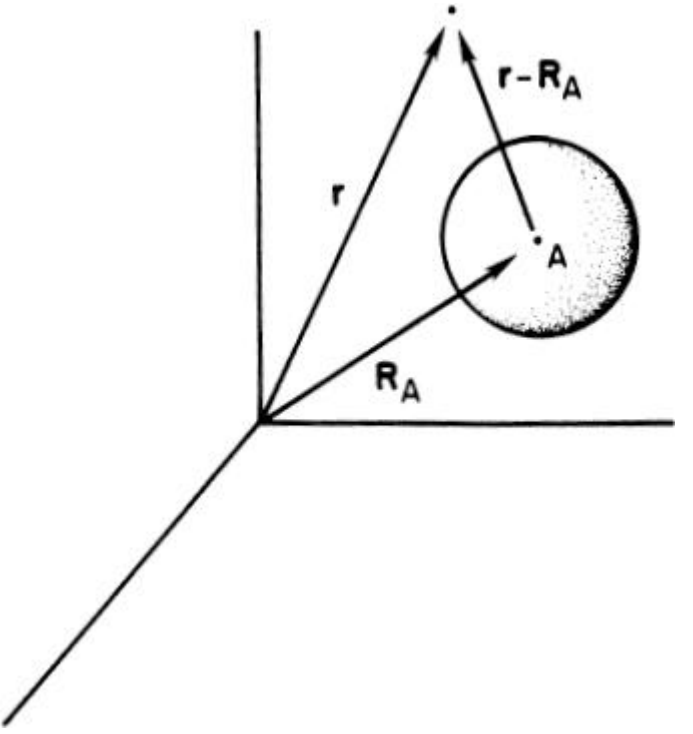

Figure A.1 Molecular coordinate system.

In a Gaussian calculation the contracted Gaussian basis functions ϕ_μ^{CGF} are normally expanded in a set of primitive Gaussian functions $g \equiv \phi_p^{\mathrm{GF}}$ (see Eq. (3.283) or Eq. (3.212)), and thus we need only consider integral evaluation over the primitive functions. The integrals for contracted functions ϕ_μ^{CGF} are obtained just by summing up integrals over primitives using the appropriate contraction coefficients. One commonly uses only 1*s*, 2*p*, 3*d*, etc. primitive Gaussians, since any function of *s*, *p*, *d*, etc. symmetry can be expanded

in just these Gaussians. Here we consider integral evaluations only for 1*s* primitive Gaussians. Shavitt[1] has given a similar, but complementary, discussion of integral evaluation methods for the Gaussian function. Integrals involving *p*, *d*, etc. symmetry functions could be obtained by differentiating our results with respect to the Cartesian coordinates of the centers $\mathbf{R}_A$, $\mathbf{R}_B$, etc. However, integrals for higher angular quantum numbers are more efficiently formulated for computation using newer methods based on Rys polynomials.[2]

The unnormalized 1*s* primitive Gaussian at $\mathbf{R}_A$ is

$$\tilde{g}_{1s}(\mathbf{r} - \mathbf{R}_A) = e^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2} \tag{A.1}$$

We will use α, β, γ, and δ for orbital exponents of functions centered at $\mathbf{R}_A$, $\mathbf{R}_B$, $\mathbf{R}_C$, $\mathbf{R}_D$, respectively. The reason why Gaussians simplify multicenter integrations is that the product of two 1*s* Gaussians, each on different centers, is proportional to a 1*s* Gaussian on a third center. Thus

$$\tilde{g}_{1s}(\mathbf{r} - \mathbf{R}_A)\tilde{g}_{1s}(\mathbf{r} - \mathbf{R}_B) = \tilde{K}\tilde{g}_{1s}(\mathbf{r} - \mathbf{R}_P) \tag{A.2}$$

where the proportionality constant $\tilde{K}$ is

$$\tilde{K} = \exp[-\alpha\beta/(\alpha + \beta)|\mathbf{R}_A - \mathbf{R}_B|^2] \tag{A.3}$$

The third center *P* is on a line joining the centers *A* and *B*,

$$\mathbf{R}_P = (\alpha\mathbf{R}_A + \beta\mathbf{R}_B)/(\alpha + \beta) \tag{A.4}$$

The exponent of the new Gaussian centered at $\mathbf{R}_P$ is

$$p = \alpha + \beta \tag{A.5}$$

Thus for 1*s* Gaussians any 2-center distribution, i.e., product of functions on 2 different centers, can immediately be converted to a one-center distribution. We now evaluate the basic integrals that we need for any *ab initio* calculation that uses only contractions of primitive 1*s* Gaussians. We will evaluate integrals for *unnormalized* functions and, if we require integrals for normalized functions, we can easily multiply by the appropriate normalization constants.

Consider the 2-center overlap integral first

$$(A|B) = \int d\mathbf{r}_1\, \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_A)\tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_B) \tag{A.6}$$

Using (A.2) we immediately have

$$(A|B) = \tilde{K} \int d\mathbf{r}_1\, \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_P) = \tilde{K} \int d\mathbf{r}_1\, \exp[-p|\mathbf{r}_1 - \mathbf{R}_P|^2] \tag{A.7}$$

If we now let $\mathbf{r} = \mathbf{r}_1 - \mathbf{R}_P$ and $d\mathbf{r} = d\mathbf{r}_1$, then

$$(A|B) = \tilde{K} \int d\mathbf{r}\, e^{-pr^2} = 4\pi\tilde{K} \int_0^\infty dr\, r^2 e^{-pr^2} \tag{A.8}$$

This last integral is just $(\pi/p)^{3/2}/4\pi$, so that

$$(A|B) = [\pi/(\alpha + \beta)]^{3/2} \exp[-\alpha\beta/(\alpha + \beta)|\mathbf{R}_A - \mathbf{R}_B|^2] \tag{A.9}$$

The kinetic energy integral

$$(A|-\tfrac{1}{2}\nabla^2|B) = \int d\mathbf{r}_1\, \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_A)(-\tfrac{1}{2}\nabla_1^2)\tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_B) \tag{A.10}$$

can be evaluated in a very similar way (after letting ∇_1^2 operate) to give

$$(A|-\tfrac{1}{2}\nabla^2|B) = \alpha\beta/(\alpha+\beta)[3 - 2\alpha\beta/(\alpha+\beta)|\mathbf{R}_A - \mathbf{R}_B|^2][\pi/(\alpha+\beta)]^{3/2} \times \exp[-\alpha\beta/(\alpha+\beta)|\mathbf{R}_A - \mathbf{R}_B|^2] \quad \text{(A.11)}$$

In order to evaluate the nuclear attraction and two-electron repulsion integrals, we now introduce here a powerful and general technique that is often useful for evaluating integrals, particularly of the type that we will be considering. The technique is to replace each quantity in the integrand by its Fourier transform. If we are given a function $f(\mathbf{r})$ of the vector **r,** then its three-dimensional Fourier transform $F(\mathbf{k})$ is defined by

$$F(\mathbf{k}) = \int d\mathbf{r}\, f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} \quad \text{(A.12)}$$

where the vector **k** is the transform variable. The Fourier integral theorem states that

$$f(\mathbf{r}) = (2\pi)^{-3} \int d\mathbf{k}\, F(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \quad \text{(A.13)}$$

$F(\mathbf{k})$ and $f(\mathbf{r})$ are said to be a Fourier transform pair. All the Fourier transform pairs we shall need here are given in Table A.1. In particular, the Fourier representation of the three-dimensional Dirac delta function is

$$\delta(\mathbf{r}_1 - \mathbf{r}_2) = (2\pi)^{-3} \int d\mathbf{k}\, e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} \quad \text{(A.14)}$$

Table A.1 Fourier transform pairs

$f(\mathbf{r})$	$F(\mathbf{k})$

$\frac{1}{r}$	$\frac{4\pi}{k^2}$
$e^{-\alpha r^2}$	$\left(\frac{\pi}{\alpha}\right)^{3/2} e^{-k^2/4\alpha}$
$\delta(\mathrm{r})$	1

Recall that the Dirac δ function has the property that

$$\int d\mathbf{r}_1\, \delta(\mathbf{r}_1 - \mathbf{r}_2) h(\mathbf{r}_1) = h(\mathbf{r}_2) \tag{A.15}$$

for any function $h(\mathbf{r})$.

Let us now consider the nuclear attraction integral for our primitive 1*s* Gaussians.

$$\begin{aligned}(A|-Z_C/r_{1C}|B) &= \int d\mathbf{r}_1\, \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_A)[-Z_C/|\mathbf{r}_1 - \mathbf{R}_C|]\tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_B) \\ &= -Z_C \int d\mathbf{r}_1\, e^{-\alpha|\mathbf{r}_1 - \mathbf{R}_A|^2} |\mathbf{r}_1 - \mathbf{R}_C|^{-1} e^{-\beta|\mathbf{r}_1 - \mathbf{R}_B|^2}\end{aligned} \tag{A.16}$$

We first combine the two Gaussians to obtain a single Gaussian at $\mathbf{R}_P$,

$$(A|-Z_C/r_{1C}|B) = -Z_C \tilde{K} \int d\mathbf{r}_1\, e^{-p|\mathbf{r}_1 - \mathbf{R}_P|^2} |\mathbf{r}_1 - \mathbf{R}_C|^{-1} \tag{A.17}$$

We then substitute for the two terms in the above integrand using (A.13) and Table A.1,

$$\begin{aligned}(A|-Z_C/r_{1C}|B) = -Z_C \tilde{K} (2\pi)^{-6} (\pi/p)^{3/2} \int d\mathbf{r}_1\, d\mathbf{k}_1\, d\mathbf{k}_2\, e^{-k_1^2/4p} \\ \times e^{i\mathbf{k}_1 \cdot (\mathbf{r}_1 - \mathbf{R}_P)} 4\pi k_2^{-2} e^{i\mathbf{k}_2 \cdot (\mathbf{r}_1 - \mathbf{R}_C)}\end{aligned} \tag{A.18}$$

If we collect all the exponential terms involving our original variable of integration $\mathbf{r}_1$, we obtain

$$(A|-Z_C/r_{1C}|B) = -4\pi Z_C\tilde{K}(2\pi)^{-6}(\pi/p)^{3/2}\int d\mathbf{r}_1\, d\mathbf{k}_1\, d\mathbf{k}_2\, k_2^{-2}e^{-k_1^2/4p} \times e^{-i\mathbf{k}_1\cdot\mathbf{R}_P}e^{-i\mathbf{k}_2\cdot\mathbf{R}_C}e^{i\mathbf{r}_1\cdot(\mathbf{k}_1+\mathbf{k}_2)} \tag{A.19}$$

We can now use the definition (A.14) of the delta function to perform the integration over $\mathbf{r}_1$ to obtain

$$\begin{aligned}(A|-Z_C/r_{1C}|B) &= -4\pi Z_C\tilde{K}(2\pi)^{-3}(\pi/p)^{3/2}\int d\mathbf{k}_1\, d\mathbf{k}_2\, e^{-k_1^2/4p}k_2^{-2} \\ &\quad\times e^{-i\mathbf{k}_1\cdot\mathbf{R}_P}e^{-i\mathbf{k}_2\cdot\mathbf{R}_C}\delta(\mathbf{k}_1+\mathbf{k}_2) \\ &= -Z_C\tilde{K}/(2\pi^2)(\pi/p)^{3/2}\int d\mathbf{k}\, e^{-k^2/4p}k^{-2}e^{-i\mathbf{k}\cdot(\mathbf{R}_P-\mathbf{R}_C)}\end{aligned} \tag{A.20}$$

where we have set $\mathbf{k}_2 = -\mathbf{k}_1$ because of the delta function and relabeled the variable as $\mathbf{k}$. If we let $\mathbf{R}_P - \mathbf{R}_C$ lie along the z axis so that $\mathbf{k}\cdot(\mathbf{R}_P - \mathbf{R}_C) = k|\mathbf{R}_P - \mathbf{R}_C|\cos\theta$, then we can easily perform the angular part of the integration over $\mathbf{k}$ to obtain

$$(A|-Z_C/r_{1C}|B) = N\int_0^\infty dk\, e^{-k^2/4p}k^{-1}\sin(k|\mathbf{R}_P-\mathbf{R}_C|) \tag{A.21}$$

$$N = -2Z_C\tilde{K}(\pi|\mathbf{R}_P-\mathbf{R}_C|)^{-1}(\pi/p)^{3/2} \tag{A.22}$$

To evaluate the integral in (A.21), we consider the general integral:

$$S_{\mu\nu} = \int d\mathbf{r} \sum_{p=1}^{L} d_{p\mu}^{*} \phi_p^{\mathrm{GF}*}(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_A) \sum_{q=1}^{L} d_{q\nu} \phi_q^{\mathrm{GF}}(\alpha_{q\nu}, \mathbf{r} - \mathbf{R}_B)$$
$$= \sum_{p=1}^{L} \sum_{q=1}^{L} d_{p\mu}^{*} d_{q\nu} \int d\mathbf{r}\, \phi_p^{\mathrm{GF}*}(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_A) \phi_q^{\mathrm{GF}}(\alpha_{q\nu}, \mathbf{r} - \mathbf{R}_B)$$
$$= \sum_{p=1}^{L} \sum_{q=1}^{L} d_{p\mu}^{*} d_{q\nu} S_{pq} \tag{3.228}$$

and its derivative with respect to x,

$$I'(x) = \int_0^\infty dk\, e^{-ak^2} \cos kx \tag{A.24}$$

Note that the integrand in Eq. (A.24) is an even function of k. Since $I(0) = 0$, we have

$$\int_0^x dy\, I'(y) = I(x) - I(0) = I(x) \tag{A.25}$$

The integral in (A.24) can be evaluated by noting that $\cos\theta$ is the real part of $e^{i\theta}$ (i.e., $\cos\theta = \mathscr{R}e[e^{i\theta}]$), so that

$$I'(x) = \frac{1}{2} \int_{-\infty}^{\infty} dk\, e^{-ak^2} \cos kx = \frac{1}{2} \mathscr{R}e\left[\int_{-\infty}^{\infty} dk\, e^{-ak^2} e^{ikx} \right] \tag{A.26}$$

By completing the square, we have

$$I'(x) = \frac{1}{2} e^{-x^2/4a} \mathscr{R}e\left[\int_{-\infty}^{\infty} dk\, e^{-(a^{1/2}k - 1/2ia^{-1/2}x)^2} \right] \tag{A.27}$$

Letting $u = \alpha^{1/2}k - \frac{1}{2}i\alpha^{-1/2}x$, we have

$$I'(x) = \frac{1}{2} e^{-x^2/4a} a^{-1/2} \int_{-\infty}^{\infty} du\, e^{-u^2} = \frac{1}{2} (\pi/a)^{1/2} e^{-x^2/4a} \tag{A.28}$$

so that

$$I(x) = \frac{1}{2}(\pi/a)^{1/2} \int_0^x dy\, e^{-y^2/4a} \tag{A.29}$$

Therefore

$$\begin{aligned}(A|-Z_C/r_{1C}|B) &= -2\pi Z_C \tilde{K}(p|\mathbf{R}_P - \mathbf{R}_C|)^{-1} \int_0^{|\mathbf{R}_P - \mathbf{R}_C|} dy\, e^{-py^2} \\ &= -2\pi Z_C \tilde{K} p^{-1}(p^{1/2}|\mathbf{R}_P - \mathbf{R}_C|)^{-1} \int_0^{p^{1/2}|\mathbf{R}_P - \mathbf{R}_C|} dy\, e^{-y^2}\end{aligned} \tag{A.30}$$

We now introduce the F_0 function, which is defined by

$$F_0(t) = t^{-1/2} \int_0^{t^{1/2}} dy\, e^{-y^2} \tag{A.31}$$

It is related to the error function by

$$F_0(t) = \tfrac{1}{2}(\pi/t)^{1/2} erf(t^{1/2}) \tag{A.32}$$

Therefore, our nuclear attraction integral can be written in terms of the F_0 function as

$$\begin{aligned}(A|-Z_C/r_{1C}|B) = &-2\pi/(\alpha+\beta)Z_C \exp[-\alpha\beta/(\alpha+\beta)|\mathbf{R}_A - \mathbf{R}_B|^2] \\ &\times F_0[(\alpha+\beta)|\mathbf{R}_P - \mathbf{R}_C|^2]\end{aligned} \tag{A.33}$$

The error function (hence $F_0(t)$) is a built-in function on IBM FORTRAN compilers.

Let us now consider the two-electron integral

$$(AB|CD) = \int d\mathbf{r}_1\, d\mathbf{r}_2\, \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_A)\tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_B) r_{12}^{-1} \tilde{g}_{1s}(\mathbf{r}_2 - \mathbf{R}_C)\tilde{g}_{1s}(\mathbf{r}_2 - \mathbf{R}_D) \tag{A.34}$$

The first step is to combine the Gaussian at $\mathbf{R}_A$ and $\mathbf{R}_B$ into a new Gaussian at $\mathbf{R}_P$ and to combine those at $\mathbf{R}_C$ and $\mathbf{R}_D$ into

a new Gaussian at $\mathbf{R}_Q$ as shown in Fig. A.2. Then (A.34) becomes

$$(AB|CD) = \exp[-\alpha\beta/(\alpha+\beta)|\mathbf{R}_A - \mathbf{R}_B|^2 - \gamma\delta/(\gamma+\delta)|\mathbf{R}_C - \mathbf{R}_D|^2] \times \int d\mathbf{r}_1\, d\mathbf{r}_2\, e^{-p|\mathbf{r}_1 - \mathbf{R}_P|^2} r_{12}^{-1} e^{-q|\mathbf{r}_2 - \mathbf{R}_Q|^2} \tag{A.35}$$

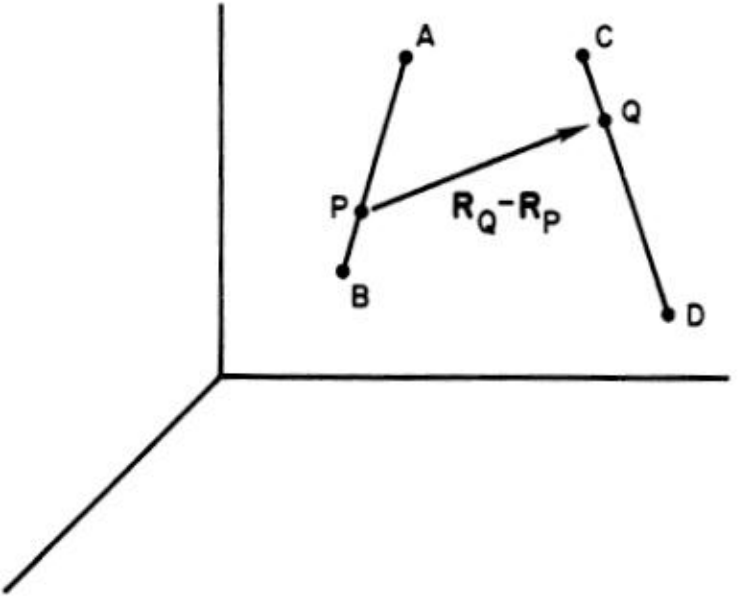

Figure A.2 The six centers involved in a two-electron integral.

Replacing the three terms in the integrand by their Fourier representation gives

$$(AB|CD) = M(2\pi)^{-9} \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{k}_1\, d\mathbf{k}_2\, d\mathbf{k}_3\, (\pi/p)^{3/2} e^{-k_1^2/4p} e^{i\mathbf{k}_1 \cdot (\mathbf{r}_1 - \mathbf{R}_P)} \times 4\pi k_2^{-2} e^{i\mathbf{k}_2 \cdot (\mathbf{r}_1 - \mathbf{r}_2)} (\pi/q)^{3/2} e^{-k_3^2/4q} e^{i\mathbf{k}_3 \cdot (\mathbf{r}_2 - \mathbf{R}_Q)} \tag{A.36}$$

where

$$M = \exp[-\alpha\beta/(\alpha+\beta)|\mathbf{R}_A - \mathbf{R}_B|^2 - \gamma\delta/(\gamma+\delta)|\mathbf{R}_C - \mathbf{R}_D|^2] \quad \text{(A.37)}$$

After collecting the exponential terms in the original variables of integration $\mathbf{r}_1$ and $\mathbf{r}_2$, we have

$$(AB|CD) = 4\pi M(2\pi)^{-9}(\pi^2/pq)^{3/2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{k}_1\, d\mathbf{k}_2\, d\mathbf{k}_3\, e^{-k_1^2/4p} e^{-k_3^2/4q} \times k_2^{-2} e^{-i\mathbf{k}_1\cdot\mathbf{R}_P} e^{-i\mathbf{k}_3\cdot\mathbf{R}_Q} e^{i\mathbf{r}_1\cdot(\mathbf{k}_1+\mathbf{k}_2)} e^{i\mathbf{r}_2\cdot(\mathbf{k}_3-\mathbf{k}_2)} \quad \text{(A.38)}$$

The integral over $\mathbf{r}_1$ and $\mathbf{r}_2$ now introduces two delta functions (see Eq. (A.14))

$$(AB|CD) = 4\pi M(2\pi)^{-3}(\pi^2/pq)^{3/2}\int d\mathbf{k}_1\, d\mathbf{k}_2\, d\mathbf{k}_3\, e^{-k_1^2/4p} e^{-k_3^2/4q} \times k_2^{-2} e^{-i\mathbf{k}_1\cdot\mathbf{R}_P} e^{-i\mathbf{k}_3\cdot\mathbf{R}_Q} \delta(\mathbf{k}_1+\mathbf{k}_2)\delta(\mathbf{k}_3-\mathbf{k}_2) \quad \text{(A.39)}$$

We can now set $\mathbf{k}_1 = -\mathbf{k}_2$ and $\mathbf{k}_3 = \mathbf{k}_2$ and relabel $\mathbf{k}_2$ as $\mathbf{k}$ to obtain

$$(AB|CD) = M/(2\pi^2)(\pi^2/pq)^{3/2}\int d\mathbf{k}\, k^{-2} e^{-(p+q)k^2/4pq} e^{i\mathbf{k}\cdot(\mathbf{R}_P-\mathbf{R}_Q)} \quad \text{(A.40)}$$

This integral is identical in form to that of (A.20) which we encountered in evaluating the nuclear attraction integral. Performing the rest of the algebra we finally obtain

$$(AB|CD) = 2\pi^{5/2}/[(\alpha+\beta)(\gamma+\delta)(\alpha+\beta+\gamma+\delta)^{1/2}] \times \exp[-\alpha\beta/(\alpha+\beta)|\mathbf{R}_A-\mathbf{R}_B|^2 - \gamma\delta/(\gamma+\delta)|\mathbf{R}_C-\mathbf{R}_D|^2] \times F_0[(\alpha+\beta)(\gamma+\delta)/(\alpha+\beta+\gamma+\delta)|\mathbf{R}_P-\mathbf{R}_Q|^2] \quad \text{(A.41)}$$

These then are the explicit formulas for all the integrals required in a Hartree-Fock calculation provided we are using

only 1*s*-type primitive Gaussian functions. They are used in the computer program listed in Appendix B.

NOTES

1. I. Shavitt, The Gaussian function in calculations of statistical mechanics and quantum mechanics, in *Methods in Computational Physics*, B. Alder, S. Fernbach, and M. Rotenberg (Eds.), Academic Press, New York, 1963.

2. M. Dupuis, J. Rys, and H. King, Evaluation of molecular integrals over Gaussian basis functions, *J. Chem. Phys*. **65:** 111 (1976).