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A Numerical Method for Evaluating Matrix Elements of Hermitian Operators

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A method for determining weights and points for the numerical calculation of the matrix elements of a hermitian operator is proposed. For local non-negative operators, this method reduces to the Gauss' method of quadrature, while it is completely novel for non-local operators. Analogously with Gauss' method of quadrature, the best n points are the zero of the polynomial of degree n belonging to the sequence of polynomials which are orthogonal with respect to the given operator. The method for obtaining the weights, which are $n(n+1)/2$, is indicated, and it is proved that $(n+1)(n+2)/2-1$ distinct matrix elements are exactly reproduced using the above determined weights and points. Some sufficient conditions in order that the zeros of the polynomial are internal to the interval of integration are examined. As a practical example the evaluation of exchange integrals generated by an atomic inner shell is given.

In many problems of quantum mechanics one must evaluate integrals such as $\int_c \bar{f}_1 \alpha f_2 \, d\tau$, where α is a hermitian operator in the space $L^2_\alpha(C) = \{ g: C \to \mathbb{C}: \int_c \bar{g} \alpha g \, d\tau < \infty \}$, $C \subset R^n$ [1]. If the functions are subjected to special conditions, it is possible to modify the operator, without its physical meaning being substantially changed, in such a way that these restrictions are no longer demanded. For example, if the integral were $\int_a^b \overline{f_1(x)}\, \alpha f_2(x) \, dx$ and the functions f_1, f_2 had to vanish at the endpoints, by taking the operator $\alpha' = (x-a)(b-x)\ \alpha(x-a)(b-x)$ such a restriction is unnecessary. Similarly, for an infinite interval, it can be useful to modify the operator by taking $\alpha' = e^{-x} \alpha e^{-x}$, or $\alpha' = e^{-x^2} \alpha e^{-x^2}$, depending on the extremes of integration. In the same manner, one can change α so that the set of all polynomials is contained in $L^2_\alpha(C)$.

Therefore, we shall examine the numerical integration of integrals of the kind

$$\langle f | \alpha | g \rangle = \int_a^b \overline{f(x)}\, \alpha g(x) \, dx$$

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with functions f and g having the form $\sum_{s=0}^{m} a_s x^s$ (the restriction to a single variable is only for brevity). The question is analogous to that of the numerical integration using Gauss' method, and it consists in determining a set of values of $x, x_0, x_1, \ldots, x_{n-1}$, belonging to the interval $[a, b]$, and a set of numerical constants H_{ij} $(0 \leqslant i, j \leqslant n-1)$ so that the sum $\sum_{ij} H_{ij} \overline{f(x_i)} \cdot g(x_j)$ is equal to $\langle f | \alpha | g \rangle$ for polynomials having the highest degree. The utility of the technique proposed is substantially for non-local operators, for which it is completely novel, while, for local non-negative operators it leads to standard Gaussian quadrature [2].

Starting from the knowledge of the values $I_{rs} = \langle x^r | \alpha | x^s \rangle$ and assuming that the determinant

$$D_{(n)} = \begin{vmatrix} I_{00} & I_{01} & \cdots & I_{0,n-1} \\ I_{10} & I_{11} & \cdots & I_{1,n-1} \\ & \vdots & & \\ I_{n-1,0} & I_{n-1,1} & \cdots & I_{n-1,n-1} \end{vmatrix}$$

is not zero for all n, it is possible to find polynomials $P_0, P_1, \ldots, P_i, \ldots$, of degree $0, 1, \ldots, i, \ldots$, orthogonal with respect to α, i.e., which satisfy the relation $\langle P_i | \alpha | P_j \rangle = \delta_{ij} \langle P_i | \alpha | P_i \rangle$. As an example, one can follow the Gram–Schmidt orthogonalization method. We denote with $\mathbb{I}$ the matrix $(\infty \times \infty)$ having entries I_{rs}, and with $\mathbb{J}$ the diagonal matrix with entries $J_{ij} = \langle P_i | \alpha | P_j \rangle$; then one has: $\mathbb{J} = \bar{L} \mathbb{I} {}^t L$, where L is the triangular (inferior) matrix composed by the coefficients of the P_i.

If f and g are polynomials of degree p and q respectively, one can write $f(x) = \sum_{i=0}^{p} f_i P_i(x)$, $g(x) = \sum_{j=0}^{q} g_j P_j(x)$, where f_i, g_j are univocally determined constants. Putting $\mathbf{f} = {}^t(f_0, f_1, \ldots, f_p, 0, \ldots)$, $\mathbf{g} = {}^t(g_0, g_1, \ldots, g_q, 0, \ldots)$, as the vectors of the components of f and g with respect to $\mathbf{P}(x) = {}^t(P_0(x), P_1(x), \ldots)$ $[= {}^t\mathbf{x} {}^t L$, with $\mathbf{x} = {}^t(1, x, x^2, \ldots)]$ the precedent equalities can be written in matrix form as

$$f(x) = {}^t\mathbf{f}\mathbf{P}(x), \qquad g(x) = {}^t\mathbf{g}\mathbf{P}(x).$$

With these notations, one has:

$$\int_a^b \overline{f(x)}\, \alpha g(x)\, dx = {}^t\bar{\mathbf{f}} \left[\int_a^b \overline{\mathbf{P}(x)}\, \alpha\, {}^t\mathbf{P}(x)\, dx \right] \mathbf{g} = {}^t\bar{\mathbf{f}} \mathbb{J} \mathbf{g} [= {}^t\mathbf{f} L \mathbb{I} {}^t L \mathbf{g}] \tag{1}$$

Analogously, one can write:

$$\sum_{i,j=0}^{n-1} H_{ij} \overline{f(x_i)}\, g(x_j) = \sum_{i,j=0}^{n-1} {}^t\bar{\mathbf{f}} \overline{\mathbf{P}(x_i)}\, H_{ij} {}^t\mathbf{P}(x_j)\, \mathbf{g}$$
$$= {}^t\bar{\mathbf{f}} \bar{\mathbb{P}} \mathbb{H} {}^t\mathbb{P} \mathbf{g} [= {}^t\mathbf{f} \bar{L} \mathbb{X} \mathbb{H} {}^t\mathbb{X} {}^t L \mathbf{g}], \tag{2}$$

where $\mathbb{P} = \mathbb{P}(x_0, \ldots, x_{n-1})$ is the matrix $(\infty \times n)$ with entries $\mathbb{P}_{\mu\nu} = P_\mu(x_\nu)$ [and $\mathbb{X}_{\mu\nu} = (x_\nu)^\mu$] and $\mathbb{H}$ is the matrix $n \times n$ of the H_{ij}.

In order that (2) gives the best approximation of (1) for every choice of f and g,

one must find the points $x_0,\ldots, x_{n-1} \in [a, b]$ so that the matrices $\mathbb{J}$ and $\bar{\mathbb{P}}\mathbb{H}'\mathbb{P}$ have the greatest number of elements equal. It is very easy to show that the approximation (2) of (1) is exact for all polynomials f and g of degrees p and q respectively, if and only if the minors $(p+1)\times(q+1)$ given by the first $(p+1)$-rows and the first $(q+1)$-columns of the above-mentioned matrices are equal.

Note that the minor of order n of $\mathbb{P}$

$$P_{(n)} = \begin{vmatrix} P_0(x_0) & P_0(x_1) & \cdots & P_0(x_{n-1}) \\ P_1(x_0) & P_1(x_1) & \cdots & P_1(x_{n-1}) \\ & \vdots & & \\ P_{n-1}(x_0) & P_{n-1}(x_1) & \cdots & P_{n-1}(x_{n-1}) \end{vmatrix}$$

does not vanish if we take $x_0,\ldots, x_{n-1}$ different among them; thus it is possible to determine $\mathbb{H}$ so that $\mathbb{J}$, $\bar{\mathbb{P}}\mathbb{H}'\mathbb{P}$ have the corresponding minors of order n $\mathbb{J}_{(n)}$, $\bar{\mathbb{P}}_{(n)}\mathbb{H}'\mathbb{P}_{(n)}$ equal by setting

$$\mathbb{H} = \bar{\mathbb{P}}_{(n)}^{-1}\mathbb{J}_{(n)}{}^{t}\mathbb{P}_{(n)}^{-1} \qquad [= \mathbb{X}_{(n)}^{-1}\mathbb{I}_{(n)}{}^{t}\mathbb{X}_{(n)}^{-1}]. \tag{3}$$

In that case $\mathbb{H}$ is a hermitian matrix. From what we have said before, the approximation (2) of (1) is exact at least for all polynomials f and g of degree up to $n-1$. By examining the equality

$$\mathbb{J} = \bar{\mathbb{P}}\mathbb{H}'\mathbb{P} \qquad [\mathbb{I} = \mathbb{X}\mathbb{H}'\mathbb{X}] \tag{*}$$

as a system in the unknowns $x_0,\ldots, x_{n-1}$, H_{ij} (which are n^2+n) it is reasonable to require that besides the equations concerning the mentioned minor of order n, other n equations (and their symmetrics) are solvable by a suitable choice of the x_i. However, one must bear in mind that it is always necessary that $x_0,\ldots, x_{n-1}$ be located in the interval $[a, b]$. For example, let us suppose that the two matrices in (*) have, besides $\mathbb{J}_{(n)}$, the elements $J_{n,0}, J_{n+1,0},\ldots, J_{2n-1,0}$ (and their symmetrics) equal; moreover, let us suppose that α is such that the function $\alpha(1)(x) \geqslant 0$ in $[a, b]$ ($\alpha(1)$ is not identically zero if $D_{(n)} \neq 0$). Then consider the product $(f, g)_0 = \int_a^b \alpha(1)(x)\,\overline{f(x)}\,g(x)\,dx$, and let $p_{01}, p_{02},\ldots, p_{0n},\ldots$, be orthogonal polynomials (of degree 0, 1,..., n,...) with respect to this product. It is known [2, 3] that the zeros $\xi_{00}, \xi_{01},\ldots, \xi_{0,n-1}$ of p_{0n} are contained in (a, b) and are distinct, and that $\int_a^b \alpha(1)(x)\,\overline{f(x)}\,dx = \langle f|\,\alpha\,|1\rangle = \sum_{i=0}^{n-1} h_{0i}\,\overline{f(\xi_{0i})}$, with suitable weights h_{0i}, for polynomials f having degree $\leqslant 2n-1$. Hence, by chosing $x_0 = \xi_{00},\ldots, x_{n-1} = \xi_{0,n-1}$ we obtain the desired equalities.

Analogously, if $\alpha(P_j) \geqslant 0$ [$\alpha(x^j) \geqslant 0$] in $[a, b]$, and if we take $x_0 = \xi_{j0},\ldots, x_{n-1} = \xi_{j,n-1}$ [$x_0 = \eta_{j0},\ldots, x_{n-1} = \eta_{j,n-1}$] as the zeros of the nth orthogonal polynomial p_{jn}[p'_{jn}] with respect to the product $(f, g)_j = \int_a^b \alpha(P_j)(x)\,\overline{f(x)}\,g(x)\,dx$, [$(f, g)'_j = \int_a^b \alpha(x^j)(x)\,\overline{f(x)}\,g(x)\,dx$], the matrices in (*) will have the elements $J_{n,j},\ldots, J_{2n-1,j}$ [$I_{n,j},\ldots, I_{2n-1,j}$] equal. (However, this last condition is less significant than the preceding one, because it depends on the polynomials that are considered.)

The most reasonable requirements are that the matrices have, besides $\mathbb{J}_{(n)}$[$\mathbb{I}_{(n)}$],

the elements $J_{n,0},\ldots, J_{n,n-1}$ $[I_{n,0},\ldots, I_{n,n-1}]$ (and their symmetrics) equal. This is satisfied, as it is easily verified, by taking $x_0,\ldots, x_{n-1}$ as the zeros of P_n, when these are contained in $[a, b]$. Moreover in this manner the matrices will have the entire $(n+1)$th row and column equal, except J_{nn} $[I_{nn}]$. With this choice the approximation (2) of (1) is exact for polynomials f, g of highest degree $n+1$, n (or $n, n+1$), respectively.

One condition which guarantees that, for each n, P_n has all its zeros in (a, b), is that, setting $\alpha(\mathbf{P}(x)) = {}^t(\alpha P_0, \alpha P_1,\ldots)$ $[\alpha(\mathbf{x}) = {}^t(\alpha(1), \alpha(x),\ldots)]$, the following equality is verified

$$\alpha(\mathbf{P}(x)) = \omega(x)\, \mathbb{D}\mathbf{P}(x) \qquad [\alpha(\mathbf{x}) = \omega(x)\, L^{-1}\mathbb{D}L\mathbf{x} = \omega(x)\, \mathbb{T}\mathbf{x}], \tag{4}$$

where $\omega(x)$ is a function $\geqslant 0$ in (a, b) and $\mathbb{D}$ is a diagonal matrix [while $\mathbb{T}$ is a triangular matrix]. In fact, setting $f \cdot g = \int_a^b \omega(x)\, \overline{f(x)}\, g(x)\, dx$, one has

$$\begin{aligned} \mathbb{J} &= \langle \mathbf{P}(x)\, |\alpha|^t\, \mathbf{P}(x) \rangle = \langle \mathbf{P}(x) \mid \omega(x)^t\, \mathbf{P}(x)^t\, \mathbb{D} \rangle \\ &= \mathbf{P}(x)^t \cdot \mathbf{P}(x)\, \mathbb{D} = \Lambda\mathbb{D} \quad [\mathbb{I} = \Gamma^t\mathbb{T}], \end{aligned} \tag{5}$$

where Λ is given by $\Lambda_{ij} = \int_a^b \omega(x)\, \overline{P_i(x)}\, P_j(x)\, dx$ $[\Gamma_{ij} = \int_a^b \omega(x)\, x^{i+j}\, dx]$. Since $\mathbb{D}$ and $\mathbb{J}$ are diagonal matrices, so is Λ, that is the P_js are orthogonal with respects to the product $f \cdot g$; hence they have simple zeros contained in (a, b).

If the operator α is real, and the interval is all $\mathbb{R}$, (4) can be modified by an analogue relation, in which D is the inverse of a tridiagonal symmetric matrix. In fact, in that case, each polynomial $p(x)$ of degree r is expressed as

$$\omega(x)\, p(x) = \sum_{j=0}^{n+1} c_j \alpha(P_j)$$

with suitable constants c_j. If x_0 was a complex zero of P_n (which we can choose to have real coefficients) and if $P_n(x) = \gamma_n(x-x_0)(x-x_0)(x-x_2)\cdots(x-x_{n-1})$ then one would have

$$\begin{aligned} \int_a^b \omega(x)\, \gamma_n(x-x_0)(x-\bar{x}_0)(x-x_2)^2\cdots(x-x_{n-1})^2\, dx &= \int_a^b P_n \sum_{j=0}^{n-1} c_j \alpha P_j\, dx \\ &= \sum_{j=0}^{n-1} c_j \int_a^b P_n \alpha P_j\, dx = 0, \end{aligned}$$

because of the orthogonality of P_n, P_j when $j \leqslant n-1$; hence $(x-x_0)(x-\bar{x}_0)$ would have to vanish for real x, which is absurd. Therefore all of the zeros of P_n are real.

The technique that we have exposed above has turned out to be very useful for some problems of chemical physics connected with non-local operators. As an example we propose there the numerical evaluation of exchange integrals.

The exchange operator of the inner shell of a given heavy atom can be written as

$$\begin{aligned} K &= \sum_n K_n, \qquad (n = 1, 2, \ldots) \\ K_n &= \sum_{l=0}^{n-1} \sum_{m=-l}^{l} K_{nlm} \\ K_{nlm}\varphi(r_1) &= \psi_{nlm}(r_1) \int \psi^*_{nlm}(r_1)\, \varphi(r_2)(|r_2 - r_1|)^{-1}\, dr_2 \\ \psi_{nlm}(r) &= \left[\frac{(2\zeta)^{2n+1}}{(2n)!}\right]^{1/2} r^{n-1} e^{-\zeta r} Y_{l,m}(\theta, \varphi) = R_n(r)\, Y_{l,m}(\theta, \varphi). \end{aligned} \tag{6}$$

In (6) we suppose that each inner shell can be represented by only one Slater function, and we derive formulas for such a case, but the generalisation to two or more Slater functions, or different radial parts for different l, is straightforward.

Let us assume that we have two functions $\Phi_1(r - R_1)$ and $\Phi_2(r - R_2)$; we can expand them in spherical harmonics, with the same centre as K_n, and write

$$\begin{aligned} \Phi_1(r - R_1) &= \sum_{p=0}^{\infty} \sum_{q=-p}^{p} \varphi_{pq}(r)\, r^p Y_{pq}(\omega) \\ \Phi_2(r - R_2) &= \sum_{p'=0}^{\infty} \sum_{q=-p'}^{p'} f_{p'q}(r)\, r^{p'} Y_{p'q'}(\omega). \end{aligned} \tag{7}$$

Using the expansion [4] of $(|r_2 - r_1|)^{-1}$ from (6) and (7), and after the angular integration we obtain [5]:

$$\int \Phi_1 K_n \Phi_2\, d\tau = \sum_{pq} \int \varphi_{pq}(r_1)\, R_n(r_1)\, r_1^{2+p}\, dr_1 \int f_{pq}(r_2)\, R_n(r_2)\, r_2^{2+p} \gamma_{np}(r_1 r_2)\, dr_2 \tag{8}$$

with

$$\gamma_{n,p}(r_1 r_2) = \sum_{l=0}^{n-1} \sum_{i=0}^{\infty} \frac{r_<^i}{r_>^{i+1}} \frac{(2p+1)(2l+1)}{(2i+1)^2} C^2(p, l, i, 0, 0, 0). \tag{9}$$

The different contributions to the integral (8) are thus characterized by different expressions for $\gamma_{n,p}$. Let us consider a term of (8), putting

$$\begin{aligned} \varphi_{pq}(r) &= \sum_s \alpha_s r^s \\ f_{pq}(r) &= \sum_t \beta_t r^t. \end{aligned} \tag{10}$$

Any of the integrals inside the summation (8), i.e.,

$$I_{pq} = \int \varphi_{pq}(r_1)\, R_n(r_1)\, f_{pq}(r_2)\, R_n(r_2)\, \gamma_{np}(r_1, r_2)\, r_1^{2+p} r_2^{2+p}\, dr_1\, dr_2$$

then becomes

$$I_{pq} = \sum_{st} \alpha_s \beta_t Q_{st}(n, p), \tag{11}$$

where

$$Q_{st}(n, p) = \int R_n(r_1)\, R_n(r_2)\, \gamma_{np}(r_1 r_2)\, r_1^{s+p+2} r_2^{t+p+2}\, dr_1\, dr_2$$

$$= \int e^{-p_1 - p_2} p_1^{n+s+p+1} p_2^{n+p+t+1} \gamma_{np}(p_1 p_2)\, dp_1\, dp_2, \tag{12}$$

where $\zeta r_1 = p_1$ and $\zeta r_2 = p_2$.

If we now set

$$I_{pq} \simeq \sum_{ij} H_{ij} f_{pq}(r_i)\, \varphi_{pq}(r_j) \tag{13}$$

we obtain, from (10), (11), (12), and (13),

$$\sum_{st} \frac{\alpha_s \beta_t}{\zeta^{s+t}} \left[q_{st}(n, p) - \sum_{ij} h_{ij} v_i^s v_j^t \right] = 0, \tag{14}$$

TABLE I

Points and Weights for Integrals of the Type $\langle s|\, K_1\, |s\rangle$

$N_p = 1$	$P_1 = 2.5$	$H_{11} = 1.25$
$N_p = 2$	$P_1 = 1.45080666151$	$H_{11} = 0.592342882607$
	$P_2 = 4.54919333846$	$H_{12} = 0.234375000001$
		$H_{22} = 0.188907117389$
$N_p = 3$	$P_1 = 1.06710649908$	$H_{11} = 0.240656423163$
	$P_2 = 2.93658305757$	$H_{12} = 0.213009553935$
	$P_3 = 6.49631044424$	$H_{13} = 0.025990411916$
		$H_{22} = 0.400383162779$
		$H_{23} = 0.058354143652$
		$H_{33} = 0.014252195055$
$N_p = 4$	$P_1 = 0.85142460521$	$H_{11} = 0.118885638116$
	$P_2 = 2.26616210162$	$H_{12} = 0.143666899247$
	$P_3 = 4.46282779200$	$H_{13} = 0.049888875751$
	$P_4 = 8.41958553569$	$H_{14} = 0.003635803326$
		$H_{22} = 0.347113462687$
		$H_{23} = 0.134206486184$
		$H_{24} = 0.009212922182$
		$H_{33} = 0.088296738661$
		$H_{34} = 0.008641307252$
		$H_{44} = 0.000799572045$

with

$$H_{ij} = \frac{2^{2n+1}}{(2n)!} \frac{h_{ij}}{\zeta^{2p+2}},$$

$$r_i = \frac{v_i}{\zeta}.$$

Points v_i and weights h_{ij} independent of α_s and β_t are obtained in the way described in the first part of this paper.

By the method explained above we have calculated the points $v_1 \cdots v_N$ and the weights h_{ij} for the operators k_n ($n = 1,..., 4$) and for N (number of points) from 1 to 4. These points and weights are reported in Tables I–VIII.

When the angular part of the functions f and φ is not explicitly given, one must calculate these functions at a certain number of points on a given sphere. If we take the six points P_i on the 3-coordinate axis, then the expression $\sqrt{\pi}/3 \sum_{i=1}^{6} f(p_i)$ gives the spherical contribution correctly up to $l = 4$, while the total p-type contribution, correct up to $l = 3$, can be obtained by using $(1/r_i)\sqrt{\pi/3}(f(P_1) - f(P_2) + f(P_3) - f(P_4) + f(P_5) - f(P_6))$. Our experience shows that these expressions are quite simple and accurate.

TABLE II

Points and Weights for Integrals of the Type $\langle s| K_2 |s\rangle$

$N_p = 1$	$P_1 = 3.5$	$H_{11} = 10$
$N_p = 2$	$P_1 = 2.20417150038$	$H_{11} = 4.49289030971$
	$P_2 = 5.79582849959$	$H_{12} = 1.89922480622$
		$H_{22} = 1.70866007786$
$N_p = 3$	$P_1 = 1.70686399052$	$H_{11} = 1.74517772185$
	$P_2 = 3.94935189695$	$H_{12} = 1.61463423957$
	$P_3 = 7.84378411129$	$H_{13} = 0.22026264522$
		$H_{22} = 3.36457403385$
		$H_{23} = 0.53307388845$
		$H_{33} = 0.15430669784$
$N_p = 4$	$P_1 = 1.39130720352$	$H_{11} = 0.78246320695$
	$P_2 = 3.14594635457$	$H_{12} = 1.03024089486$
	$P_3 = 5.60983247045$	$H_{13} = 0.38244357032$
	$P_4 = 9.85291398871$	$H_{14} = 0.03256526658$
		$H_{22} = 2.83721017743$
		$H_{23} = 1.14478563167$
		$H_{24} = 0.08703518627$
		$H_{33} = 0.86867423187$
		$H_{34} = 0.07363607402$
		$H_{44} = 0.01023913636$

TABLE III

Points and Weights for Integrals of the Type $\langle s|\ K_3\ |s\rangle$

$N_p = 1$	$P_1 = 4.5$	$H_{11} = 137.875$
$N_p = 2$	$P_1 = 2.98442150646$	$H_{11} = 59.5236549842$
	$P_2 = 7.01557849355$	$H_{12} = 26.5150147847$
		$H_{22} = 25.3213154466$
$N_p = 3$	$P_1 = 2.38571000425$	$H_{11} = 22.3214011507$
	$P_2 = 4.95699822302$	$H_{12} = 21.5080609440$
	$P_3 = 9.15729176967$	$H_{13} = 3.21398391467$
		$H_{22} = 47.5169515496$
		$H_{23} = 8.00902285976$
		$H_{33} = 2.57451186326$
$N_p = 4$	$P_1 = 1.97795750421$	$H_{11} = 9.33618260333$
	$P_2 = 4.03642409320$	$H_{12} = 13.1560654650$
	$P_3 = 6.73669720718$	$H_{13} = 5.18234923422$
	$P_4 = 11.2489211851$	$H_{14} = 0.49577053909$
		$H_{22} = 39.1551932788$
		$H_{23} = 16.3711122141$
		$H_{24} = 1.35853988964$
		$H_{33} = 13.5964690681$
		$H_{34} = 1.23372115161$
		$H_{44} = 0.19203806328$

TABLE IV

Points and Weights for Integrals of the Type $\langle s|\ K_4\ |s\rangle$

$N_p = 1$	$P_1 = 5.5$	$H_{11} = 3010.5$
$N_p = 2$	$P_1 = 3.78475185035$	$H_{11} = 1259.95362836$
	$P_2 = 8.21524814976$	$H_{12} = 585.043862312$
		$H_{22} = 580.458647015$
$N_p = 3$	$P_1 = 3.09320767247$	$H_{11} = 459.363306668$
	$P_2 = 5.96215731522$	$H_{12} = 458.023820293$
	$P_3 = 10.4446350130$	$H_{13} = 73.5849154651$
		$H_{22} = 1051.63493794$
		$H_{23} = 186.002715769$
		$H_{33} = 64.2788523281$
$N_p = 4$	$P_1 = 2.59933420998$	$H_{11} = 182.109127408$
	$P_2 = 4.93508289110$	$H_{12} = 270.878301366$
	$P_3 = 7.85018745280$	$H_{13} = 112.058746459$
	$P_4 = 12.6153954062$	$H_{14} = 11.7073912375$
		$H_{22} = 850.323150111$
		$H_{23} = 366.126554626$
		$H_{24} = 32.6598090752$
		$H_{33} = 323.947323613$
		$H_{34} = 31.0141030701$
		$H_{44} = 5.23058720783$

TABLE V

Points and Weights for Integrals of the Type $\langle p| K_1 |p\rangle$

$N_p = 1$	$P_1 = 3.5$	$H_{11} = 1.75$
$N_p = 2$	$P_1 = 2.33095407918$	$H_{11} = 0.890330929842$
	$P_2 = 5.66904592073$	$H_{12} = 0.246794871798$
		$H_{22} = 0.366079326560$
$N_p = 3$	$P_1 = 1.80190654436$	$H_{11} = 0.386113160475$
	$P_2 = 3.98977659082$	$H_{12} = 0.221091970685$
	$P_3 = 7.70831686636$	$H_{13} = 0.015314691567$
		$H_{22} = 0.686909691489$
		$H_{23} = 0.083703882550$
		$H_{33} = 0.036756050435$
$N_p = 4$	$P_1 = 1.48118475461$	$H_{11} = 0.180336107386$
	$P_2 = 3.18304866743$	$H_{12} = 0.149464453892$
	$P_3 = 5.63524421477$	$H_{13} = 0.030480366294$
	$P_4 = 9.70052229473$	$H_{14} = 0.002018787696$
		$H_{22} = 0.616150942836$
		$H_{23} = 0.179178816543$
		$H_{24} = 0.008560466225$
		$H_{33} = 0.185646649000$
		$H_{34} = 0.012928574601$
		$H_{44} = 0.002603370244$

TABLE VI

Points and Weights for Integrals of the Type $\langle p| K_2 |p\rangle$

$N_p = 1$	$P_1 = 4.5$	$H_{11} = 349.15$
$N_p = 2$	$P_1 = 2.95833181119$	$H_{11} = 147.454247660$
	$P_2 = 7.04166818887$	$H_{12} = 69.8737816920$
		$H_{22} = 61.9481889556$
$N_p = 3$	$P_1 = 2.34459171512$	$H_{11} = 52.4057946143$
	$P_2 = 4.94304090496$	$H_{12} = 56.4795525848$
	$P_3 = 9.21236738202$	$H_{13} = 8.62607881591$
		$H_{22} = 119.195327098$
		$H_{23} = 20.6748171066$
		$H_{33} = 5.98798127323$
$N_p = 4$	$P_1 = 1.94857369502$	$H_{11} = 21.8022509632$
	$P_2 = 4.01024967129$	$H_{12} = 33.7180302590$
	$P_3 = 6.73880190174$	$H_{13} = 14.1937335998$
	$P_4 = 11.3023748753$	$H_{14} = 1.32104042221$
		$H_{22} = 95.5691236084$
		$H_{23} = 43.0705834765$
		$H_{24} = 3.67535281145$
		$H_{33} = 33.2006789883$
		$H_{34} = 3.09022329819$
		$H_{44} = 0.44001869920$

TABLE VII

Points and Weights for Integrals of the Type $\langle p| K_3 |p\rangle$

$N_p = 1$	$P_1 = 5.5$	$H_{11} = 8422.45714286$
$N_p = 2$	$P_1 = 3.76781902785$	$H_{11} = 3478.84375803$
	$P_2 = 8.23218097208$	$H_{12} = 1675.68390602$
		$H_{22} = 1592.24557278$
$N_p = 3$	$P_1 = 3.06073231235$	$H_{11} = 1220.25198262$
	$P_2 = 5.95211688356$	$H_{12} = 1310.38215957$
	$P_3 = 10.4871508025$	$H_{13} = 210.116790797$
		$H_{22} = 2935.83210755$
		$H_{23} = 527.752340554$
		$H_{33} = 169.\ 870470886$
$N_p = 4$	$P_1 = 2.57437967603$	$H_{11} = 479.403020526$
	$P_2 = 4.91029198107$	$H_{12} = 759.884073918$
	$P_3 = 7.85502851969$	$H_{13} = 325.525931763$
	$P_4 = 12.6602998117$	$H_{14} = 32.8530793161$
		$H_{22} = 2329.76035654$
		$H_{23} = 1057.14138339$
		$H_{24} = 94.5148357954$
		$H_{33} = 887.672781772$
		$H_{34} = 86.0871710229$
		$H_{44} = 13.6080333927$

TABLE VIII

Points and Weights for Integrals of the Type $\langle p| K_4 |p\rangle$

$N_p = 1$	$P_1 = 6.5$	$H_{11} = 277369.928571$
$N_p = 2$	$P_1 = 4.58842573343$	$H_{11} = 112217.444670$
	$P_2 = 9.41157426668$	$H_{12} = 55221.5510015$
		$H_{22} = 54709.3818987$
$N_p = 3$	$P_1 = 3.79681850907$	$H_{11} = 38851.3668961$
	$P_2 = 6.95847649921$	$H_{12} = 42022.0432165$
	$P_3 = 11.7447049656$	$H_{13} = 7102.86321170$
		$H_{22} = 97672.3207730$
		$H_{23} = 18153.9325877$
		$H_{33} = 6288.56287268$
$N_p = 4$	$P_1 = 3.22670816096$	$H_{11} = 14618.0234416$
	$P_2 = 5.81876229681$	$H_{12} = 23795.8795773$
	$P_3 = 8.95954737781$	$H_{13} = 10469.9870176$
	$P_4 = 13.9949830515$	$H_{14} = 1137.05835081$
		$H_{22} = 76684.1141546$
		$H_{23} = 35185.8351013$
		$H_{24} = 3312.67553856$
		$H_{33} = 31396.3331735$
		$H_{34} = 3164.27196324$
		$H_{44} = 540.042726520$

TABLE IX

Values of Some Typical Integrals

	N_p				
	1	2	3	4	Exact
$\langle 1s(z_2)\vert K_1(z_1)\vert 1s(z_2)\rangle$	3.007	4.372	4.358	4.367	4.366
$\langle 1s(z_4)\vert K_1(z_1)\vert 1s(z_4)\rangle$	0.3345	0.3471	0.3468	0.3468	0.3468
$\langle 2s(z_3)\vert K_1(z_1)\vert 2s(z_3)\rangle$	0.1865	0.1413	0.1446	0.1442	0.1442
$\langle 3s(z_3)\vert K_1(z_1)\vert 3s(z_3)\rangle$	0.00971	0.00982	0.00969	0.00976	0.00975
$\langle 3s(z_3)\vert K_2(z_2)\vert 3s(z_3)\rangle$	0.9073	0.5781	0.6104	0.6081	0.6099
$\langle 4s(z_4)\vert K_2(z_2)\vert 4s(z_4)\rangle$	0.00374	0.00498	0.00468	0.00474	0.00473
$\langle 4s(z_4)\vert K_3(z_3)\vert 4s(z_4)\rangle$	0.2243	0.1432	0.1553	0.1559	0.1557
$\langle 5s(z_5)\vert K_4(z_4)\vert 5s(z_5)\rangle$	0.0721	0.0502	0.0533	0.0538	0.0537
$\langle 2p(z_3)\vert K_1(z_1)\vert 2p(z_3)\rangle$	0.0253	0.0305	0.0306	0.0306	0.0306
$\langle 3p(z_5)\vert K_2(z_2)\vert 3p(z_5)\rangle$	0.00394	0.00335	0.00338	0.00337	0.00337
$\langle 3p(z_4)\vert K_2(z_2)\vert 3p(z_4)\rangle$	0.1394	0.1187	0.1188	0.1181	0.1182
$\langle 4p(z_4)\vert K_3(z_3)\vert 4p(z_4)\rangle$	0.5555	0.4609	0.4561	0.4529	0.4536
$\langle 5p(z_5)\vert K_3(z_3)\vert 5p(z_5)\rangle$	0.00143	0.00139	0.00138	0.00139	0.00139
$\langle 5p(z_5)\vert K_4(z_4)\vert 5p(z_5)\rangle$	0.2201	0.1531	0.1588	0.1588	0.1589
$\langle 5p(z_6)\vert K_4(z_4)\vert 5p(z_6)\rangle$	0.00277	0.00245	0.00247	0.00248	0.00248

Note. N_p = number of radial points for the numerical integration; values of the orbital exponents: $z_1 = 16$, $z_2 = 7$, $z_3 = 4$, $z_4 = 2$, $z_5 = 1$, $z_6 = 0.5$.

In Table IX we report the approximate and the exact values of some typical integrals. These points and weights have been applied to the calculation of the matrix elements of the exchange integral K generated by the orbitals representing the inner shells of heavy atoms [6]. This approximate calculation constitutes a remarkable simplification in the calculations of electronic structure of molecules or complexes involving pseudopotentials [7].

REFERENCES

1. A. MESSIAH, "Quantum Mechanics," Vol. 2, Chap. 28, North–Holland, Amsterdam, 1970.
2. G. SZEGÖ, "Orthogonal polynomials," Amer. Math. Soc. Coll. Publ. Vol. 23, 1939.
3. J. STOER AND R. BULIRSCH, "Introduction to Numerical Analysis," Springer-Verlag, Berlin, 1980.
4. H. EYRING, J. WALTER, AND G. E. KIMBALL, "Quantum Chemistry," p. 371, Wiley, New York, 1944.
5. M. E. ROSE, "Elementary Theory of Angular Momentum," pp. 34, 40, 62, Wiley, New York, 1957.
6. R. MONTAGNANI AND O. SALVETTI, *Theor. Chim. Acta* **65** (1984), 120.
7. J. C. PHILLIPS AND L. KLEINMAN, *Phys. Rev.* **116** (1959), 287; J. D. WEEKS, A. HAZI, AND S. A. RICE, *Adv. Chem. Phys.* **16** (1969), 283; R. N. DIXON, P. W. TASKER, AND G. G. BALINT-KURTI, *Mol. Phys.* **32** (1976), 1651; **34** (1977), 1455; R. N. DIXON AND I. L. ROBERTSON, *Mol. Phys.* **37** (1979), 1223; M. KLEINER AND R. MCWEENY, *Chem. Phys. Lett.* **19** (1973), 476.