

Determination of Many-Particle Integrals by the Method of Distance Functions

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An interpolative method for determining many-particle integrals needed in quantumchemical calculations is proposed. The basic idea is that integrals of the form $\int dr_I \int dr_J \varrho(r_I, r_J) r_{IJ}^{2h}$ ($h=0, 1, 2, \dots$, r_I and r_J are coordinates of the I -th and the J -th particle, respectively, r_{IJ} is their distance and $\varrho(r_I, r_J)$ is a charge distribution) can be easily calculated and can be used to determine integrals $\int dr_I \int dr_J \varrho(r_I, r_J) r_{IJ}^{2h-1}$ by interpolation (or for $h=0$ by extrapolation). By making use of the identity $\Delta_I \Delta_J r_{IJ}^{h+4} = (h+2)(h+3)(h+4)(h+5)r_{IJ}^h$ (where Δ is the Laplacian operator) the extrapolation can be replaced by interpolation definitely improving the accuracy. As a probably most natural tool for interpolation the use of an auxiliary quantity called the distance function is discussed. The method can be considerably generalized (e.g. to many-particle integrals). Numerical results obtained by applying a preliminary form of the method to two-center integrals resulting from a Slater-type base are given.

Key words: Many-particle integrals – Method of distance functions

1. Introduction

In quantumchemical calculations based on variational or perturbative techniques a high number of integrals is needed the integrands of which depend on the coordinates of the particles making up the molecular system. In the case of all but the very simplest systems it is the difficulties of integration and not the physical considerations that fundamentally influence the choice of the analytical form of the variational wave functions.

The aim of this paper is to outline the basic principles of an integration technique which may be helpful in overcoming some of the difficulties of integration. The new method is fundamentally different from the standard techniques and it has the attractive feature that it probably works better in the case of integrals that result from variational wave functions involving terms explicitly depending on the distances of the particles than in the case of integrals resulting from self-consistent-field or configuration interaction wave functions.

The method, as presented here, is far from having reached its final stage, and must undergo similar sophisticated refinements both in its algorithm as in programming techniques as the standard methods did.

2. The Basic Principles of the Method

Let us consider a molecular system that consists of N particles. The coordinates of the I -th particle in a "global" rectangular coordinate system common for all particles are $\{x_I, y_I, z_I\} = \mathbf{r}_I$. The integrals emerging in quantumchemical calculations have the forms

$$H_K = \int d\mathbf{r}_I \varrho_K(\mathbf{r}_I) f(r_{IA}) \quad (2.1)$$

$$I_{KL} = \int d\mathbf{r}_I \int d\mathbf{r}_J \varrho_K(\mathbf{r}_I) \varrho_L(\mathbf{r}_J) f(r_{IJ}) \quad (2.2)$$

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Here $\varrho(r)$ denotes some function of the coordinates of the particle and is briefly referred to as the charge distribution of the particle, r_{IA} is the distance of the I -th particle from some fixed point A , r_{IJ} is the distance between the I -th and the J -th particle and $f(r)$ is some function of r , in most cases a power of $r: r^{-1}, r^0, r^{+1}, \dots$

For simplicity only integrals depending on the coordinates of not more than two particles will be considered. It will also be assumed that the charge distributions are a product of two orbitals which may be Slater-type orbitals

$$X^{N_x} Y^{N_y} Z^{N_z} R^{N_R} \exp(-CR) \quad (2.3)$$

or Boys-type orbitals

$$X^{N_x} Y^{N_y} Z^{N_z} R^{2N_R} \exp(-CR^2). \quad (2.4)$$

Here X, Y, Z denote coordinates of arbitrary "local" rectangular coordinate systems which may have different centers and different orientation, N_x, N_y, N_z , and N_R are non-negative integers, C is a positive real and $R^2 = X^2 + Y^2 + Z^2$. A generalization of the method to more complicated cases is in principle straightforward although in practice technical difficulties may emerge. Some hint for possible generalizations will be given. It will prove advantageous to use products of powers of X, Y, Z to describe the angular dependence of the orbitals instead of spherical harmonics.

It will be assumed that the calculation of the one-particle integrals (2.1) is solved and we must concentrate on the two-particle integrals (2.2).

Let us define the auxiliary one-particle integrals

$$\mathcal{O}(K, M_x, M_y, M_z, M_r) = \int d\mathbf{r} \varrho_K(\mathbf{r}) x^{M_x} y^{M_y} z^{M_z} r^{2M_r}, \quad (2.5)$$

where $r^2 = x^2 + y^2 + z^2$. In principle the \mathcal{O} -s can be calculated in closed analytical form (although this may not be the best way for calculating them in practice). This has the consequence that for $f(r_{IJ}) = r_{IJ}^0, r_{IJ}^2, r_{IJ}^4, \dots$ the two-particle integrals (2.2) can also be calculated. By $r_{IJ}^2 = r_I^2 + r_J^2 - 2(x_I x_J + y_I y_J + z_I z_J)$ we obtain for $n = 0, 1, 2, \dots$

$$\begin{aligned} I_{KL}(2n) &= \int d\mathbf{r}_I \int d\mathbf{r}_J \varrho_K(\mathbf{r}_I) \varrho_L(\mathbf{r}_J) r_{IJ}^{2n} \\ &= \sum_{l=0}^n (-2)^l \binom{n}{l} \sum_{i=0}^l \binom{l}{i} \sum_{j=0}^i \binom{i}{j} \sum_{k=0}^{n-l} \binom{n-l}{k} \\ &\quad \times \mathcal{O}(K, j, i-j, l-i, n-l-k) \mathcal{O}(L, j, i-j, l-i, k). \end{aligned} \quad (2.6)$$

We disregard for a while the problems connected with the calculation of the \mathcal{O} -s. If the \mathcal{O} -s are given, the idea may emerge to calculate the two-particle integrals

with $r_{IJ}^{+1}, r_{IJ}^{+3}, \dots$ by interpolating between, and the integrals with r_{IJ}^{-1} by extrapolating from the integrals with $r_{IJ}^0, r_{IJ}^2, \dots$. Essentially this is the basic idea of the present method.

Before considering the problem of how to interpolate it will be shown that without loss of generality the calculation of the integrals with $r_{IJ}^{-1}, r_{IJ}^{+1}, \dots$ can always be done by interpolation.

Let us make use of the identity

$$r_{IJ}^h = \Delta_I \Delta_J r_{IJ}^{h+4} / ((h+2)(h+3)(h+4)(h+5)), \quad (2.7)$$

where $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. Integrating by parts we obtain

$$\begin{aligned} I_{KL}(h) &= \int d\mathbf{r}_I \int d\mathbf{r}_J \varrho_K(\mathbf{r}_I) \varrho_L(\mathbf{r}_J) r_{IJ}^h \\ &= \int d\mathbf{r}_I \int d\mathbf{r}_J \Delta_I \varrho_K(\mathbf{r}_I) \Delta_J \varrho_L(\mathbf{r}_J) r_{IJ}^{h+4} / ((h+2)(h+3)(h+4)(h+5)). \end{aligned} \quad (2.8)$$

Consequently instead of calculating the integrals $I_{KL}(-1)$ we can calculate similar integrals with r_{IJ}^{+3} but with charge distribution $\Delta \varrho(\mathbf{r})$ instead of $\varrho(\mathbf{r})$. The corresponding auxiliary integrals with $r_{IJ}^0, r_{IJ}^2, r_{IJ}^4, \dots$ can be calculated without additional effort by reverting (2.8) giving

$$\begin{aligned} &\int d\mathbf{r}_I \int d\mathbf{r}_J \Delta_I \varrho_K(\mathbf{r}_I) \Delta_J \varrho_L(\mathbf{r}_J) r_{IJ}^{2h} \\ &= (2h-2)(2h-1)(2h+0)(2h+1) \int d\mathbf{r}_I \int d\mathbf{r}_J \varrho_K(\mathbf{r}_I) \varrho_L(\mathbf{r}_J) r_{IJ}^{2h-4} \end{aligned} \quad (2.9)$$

where the right-hand side of (2.9) vanishes for $h=0, 1$.

This procedure will be referred to as the pre-manipulation of the (two-particle) integrals.

Summarizing: In order to calculate the integrals $I_{KL}(-1), I_{KL}(+1), \dots$ we a) calculate the auxiliary two-particle integrals

$$T_{KL}(2h) = \int d\mathbf{r}_I \int d\mathbf{r}_J \varrho_{KL}(\mathbf{r}_I, \mathbf{r}_J) r_{IJ}^{2h} \quad (2.10)$$

$$\varrho_{KL}(\mathbf{r}_I, \mathbf{r}_J) = \Delta_I \varrho_K(\mathbf{r}_I) \Delta_J \varrho_L(\mathbf{r}_J) \quad (2.11)$$

by (2.9) and (2.6), b) calculate the integrals $T_{KL}(2h+3)$ ($h=0, 1, \dots$) by interpolating between the integrals $T_{KL}(2h)$, and c) calculate the integrals $I_{KL}(h)$ ($h=-1, +1, \dots$) by (2.8).

At this point three brief remarks must be made.

1) The pre-manipulation is by no means an identical re-formulation of the problem. This can be seen both from the fact that by pre-manipulation we obtain two additional auxiliary two-electron integrals [namely $T_{KL}(0)$ and $T_{KL}(2)$] and from the numerical experience.

2) If the wave functions contain terms explicitly depending on the distance of two particles and the nuclei are kept fixed the charge distributions $\varrho_{KL}(\mathbf{r}_I, \mathbf{r}_J)$ defined in (2.11) may contain Dirac-delta-function terms located at the nuclei. (This is an example of charge distributions more general than those defined at the beginning of this section.) The emerging of Dirac-delta-terms causes no difficulties of principle but in practice more sophisticated interpolation procedures are needed (cf. Remark 3)).

3) It is an obvious idea to repeat the pre-manipulation in order to increase its benefits. No difficulties of principle prevent us from doing it, but if the charge

distributions $\varrho(\mathbf{r})$ involve 1s or 2s Slater-type orbitals Dirac-delta-function terms appear at the centers of these orbitals. This has the effect, that the behaviour of the manipulated charge distributions becomes fundamentally different from that of the non-manipulated ones and this drastically changes the interpolation procedure. The numerical experience indicates that if the interpolation procedure is adequately chosen the second pre-manipulation generally improves the results, but if the results become inaccurate because of an unskillful way of interpolation, the second pre-manipulation causes an earlier breakdown of the approximation.

We turn now to the problem of how to interpolate.

The trivial idea of interpolating by polynomials or similar simple functions gave unstable results the accuracy of which strongly depended on the actual integral. Although this possibility can not be excluded for once and ever, at present it does not appear to be the best choice.

Probably the most natural way of interpolating is provided by an auxiliary quantity referred to as the distance function $D_{KL}(r_{IJ})$ belonging to the charge distribution $\varrho_{KL}(\mathbf{r}_I, \mathbf{r}_J)$.

Let us introduce new variables of integration in

$$T_{KL}(h) = \int d\mathbf{r}_I \int d\mathbf{r}_J \varrho_{KL}(\mathbf{r}_I, \mathbf{r}_J) r_{IJ}^h. \quad (2.12)$$

Be one variable the distance r_{IJ} and five other independent variables which need not be specified in detail and will be denoted by \mathbf{q}_{IJ} . As in our case the integral $T_{KL}(h)$ is absolutely convergent we can write

$$T_{KL}(h) = \int_0^\infty dr_{IJ} [r_{IJ}^2 \int d\mathbf{q}_{IJ} \sigma_{KL}(r_{IJ}, \mathbf{q}_{IJ})] r_{IJ}^h \quad (2.13)$$

where $\sigma_{KL}(r_{IJ}, \mathbf{q}_{IJ})$ denotes the charge distribution $\varrho_{KL}(\mathbf{r}_I, \mathbf{r}_J)$ expressed as a function of the new variables. We define the distance function $D_{KL}(r_{IJ})$ belonging to the charge distribution $\varrho_{KL}(\mathbf{r}_I, \mathbf{r}_J)$ by

$$D_{KL}(r_{IJ}) = r_{IJ}^2 \int d\mathbf{q}_{IJ} \sigma_{KL}(r_{IJ}, \mathbf{q}_{IJ}). \quad (2.14)$$

Thus for any function $f(r_{IJ})$ for which an integral analogous to (2.13) is absolutely convergent we have

$$T_{KL}(f) = \int_0^\infty dr_{IJ} D_{KL}(r_{IJ}) f(r_{IJ}) \quad (2.15)$$

(the notation is obvious).

If the distance function is known, any integral satisfying the above conditions can be calculated at worst by a one-dimensional numerical quadrature.

The Eq. (2.15) will be considered as the basic equation of the method of distance functions. Our aim will be to determine approximations to the distance functions belonging to the emerging charge distributions.

In order to solve this task we combine three sources of information.

1) Starting from the definition Eq. (2.14) of the distance function and taking into account only qualitative features of the charge distribution the following conclusions can be drawn.

The distance function and at least its first derivative are continuous functions of r_{IJ} . Higher derivatives may have discontinuities at values of r_{IJ} equal to the

distances of the centers of the orbitals making up the charge distribution. Thus the distance functions are fairly smooth functions.

At $r_{IJ} \rightarrow 0$ the distance functions vanish at least in the same order as r_{IJ}^2 . At $r_{IJ} \rightarrow \infty$ the distance functions vanish more rapidly than any negative power of r_{IJ} .

2) If we substitute explicit expressions in the place of the charge distributions in some special cases the explicit form of the distance function can be determined from (2.14). The cases in which we succeeded are:

2.1) All orbitals are Slater-type orbitals centered at the same point (one-center Slater integrals). The result is:

Be C_I and C_J the sum of the orbital exponents associated with the orbitals occupied by the I -th and the J -th particle, respectively. Then for $C_I = C_J$

$$D_{KL}(r_{IJ}) = \sum_{i=0}^n a_i r_{IJ}^{i+2} \exp(-ar_{IJ}), \quad (2.16)$$

and for $C_I \neq C_J$

$$D_{KL}(r_{IJ}) = \sum_{i=0}^{n_I} a_i^{(I)} r_{IJ}^{i+1} \exp(-a^{(I)} r_{IJ}) + \sum_{i=0}^{n_J} a_i^{(J)} r_{IJ}^{i+1} \exp(-a^{(J)} r_{IJ}), \quad (2.17)$$

where $a = C_I = C_J$, $a^{(I)} = C_I$, $a^{(J)} = C_J$, n is the sum of the exponents N_X, N_Y, N_Z, N_R of the Slater-type orbitals making up the charge distribution, n_I and n_J denotes the sum of the N -exponents associated with the I -th and the J -th particle, respectively, and $a_0^{(I)} = -a_0^{(J)}$.

2.2) Two-center Coulomb and hybrid integrals based on Slater-type orbitals. If the distance of the two centers is R , the result is similar to that of 2.1) for $r_{IJ} > R$, and involves additional terms with $\exp(+ar_{IJ})$ and $\exp(+a^{(I)}r_{IJ})$, $\exp(+a^{(J)}r_{IJ})$ for $r_{IJ} < R$.

2.3) All orbitals making up the charge distribution are Boys-type orbitals. The result can be expressed in terms of a special set of "elementary functions" but it is a very complicated expression and we have failed to bring it to a practically useful form.

The results 2.1)–2.3) can be used for obtaining a more definite picture of the possible analytical form of the distance function.

In all the cases 2.1)–2.3) the integral (2.14) has been evaluated by using polar coordinates for both particles, the origin of the coordinate system for Particle I being at the center of an orbital, the origin of the coordinate system for particle J being at the actual position of Particle I.

3) From more or less qualitative considerations similar to those described in 1)–2) we can choose a variational function $D_{KL}(r_{IJ}; a_0, a_1, \dots, a_n)$ in order to approximate to the distance function $D_{KL}(r_{IJ})$. The variational parameters a_0, a_1, \dots, a_n can be determined from the criterion that for $h = 0, 1, \dots, n$

$$\int_0^\infty dr_{IJ} D_{KL}(r_{IJ}; a_0, a_1, \dots, a_n) r_{IJ}^{2h} = T_{KL}(2h) \quad (2.18)$$

where the integrals $T_{KL}(2h)$ are assumed to be known. Having determined the parameters a_0, a_1, \dots, a_n we have for any function $f(r_{IJ})$ for which the relevant integrals are absolutely convergent

$$T_{KL}(f) \approx \int_0^\infty dr_{IJ} D_{KL}(r_{IJ}; a_0, a_1, \dots, a_n) f(r_{IJ}). \quad (2.19)$$

This procedure is justified by the fact that by Müntz's theorem a function satisfying the conditions for the distance function is uniquely determined by its non-negative even moments.

Before proceeding let us briefly summarize the critical points of the method of distance functions.

a) The determination of the auxiliary two-particle integrals $T_{KL}(2h)$. This appears to be no serious problem and can with a high probability be satisfactorily solved by a careful elaboration of existing ideas (cf. Section 3). In any case the number of auxiliary one-particle integrals entering (2.6) is proportional to the number of different one-particle charge distributions and thus increases only with the square of the number of basic functions. It appears improbable that a much better expression than (2.6) can be found for the determination of the $T_{KL}(2h) - s$.

b) The determination of the analytical form of the variational distance functions. In this context the choice proposed in Section 4 – although it gives fairly good results in many cases – is probably far from the best one. This appears to be the problem where the most important developments can be expected and the present solution must be considered as a preliminary one.

c) The solving of the Eqs. (2.18). At this point the results presented in Section 3 appear to give a solution sufficiently simple to justify the assumption that this problem will not cause major difficulties.

d) The problem of error estimates. For the moment only qualitative error estimates of the character of stability tests could be found so that this problem must be considered as open.

e) In order to increase the rate of convergence of the method of distance functions it is often advantageous to apply also auxiliary two-particle integrals other than the $T_{KL}(2h) - s$. The simplest possibility is to use as auxiliary two-particle functions $f(r_{IJ}) = \delta^{(3)}(r_{IJ})$ and $f(r_{IJ}) = \Delta_I \delta^{(3)}(r_{IJ})$, where $\delta^{(3)}$ denotes the three-dimensional Dirac-delta-function. If these functions are substituted into the integrals (2.2) the pre-manipulated integrals can be easily obtained by the identity $\Delta_I r_{IJ}^{-1} = -4\pi \delta^{(3)}(r_{IJ})$, giving

$$T_{KL}(+1) = -8\pi \int d\mathbf{r} \varrho_K(\mathbf{r}) \varrho_L(\mathbf{r}), \quad (2.20)$$

$$T_{KL}(-1) = -4\pi \int d\mathbf{r} \varrho_K(\mathbf{r}) \Delta \varrho_L(\mathbf{r}). \quad (2.21)$$

In any case for multi-center integrals the calculation of $T_{KL}(+1)$ and $T_{KL}(-1)$ may be a harder task than the calculation of $T_{KL}(2h)$.

3. Selected Technical Problems

This section deals with two problems: the calculation of the auxiliary one-electron integrals (2.5) and the solving of the set of Eq. (2.18).

1) In the one- and two-center case the calculation of the integrals (2.5) is a routine task. In multi-center problems difficulties emerge however from the fact, that the local coordinate systems in which the orbitals are given and the global coordinate system $\{x, y, z\}$ have in general different orientations and different

origins. It is not evident that the best idea is to reduce the multi-center case to a linear combination of one- or two-center problems by appropriate rotations and translations of the coordinates.

Instead the following way appears to be helpful, at least for a pure Slater-type base. Let us introduce two-center elliptical coordinates μ_I, ν_I, φ_I with focuses at the points defined by the centers of the orbitals making up the one-particle charge distribution of particle I . (The same applies to particle J .) In principle, the integrals (2.5) are a voluminous linear combination of integrals of the type

$$\int_1^{\infty} d\mu_I \int_{-1}^{+1} d\nu_I \int_0^{2\pi} d\varphi_I \sin^p \varphi_I \cos^q \varphi_I \mu_I^r \nu_I^s \exp(-\alpha_I \mu_I) \exp(-\beta_I \nu_I), \quad (3.1)$$

where $p + q + r + s$ does not exceed $M_X + M_Y + M_Z + M_R + 2$ plus the sum of the N -exponents of the orbitals making up the charge distribution of Particle I . Now for such integrals there exists a Gaussian-type numerical quadrature which is exact for every integral for which $p + q + r + s$ is less or equal to the value in (3.1). In addition, by introducing the new variable of integration $\lambda_I = \alpha_I(\mu_I - 1)$ for which the bounds are $0 \leq \lambda_I \leq \infty$ the meshpoints and weight factors of this quadrature are independent of α_I and thus can be calculated and stored for once and ever. (The same is naturally true for the φ_I -integral, where the weight factors are equal and the meshpoints are equidistant.) The set of meshpoints and weight factors must thus be generated only for the ν_I -integral, and for this purpose rapid algorithms are available which are not sensitive to round-off errors.

As such a numerical quadrature is exact for any linear combination of integrals of the type (3.1) for which $p + q + r + s$ does not exceed the order of the quadrature, specially such a numerical quadrature is exact for the auxiliary one-electron integral (2.5), without making necessary to calculate the linear combination coefficients explicitly.

The calculation of the values of the integrand of the auxiliary one-particle integrals (2.5) at the points needed by the quadrature is a relatively easy task, as it requires only the rotation and translation of one coordinate and not of products of (often high) powers of different coordinates.

There is one question that is not clear at present. Namely the calculation of the one-particle auxiliary integrals needed for calculating $T_{KL}(2h) - s$ with different $h - s$ requires Gaussian quadratures of different minimum degrees. Naturally we can calculate all integrals with the quadrature of the highest degree, but this means that we calculate at an unnecessary high number of meshpoints at lower $h - s$. On the other hand if we apply the Gaussian quadrature of minimum degree for different $h - s$, this means that we can not use the integrand values calculated for one h in the case of another h . Probably the optimum is some compromise.

It must be emphasized that as the number of auxiliary one-electron integrals (2.5) increases with the square of the number of the basic functions, for a high number of basic functions this is not likely to be a time-determining step. In addition, in calculations in series on similar systems a portion of the integrals (2.5) can often be carried from one calculation to the next one.

b) The solving of the set of Eq. (2.18) (or of analogous equations involving also other auxiliary two-particle integrals) is a highly important problem as the

number of such equations is equal to the number of integrals. This task becomes, however, very easy in the case of two important special types of variational distance functions:

- 1) when the distance function involves only linear parameters, and
- 2) when the distance function involves only linear parameters plus one common scale factor. It appears probable that the variational distance functions will either be of such types or of types which can by some tricks be handled by similar tools.

Let us assume, that the variational distance function has the form

$$D_{KL}(r_{IJ}; a_0, a_1, \dots, a_n) = \sum_{i=0}^n a_i D_i(r_{IJ}) \quad (a_i = a_i(K, L)), \quad (3.2)$$

where the functions $D_i(r_{IJ})$ are given.

As the Eq. (2.18) are in this case linear with given coefficients, the first idea is to calculate and store for once and ever the inverse of the coefficient matrix. If, however, we want to calculate only integrals involving a given function of r_{IJ} (r_{IJ}^3 , say, in order to calculate (2.2) with r_{IJ}^{-1}) the problem can be further simplified. For simplicity we shall consider only the case in which the auxiliary two-particle integrals are $T_{KL}(2h)$. A generalization to other cases is straightforward.

Let us assume, that we want to calculate $T_{KL}(m)$, and let us define the coefficients $b_{mh}^{(n)}$ by

$$\int_0^\infty dr_{IJ} D_i(r_{IJ}) r_{IJ}^m = \sum_{h=0}^n b_{mh}^{(n)} \int_0^\infty dr_{IJ} D_i(r_{IJ}) r_{IJ}^{2h} \quad (i = 0, 1, \dots, n). \quad (3.3)$$

The coefficients $b_{mh}^{(n)}$ can also be determined from the set of linear Eq. (3.3) for once and ever.

Let us multiply (3.3) by a_i and sum over i .

$$\int_0^\infty dr_{IJ} \left(\sum_{i=0}^n a_i D_i(r_{IJ}) \right) r_{IJ}^m = \sum_{h=0}^n b_{mh}^{(n)} \int_0^\infty dr_{IJ} \left(\sum_{i=0}^n a_i D_i(r_{IJ}) \right) r_{IJ}^{2h}. \quad (3.4)$$

It can immediately be observed, that the left-hand side of (3.4) is just the approximation to $T_{KL}(m)$ we want and the right-hand side is $\sum_{h=0}^n b_{mh}^{(n)} T_{KL}(2h)$. I.e. we have

$$T_{KL}(m) = \sum_{h=0}^n b_{mh}^{(n)} T_{KL}(2h). \quad (3.5)$$

It can also be easily verified, that if the terms D_i involve a common scale factor c

$$D_i = D_i(c r_{IJ}), \quad (3.6)$$

then (3.5) becomes

$$T_{KL}(m) = \sum_{h=0}^n c^{m-2h} b_{mh}^{(n)} T_{KL}(2h). \quad (3.7)$$

Thus the required approximation to $T_{KL}(m)$ is simply a linear combination of the auxiliary two particle integrals.

The coefficients $b_{mh}^{(n)}$ have an interesting interpretation that may perhaps be a starting point of some error estimate. Namely $\sum_{h=0}^n b_{mh}^{(n)} r_{IJ}^{2h}$ can be considered as some kind of approximation to r_{IJ}^m . Test calculations have shown that for not extremely small values of n this approximation is often surprizingly good for a fairly large interval of r_{IJ} .

4. Numerical Results

The method of distance functions has been applied to one- and two-center electron-interaction integrals with charge distributions resulting from a Slater-type base. In all cases the variational distance function has the form (2.16) with n being greater or equal to the value given in connection with Eq. (2.16). This value will be referred to as the minimum of n .

In the case of one-center integrals the convergence has been rapid (also in the case $C_I \neq C_J$ where this variational distance function is not exact) and a 6–7 decimal digit accuracy has been obtained with n exceeding the minimum value by 7. It even did not seem necessary to optimize the scale factor, the choice $a = \text{MIN}(C_I, C_J)$ being sufficiently close to the optimum.

In the two-center case the results have been less accurate. As an almost general rule it turned out that the most “benevolent” problems are the exchange integrals and the most “malevolent” problems are the Coulomb ones. This is not surprising, as the variational distance function (2.16) is exact for the one-center “homonuclear” case, and the charge distributions of exchange integrals resemble in general more to this case than those of the Coulomb integrals. Also this fact emphasizes the need for better types of variational distance functions. We hope to be able to come back to this problem in a subsequent paper.

In the two-center case the optimizing of the scale factor is of a greater importance than in the one-center case. The value $a = \text{MIN}(C_I, C_J)$ proved also for two-center integrals an often surprisingly good estimate, even at large distances of the centers of the orbitals, and could serve at least as a starting value for an optimization process.

The problem of how to optimize the scale factor deserves some more consideration. The simplest idea is to use one more auxiliary two-electron integral for adjusting the scale factor. This is, however, probably not the best way just because of the obvious reason that it needs one more auxiliary integral. Another possibility is to determine the scale factor from the criterion, that the distance function should show a maximum stability under small changes of the scale factor. (The reasons for this criterion are obvious.) As, however, we do not calculate explicitly the distance function [only the coefficients $b_{mn}^{(n)}$ defined in (3.3)] as an approximation to this criterion we can determine the scale factor from the maximum stability of the integral we want to calculate. The numerical experience has so definitely pointed out the equivalence of this later criterion and the criterion of determining the scale factor from an additional auxiliary integral, that we conjecture that there is – at least for variational distance functions of the form (2.16) – a deeper reason for this equivalence.

The criterion of the maximum stability of the distance function (or of the integral we approximate) under small changes of the scale factor seems still not to be the best practical criterion for determining the scale factor. Namely it turned out in all calculations, that for a fairly wide interval of the scale factor the approximate value of the integral oscillates around the exact value. Consequently some mean value between two adjacent extrema may be a better approximation than any of the extrema themselves. As an approximation to this mean value the inflexion point of the integral (as a function of the scale factor) between two adjacent extrema may be chosen. In an overwhelming part of the numerical examples this value has proved definitely better than the maximum stability value. The results given in Table 1 have been calculated by the inflexion point criterion.

Table 1. Selected values of electron-interaction integrals calculated by the method of distance functions. (All data are given in atomic units, assuming normalized basis functions)

$\int dr_I \int dr_J x_{IA} x_{IB} \exp(-2r_{IA} - r_{IB}) x_{JA} x_{JB} \exp(-3r_{JA} - 4r_{JB})$ (EXCHANGE)							
<i>R</i>	Δn	<i>I0</i>	<i>I1</i>	<i>I2</i>	<i>I1</i> δ	<i>I2</i> δ	EXACT
1	0	.14994	.15419	.15345	.15352	.15343	.15349
1	1	.15033	.15386	.15318	.15346	.15345	.15349
1	2	.15157	.15389	.15359	.15353	.15346	.15349
1	3	.15172	.15344	.15358	.15352	.15346	.15349
1	4	.15189	.15342	.15356	.15351	.15347	.15349
1	5	.15203	.15342	.15354	.15351	.15348	.15349
2	0	.09304 ₁₀ ⁻¹	.10904 ₁₀ ⁻¹	.10873 ₁₀ ⁻¹	.10845 ₁₀ ⁻¹	.10819 ₁₀ ⁻¹	.10828 ₁₀ ⁻¹
2	1	.10395 ₁₀ ⁻¹	.10747 ₁₀ ⁻¹	.10850 ₁₀ ⁻¹	.10836 ₁₀ ⁻¹	.10820 ₁₀ ⁻¹	.10828 ₁₀ ⁻¹
2	2	.10492 ₁₀ ⁻¹	.10779 ₁₀ ⁻¹	.10846 ₁₀ ⁻¹	.10836 ₁₀ ⁻¹	.10831 ₁₀ ⁻¹	.10828 ₁₀ ⁻¹
2	3	.11322 ₁₀ ⁻¹	.10795 ₁₀ ⁻¹	.10844 ₁₀ ⁻¹	.10835 ₁₀ ⁻¹	.10830 ₁₀ ⁻¹	.10828 ₁₀ ⁻¹
2	4	.11107 ₁₀ ⁻¹	.10807 ₁₀ ⁻¹	.10843 ₁₀ ⁻¹	.10825 ₁₀ ⁻¹	.10829 ₁₀ ⁻¹	.10828 ₁₀ ⁻¹
2	5	.10950 ₁₀ ⁻¹	.10809 ₁₀ ⁻¹	.10821 ₁₀ ⁻¹	.10825 ₁₀ ⁻¹	.10829 ₁₀ ⁻¹	.10828 ₁₀ ⁻¹
4	0	.29676 ₁₀ ⁻⁴	.10880 ₁₀ ⁻⁴	.11376 ₁₀ ⁻⁴	.11420 ₁₀ ⁻⁴	.11514 ₁₀ ⁻⁴	.11515 ₁₀ ⁻⁴
4	1	.22074 ₁₀ ⁻⁴	.12273 ₁₀ ⁻⁴	.11442 ₁₀ ⁻⁴	.11462 ₁₀ ⁻⁴	.11506 ₁₀ ⁻⁴	.11515 ₁₀ ⁻⁴
4	2	-.06869 ₁₀ ⁻⁴	.12010 ₁₀ ⁻⁴	.11476 ₁₀ ⁻⁴	.11484 ₁₀ ⁻⁴	.11511 ₁₀ ⁻⁴	.11515 ₁₀ ⁻⁴
4	3	.02422 ₁₀ ⁻⁴	.11856 ₁₀ ⁻⁴	.11496 ₁₀ ⁻⁴	.11559 ₁₀ ⁻⁴	.11513 ₁₀ ⁻⁴	.11515 ₁₀ ⁻⁴
4	4	.04615 ₁₀ ⁻⁴	.11760 ₁₀ ⁻⁴	.11558 ₁₀ ⁻⁴	.11546 ₁₀ ⁻⁴	.11514 ₁₀ ⁻⁴	.11515 ₁₀ ⁻⁴
4	5	.06228 ₁₀ ⁻⁴	.11697 ₁₀ ⁻⁴	.11545 ₁₀ ⁻⁴	.11537 ₁₀ ⁻⁴	.11518 ₁₀ ⁻⁴	.11515 ₁₀ ⁻⁴
$\int dr_I \int dr_J \exp(-3r_{AI} - 4r_{BJ}) z_{BJ} \exp(-2r_{AJ} - r_{BJ})$ (EXCHANGE)							
<i>R</i>	Δn	<i>I0</i>	<i>I1</i>	<i>I2</i>	<i>I1</i> δ	<i>I2</i> δ	EXACT
1	0	.10382	.10872	.10726	.10801	.10773	.10776
1	1	.10537	.10859	.10747	.10793	.10771	.10776
1	2	.10588	.10743	.10778	.10785	.10772	.10776
1	3	.10815	.10745	.10779	.10785	.10773	.10776
1	4	.10631	.10751	.10781	.10784	.10774	.10776
1	5	.10858	.10757	.10780	.10783	.10774	.10776
2	0	.87499 ₁₀ ⁻²	.82665 ₁₀ ⁻²	.91076 ₁₀ ⁻²	.84189 ₁₀ ⁻²	.85805 ₁₀ ⁻²	.84981 ₁₀ ⁻²
2	1	.98454 ₁₀ ⁻²	.84897 ₁₀ ⁻²	.82715 ₁₀ ⁻²	.84529 ₁₀ ⁻²	.85247 ₁₀ ⁻²	.84981 ₁₀ ⁻²
2	2	.95400 ₁₀ ⁻²	.84717 ₁₀ ⁻²	.83349 ₁₀ ⁻²	.84865 ₁₀ ⁻²	.85293 ₁₀ ⁻²	.84981 ₁₀ ⁻²
2	3	.85197 ₁₀ ⁻²	.86385 ₁₀ ⁻²	.84846 ₁₀ ⁻²	.84921 ₁₀ ⁻²	.85246 ₁₀ ⁻²	.84981 ₁₀ ⁻²
2	4	.84758 ₁₀ ⁻²	.86173 ₁₀ ⁻²	.84605 ₁₀ ⁻²	.84921 ₁₀ ⁻²	.85215 ₁₀ ⁻²	.84981 ₁₀ ⁻²
2	5	.84910 ₁₀ ⁻²	.85178 ₁₀ ⁻²	.84507 ₁₀ ⁻²	.85145 ₁₀ ⁻²	.84896 ₁₀ ⁻²	.84981 ₁₀ ⁻²
4	0	2.04133 ₁₀ ⁻⁵	1.12144 ₁₀ ⁻⁵	2.42889 ₁₀ ⁻⁵	.91150 ₁₀ ⁻⁵	.83884 ₁₀ ⁻⁵	.83851 ₁₀ ⁻⁵
4	1	NEGATIVE	.94869 ₁₀ ⁻⁵	.01826 ₁₀ ⁻⁵	.86616 ₁₀ ⁻⁵	.81081 ₁₀ ⁻⁵	.83851 ₁₀ ⁻⁵
4	2	NEGATIVE	.57378 ₁₀ ⁻⁵	.70507 ₁₀ ⁻⁵	.85245 ₁₀ ⁻⁵	.82171 ₁₀ ⁻⁵	.83851 ₁₀ ⁻⁵
4	3	NEGATIVE	.68960 ₁₀ ⁻⁵	.79689 ₁₀ ⁻⁵	.80724 ₁₀ ⁻⁵	.82502 ₁₀ ⁻⁵	.83851 ₁₀ ⁻⁵
4	4	3.56724 ₁₀ ⁻⁵	.74292 ₁₀ ⁻⁵	.84208 ₁₀ ⁻⁵	.82527 ₁₀ ⁻⁵	.83459 ₁₀ ⁻⁵	.83851 ₁₀ ⁻⁵
4	5	2.68452 ₁₀ ⁻⁵	.77123 ₁₀ ⁻⁵	.86445 ₁₀ ⁻⁵	.82889 ₁₀ ⁻⁵	.83928 ₁₀ ⁻⁵	.83851 ₁₀ ⁻⁵

Table 1 (continued)

$\int dr_I \int dr_J x_{AI}^2 \exp(-3r_{AI}) x_{AJ} x_{BJ} \exp(-3r_{AJ} - 4r_{BJ})$ (HYBRID)							
R	Δn	I0	I1	I2	I1 δ	I2 δ	EXACT
1	0	.17704	.18212	.18001	.18134	.18123	.18130
1	1	.17749	.18175	.18100	.18134	.18125	.18130
1	2	.17900	.18175	.18141	.18135	.18127	.18130
1	3	.17919	.18122	.18140	.18134	.18127	.18130
1	4	.17939	.18168	.18137	.18132	.18128	.18130
1	5	.17955	.18120	.18135	.18132	.18129	.18130
2	0	.15505 ₁₀ ⁻¹	.19635 ₁₀ ⁻¹	.19579 ₁₀ ⁻¹	.19508 ₁₀ ⁻¹	.19441 ₁₀ ⁻¹	.19461 ₁₀ ⁻¹
2	1	.18402 ₁₀ ⁻¹	.19210 ₁₀ ⁻¹	.19509 ₁₀ ⁻¹	.19483 ₁₀ ⁻¹	.19444 ₁₀ ⁻¹	.19461 ₁₀ ⁻¹
2	2	.18647 ₁₀ ⁻¹	.19294 ₁₀ ⁻¹	.19507 ₁₀ ⁻¹	.19481 ₁₀ ⁻¹	.19470 ₁₀ ⁻¹	.19461 ₁₀ ⁻¹
2	3	.20670 ₁₀ ⁻¹	.19365 ₁₀ ⁻¹	.19502 ₁₀ ⁻¹	.19479 ₁₀ ⁻¹	.19466 ₁₀ ⁻¹	.19461 ₁₀ ⁻¹
2	4	.20353 ₁₀ ⁻¹	.19406 ₁₀ ⁻¹	.19499 ₁₀ ⁻¹	.19447 ₁₀ ⁻¹	.19465 ₁₀ ⁻¹	.19461 ₁₀ ⁻¹
2	5	.19910 ₁₀ ⁻¹	.19408 ₁₀ ⁻¹	.19434 ₁₀ ⁻¹	.19450 ₁₀ ⁻¹	.19464 ₁₀ ⁻¹	.19461 ₁₀ ⁻¹
4	0	4.76301 ₁₀ ⁻⁴	.61665 ₁₀ ⁻⁴	.71574 ₁₀ ⁻⁴	.73139 ₁₀ ⁻⁴	.75806 ₁₀ ⁻⁴	.75642 ₁₀ ⁻⁴
4	1	3.09378 ₁₀ ⁻⁴	.97485 ₁₀ ⁻⁴	.73246 ₁₀ ⁻⁴	.74139 ₁₀ ⁻⁴	.75299 ₁₀ ⁻⁴	.75642 ₁₀ ⁻⁴
4	2	NEGATIVE	.90142 ₁₀ ⁻⁴	.74118 ₁₀ ⁻⁴	.77874 ₁₀ ⁻⁴	.75440 ₁₀ ⁻⁴	.75642 ₁₀ ⁻⁴
4	3	NEGATIVE	.85856 ₁₀ ⁻⁴	.78009 ₁₀ ⁻⁴	.77176 ₁₀ ⁻⁴	.75520 ₁₀ ⁻⁴	.75642 ₁₀ ⁻⁴
4	4	NEGATIVE	.83224 ₁₀ ⁻⁴	.77330 ₁₀ ⁻⁴	.76758 ₁₀ ⁻⁴	.75568 ₁₀ ⁻⁴	.75642 ₁₀ ⁻⁴
4	5	NEGATIVE	.63005 ₁₀ ⁻⁴	.76983 ₁₀ ⁻⁴	.76484 ₁₀ ⁻⁴	.75601 ₁₀ ⁻⁴	.75642 ₁₀ ⁻⁴
$\int dr_I \int dr_J \exp(-7r_{AI}) z_{BI} \exp(-2r_{AJ} - 1r_{BJ})$ (HYBRID)							
R	Δn	I0	I1	I2	I1 δ	I2 δ	EXACT
1	0	.55771	.54111	.51970	.53965	.55003	.53927
1	1	.52906	.54019	.52632	.53964	.53907	.53927
1	2	.53073	.53968	.52809	.53965	.53866	.53927
1	3	.53386	.53921	.52950	.53964	.53880	.53927
1	4	.53605	.53925	.53936	.53963	.53892	.53927
1	5	.53594	.53921	.54002	.53962	.53903	.53927
2	0	.52591	.51714	.54523	.52316	.51620	.52136
2	1	.53145	.51721	.53324	.52089	.51764	.52136
2	2	.53834	.51745	.52924	.52241	.52270	.52136
2	3	.52182	.52765	.52792	.52116	.52209	.52136
2	4	.52674	.52782	.52698	.52133	.52188	.52136
2	5	.52029	.52030	.51873	.52136	.52182	.52136
4	0	.18025	.17405	.16910	.17967	.17496	.17894
4	1	.18950	.17911	.17002	.17943	.18067	.17894
4	2	.18449	.17752	.17851	.17930	.17905	.17894
4	3	.16761	.17663	.17799	.17925	.17894	.17894
4	4	.17243	.17786	.17779	.17918	.17855	.17894
4	5	.17475	.17810	.17835	.17920	.17884	.17894

Table 1 (continued)

$\int dr_I \int dr_J x_{AI}^2 \exp(-3r_{AI}) x_{BJ}^2 \exp(-7r_{BJ})$ (COULOMB)							
R	Δn	I_0	I_1	I_2	$I_1\delta$	$I_2\delta$	EXACT
1	0	.40780	.42953	.42487	.42728	.42687	.42712
1	1	.41551	.42841	.42688	.42729	.42695	.42712
1	2	.41976	.42845	.42756	.42729	.42699	.42712
1	3	.42048	.42686	.42750	.42725	.42700	.42712
1	4	.42927	.42719	.42740	.42721	.42700	.42712
1	5	.42808	.42719	.42732	.42718	.42705	.42712
2	0	.07008	.30282	.30285	.29965	.29947	.29763
2	1	.26098	.27801	.30038	.29883	.29872	.29763
2	2	.27213	.28141	.30019	.29871	.29817	.29763
2	3	.40976	.29315	.30001	.29548	.29801	.29763
2	4	.36006	.29468	.29385	.29571	.29799	.29763
2	5	.31944	.29482	.29587	.29703	.29797	.29763
4	0	POSITIVE	.92217	.09730	.12682	.15485	.16901
4	1	POSITIVE	.61456	.12340	.25113	.16028	.16901
4	2	NEGATIVE	.46221	.25654	.22273	.16309	.16901
4	3	NEGATIVE	.37863	.23025	.20657	.17871	.16901
4	4	NEGATIVE	NEGATIVE	.21461	.19684	.17593	.16901
4	5	NEGATIVE	NEGATIVE	.20438	.19059	.17415	.16901
$\int dr_I \int dr_J \exp(-7r_{AI}) z_{BJ} \exp(-3r_{BJ})$ (COULOMB)							
1	0	.12448	.14757	NEGATIVE	.13269	.11014	.12776
1	1	.07120	.13614	.12956	.13159	.11557	.12776
1	2	.08914	.13656	.13428	.13024	.11927	.12776
1	3	.10860	.12190	.14424	.12917	.12180	.12776
1	4	.11163	.12497	.14196	.12914	.12211	.12776
1	5	.11294	.12315	.13894	.12906	.12257	.12776
2	0	NEGATIVE	.32679 ₁₀ ⁻¹	4.65302 ₁₀ ⁻¹	.70696 ₁₀ ⁻¹	2.49619 ₁₀ ⁻¹	.76231 ₁₀ ⁻¹
2	1	-.45271 ₁₀ ⁻¹	.55434 ₁₀ ⁻¹	5.57471 ₁₀ ⁻¹	.56311 ₁₀ ⁻¹	1.58451 ₁₀ ⁻¹	.76231 ₁₀ ⁻¹
2	2	5.54783 ₁₀ ⁻¹	.65013 ₁₀ ⁻¹	NEGATIVE	.61198 ₁₀ ⁻¹	1.21701 ₁₀ ⁻¹	.76231 ₁₀ ⁻¹
2	3	1.95436 ₁₀ ⁻¹	.69853 ₁₀ ⁻¹	NEGATIVE	.75769 ₁₀ ⁻¹	1.16959 ₁₀ ⁻¹	.76231 ₁₀ ⁻¹
2	4	1.66263 ₁₀ ⁻¹	1.24220 ₁₀ ⁻¹	-.42694 ₁₀ ⁻¹	.76417 ₁₀ ⁻¹	1.12323 ₁₀ ⁻¹	.76231 ₁₀ ⁻¹
2	5	1.47859 ₁₀ ⁻¹	1.23286 ₁₀ ⁻¹	.02074 ₁₀ ⁻¹	.76094 ₁₀ ⁻¹	1.08925 ₁₀ ⁻¹	.76231 ₁₀ ⁻¹
4	0	NEGATIVE	NEGATIVE	NEGATIVE	NEGATIVE	NEGATIVE	.22505 ₁₀ ⁻¹
4	1	POSITIVE	POSITIVE	POSITIVE	2.15006 ₁₀ ⁻¹	.54192 ₁₀ ⁻¹	.22505 ₁₀ ⁻¹
4	2	NEGATIVE	POSITIVE	POSITIVE	1.02843 ₁₀ ⁻¹	.48899 ₁₀ ⁻¹	.22505 ₁₀ ⁻¹
4	3	NEGATIVE	NEGATIVE	POSITIVE	.67870 ₁₀ ⁻¹	2.20252 ₁₀ ⁻¹	.22505 ₁₀ ⁻¹
4	4	NEGATIVE	NEGATIVE	POSITIVE	1.08563 ₁₀ ⁻¹	.92030 ₁₀ ⁻¹	.22505 ₁₀ ⁻¹
4	5	POSITIVE	NEGATIVE	NEGATIVE	.63056 ₁₀ ⁻¹	.22349 ₁₀ ⁻¹	.22505 ₁₀ ⁻¹

It may be noted, that the "best" value of the scale factor could be reached in a rapidly convergent Newton iteration scheme in general in 3–6 steps starting from the value $\text{MIN}(C_I, C_J)$.

The results listed in Table 1 involve integrals with $f(r_{IJ}) = r_{IJ}^{-1}$. Results with $f(r_{IJ}) = r_{IJ}^{+1}$ and $f(r_{IJ}) = r_{IJ}^{+3}$ showed a much greater stability than the integrals with $f(r_{IJ}) = r_{IJ}^{-1}$. This suggests, that their accuracy is higher. (This is by no means a surprising fact.) As, however we had no possibility to calculate the exact values, we did not include these data in the Table.

In the case of the twice pre-manipulated integrals the Dirac-delta-function terms discussed in Section 2 have been separated off from the charge distributions, the method of distance functions has been applied to the charge distributions truncated in this way, and finally the terms resulting from the Dirac-delta-functions have been added to the result.

Table 1 contains the values of some two-center integrals calculated by the method of distance functions. R denotes the distance of the centers called A and B . Δn is the value by which the number of variational parameters in the distance function exceeded the minimum value. The symbols $I0$, $I1$ and $I2$ refer to non pre-manipulated, once pre-manipulated and twice pre-manipulated approximations, respectively. The symbol δ indicates that the auxiliary two-electron function $f(r_{IJ}) = \delta^{(3)}(r_{IJ})$ has also been used (cf. Section 3).

The notation NEGATIVE and POSITIVE indicates that the approximate value of the integral had such a high error that it could not be written down with the format applied in the Table.

It should be noted that the integral involving the $2pz$ orbital has been the most "malevolent" example we have found in our calculations. The other example can be considered as being neither "malevolent" nor "benevolent".

The data given in the Table clearly indicate the disimprovement of accuracy with increasing R , due to the "one-center" character of the variational distance function. The disimprovement due to the change EXCHANGE \rightarrow HYBRYD \rightarrow COULOMB integrals has probably the same reason.

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