Analytic value of the atomic three-electron correlation integral with Slater wave functions

Ettore Remiddi
Dipartimento di Fisica, Università di Bologna, I-40126 Bologna, Italy
and Istituto Nazionale di Fisica Nucleare, Sezione di Bologna, I-40126 Bologna, Italy
(Received 3 April 1991)

The three-electron atomic correlation integral with Slater-type wave functions is evaluated in closed analytic form. The result is expressed in terms of rational functions, logarithms and dilogarithms of simple arguments, whose precise and fast numerical evaluation is straightforward.

PACS number(s): 31.20.Tz, 31.15.+q

I. INTRODUCTION

It is the purpose of this paper to provide a closed analytic expression for the atomic three-electron correlation integral

$$Z(w_1,w_2,w_3)\equiv\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 e^{-w_1 r_1} e^{-w_2 r_2} e^{-w_3 r_3} \times|\mathbf{r}_1-\mathbf{r}_2|\frac{1}{|\mathbf{r}_3-\mathbf{r}_1|}|\mathbf{r}_2-\mathbf{r}_3| \ . \qquad (1)$$

The integral naturally arises in the study of atoms with three or more electrons when using Hylleraas wave functions to account for two-electron correlation effects. To the author's knowledge, in all the practical applications the integral Eq. (1) is usually evaluated by means of approximated numerical techniques, by expanding for instance one of the $|\mathbf{r}_i-\mathbf{r}_j|$ factors in Legendre polynomials, performing in closed form the integration of the resulting terms, and then summing a suitable number of terms of the so-obtained infinite series.

The closed analytic formula obtained in this paper involves, besides rational fractions and logarithms, a few dilogarithmic functions of simple arguments. The basic properties of the dilogarithm are recalled in Appendix A for the benefit of the unfamiliar reader; let us just stress here that the dilogarithm of argument x has the same analytic properties in x as the logarithm of argument $(1-x)$ and, for practical purposes, its accurate numerical evaluation presents the same problems as the evaluation of the logarithm. The dilogarithm is often encountered in the calculation of radiative corrections in QED [1]; to the author's pleasure, it turned out that the techniques developed for the computational problems arising there can be used, with obvious extensions, also in the analytic evaluation of the atomic integral Eq. (1).

The result looks (perhaps is) somewhat cumbersome; but it is in fact astonishingly simple when compared to the large amount of algebra which was needed to obtain it, suggesting the existing of some underlying (and yet unknown) structure. To process the algebra, the use of an algebra-manipulating program was mandatory. The author relied, in all the steps of the calculation, on the program SCHOONSCHIP by Veltman [2], which provided the needed flexibility and computing power.

After the completion of the work, the author learned of the existence of the paper of Fromm and Hill [4], in which a similar, in fact even more general, analytic formula is given. A discussion of the relation between the present approach and the results of Ref. [4] (which are of greater generality, but correspondingly of less direct use) has been added as an independent section.

The plan of the paper is as follows. In Sec. II, which contains the essential part of the calculation, an auxiliary "fundamental" integral is introduced and evaluated by means of the "differentiate and integrate" algorithm, which is the bulk of the approach. In Sec. III the result is extended to a number of related integrals, including that of Eq. (1). Section IV discusses the relation of the present approach with the results of Ref. [4]. Section V contains the conclusions, while Appendix A recalls definition and properties of the dilogarithm and Appendix B the derivation of some of the formulas used in the text.

II. INTEGRATION OF THE AUXILIARY INTEGRAL VIA THE DIFFERENTIATE AND INTEGRATE ALGORITHM

To start with, let us introduce the auxiliary integral

$$A(w_1,w_2,w_3;u_1,u_2,u_3) \equiv\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \frac{e^{-w_1 r_1}}{r_1}\frac{e^{-w_2 r_2}}{r_2}\frac{e^{-w_3 r_3}}{r_3} \times\frac{e^{-u_3|\mathbf{r}_1-\mathbf{r}_2|}}{|\mathbf{r}_1-\mathbf{r}_2|}\frac{e^{-u_2|\mathbf{r}_3-\mathbf{r}_1|}}{|\mathbf{r}_3-\mathbf{r}_1|}\frac{e^{-u_1|\mathbf{r}_2-\mathbf{r}_3|}}{|\mathbf{r}_2-\mathbf{r}_3|} \ . \qquad (2)$$

It is obvious that the integral (1) and a wide family of related integrals with the same exponentials and different powers of the factors r_1 and $|\mathbf{r}_i-\mathbf{r}_j|$ can be obtained from it by differentiating with respect to the variables w_i and u_i and setting $u_i=0$. In this work, we will limit ourselves to providing closed analytic formulas for Eq. (2) and its first u_i derivatives only at $u_i=0$, but for arbitrary values of w_i, so that all the integrals with non-negative powers of r_i can also be obtained by differentiation. There is some hope that the $u_i\neq 0$ case, which is of interest for simple molecules, can also be worked out with similar techniques, but that generalization has not yet been attempted.

As a first step, we use the Fourier representation

$$\frac{e^{-wr}}{r}=\frac{1}{(2\pi)^3}\int d\mathbf{p}\frac{4\pi}{p^2+w^2}e^{i\mathbf{p}\cdot\mathbf{r}}$$

for the six exponentials appearing in Eq. (2), integrate over all the $d\mathbf{r}_i$, thus obtaining three Dirac δ functions, and then integrate the δ functions in three of the momenta. Equation (2) becomes

$$A(w_1,w_2,w_3;u_1,u_2,u_3)=\frac{1}{[(2\pi)^3]^3}\int d\mathbf{p}_3 d\mathbf{p}_2 d\mathbf{p}_1\frac{4\pi}{p_3^2+u_3^2}\frac{4\pi}{p_2^2+u_2^2}\frac{4\pi}{p_1^2+u_1^2}\times\frac{4\pi}{(\mathbf{p}_1-\mathbf{p}_2)^2+w_3^2}\frac{4\pi}{(\mathbf{p}_2-\mathbf{p}_3)^2+w_1^2}\times\frac{4\pi}{(\mathbf{p}_3-\mathbf{p}_1)^2+w_2^2}\ . \tag{3}$$

To perform the angular integrations, we define

$$z_1\equiv\frac{p_2^2+p_3^2+w_1^2}{2p_2p_3}\ ,\quad z_2\equiv\frac{p_3^2+p_1^2+w_2^2}{2p_3p_1}\ ,\quad z_3\equiv\frac{p_1^2+p_2^2+w_3^2}{2p_1p_2}\ , \tag{4}$$

so that

$$\frac{1}{(\mathbf{p}_2-\mathbf{p}_3)^2+w_1^2}=-\frac{1}{2p_2p_3}\frac{1}{\hat{\mathbf{p}}_2\cdot\hat{\mathbf{p}}_3-z_1}\ ,$$

where $\hat{\mathbf{p}}_i$ is the unit vector in the direction of $\mathbf{p}_i$, and similarly for the other denominators. By introducing polar coordinates through $d\mathbf{p}=p^2dp\,d\Omega(\hat{\mathbf{p}})$, Eq. (3) can be written as

$$A(w_1,w_2,w_3;u_1,u_2,u_3)=\frac{1}{32\pi^3}\int_0^\infty dp_3^2\frac{1}{p_3^2+u_3^2}\int_0^\infty dp_2^2\frac{1}{p_2^2+u_2^2}\int_0^\infty dp_1^2\frac{1}{p_1^2+u_1^2}B(z_1,z_2,z_3)\ , \tag{5}$$

where

$$B(z_1,z_2,z_3)\equiv-\frac{1}{p_1p_2p_3}\int d\Omega(\hat{\mathbf{p}}_1)d\Omega(\hat{\mathbf{p}}_2)d\Omega(\hat{\mathbf{p}}_3)\frac{1}{(\hat{\mathbf{p}}_1\cdot\hat{\mathbf{p}}_2-z_3)(\hat{\mathbf{p}}_1\cdot\hat{\mathbf{p}}_3-z_2)(\hat{\mathbf{p}}_2\cdot\hat{\mathbf{p}}_3-z_1)}\ . \tag{6}$$

The analytic integration over the spherical angle $d\Omega(\hat{\mathbf{p}}_3)$ can be performed by means of the formula

$$\int d\Omega(\hat{\mathbf{p}}_3)\frac{1}{(\hat{p}_1\hat{p}_3-z_2)(\hat{p}_2\hat{p}_3-z_1)}=\frac{2\pi}{\sqrt{\delta(z_1,z_2,z)}}\ln\left|\frac{z_1z_2-z+\sqrt{\delta(z_1,z_2,z)}}{z_1z_2-z-\sqrt{\delta(z_1,z_2,z)}}\right|\ , \tag{7}$$

where $z=\hat{\mathbf{p}}_1\cdot\hat{\mathbf{p}}_2$ is the cosine of the angle formed by $\hat{\mathbf{p}}_1$ and $\hat{\mathbf{p}}_2$, and

$$\delta(z_1,z_2,z)\equiv z_1^2+z_2^2+z^2-2z_1z_2z-1\ . \tag{8}$$

Note that $\delta(z_1,z_2,z)$ is a second-order polynomial in z, a property which will play an essential role in the following. As an aside, it is easy to verify that $\delta(z_1,z_2,z)>0$ for $w_1,w_2>0$ and $|z|\le 1$.

In terms of z one has $d\Omega(\hat{\mathbf{p}}_2)=dz\,d\phi_2$. When z and Eq. (7) are used the integrand of Eq. (6) is seen to be independent of ϕ_2 and $\hat{\mathbf{p}}_1$, so that

$$B(z_1,z_2,z_3)=-\frac{16\pi^3}{p_1p_2p_3}\int_{-1}^{1}dz\frac{1}{z-z_3}\frac{1}{\sqrt{\delta(z_1,z_2,z)}}\ln\left|\frac{z_1z_2-z+\sqrt{\delta(z_1,z_2,z)}}{z_1z_2-z-\sqrt{\delta(z_1,z_2,z)}}\right|\ . \tag{9}$$

At this point one might try direct "brute-force" analytic integration in z of Eq. (9); formulas for doing so exist in the literature, but the result is a combination of dilogarithmic functions of complicated arguments, which provide no hint for the subsequent integrations over the p_i. Our method consists instead of postponing any explicit analytic integration for a while, rewriting the required integral in a form which will be found more convenient later. Rather than explicitly integrating Eq. (9), therefore, we introduce the function

$$C(z_1,z_2,z_3)\equiv-\int_{-1}^{1}dz\frac{1}{z-z_3}\frac{\sqrt{-\delta(z_1,z_2,z_3)}}{\sqrt{\delta(z_1,z_2,z)}}\ln\left|\frac{z_1z_2-z+\sqrt{\delta(z_1,z_2,z)}}{z_1z_2-z-\sqrt{\delta(z_1,z_2,z)}}\right|\ . \tag{10}$$

$B(z_1,z_2,z_3)$ is positive definite, as $z_3>1\ge z$; $\delta(z_1,z_2,z_3)$, on the other hand, has no definite sign, and the choice of the minus sign in front of it in Eq. (10) is suggested only by aesthetics.

Let us also introduce

$$\Delta(p_1^2,p_2^2,p_3^2)\equiv -4p_1^2p_2^2p_3^2\delta(z_1,z_2,z_3)\ , \tag{11}$$

i.e., on account of Eqs. (4)

$$\begin{aligned}\Delta(p_1^2,p_2^2,p_3^2)=&w_1^2p_1^4+w_2^2p_2^4+w_3^2p_3^4+w_1^2w_2^2w_3^2\\&-(p_1^2p_2^2-w_3^2p_3^2)(w_1^2+w_2^2-w_3^2)\\&-(p_2^2p_3^2-w_1^2p_1^2)(w_2^2+w_3^2-w_1^2)\\&-(p_3^2p_1^2-w_2^2p_2^2)(w_3^2+w_1^2-w_2^2)\ .\end{aligned} \tag{12}$$

Note again that $\Delta(p_1^2,p_2^2,p_3^2)$ is a quadratic form on each of the three variables p_i^2 (as well as on the w_i^2, not explicitly written in the arguments of Δ for simplicity). With these symbols, Eq. (9) becomes

$$B(z_1,z_2,z_3)=\frac{32\pi^3}{[\Delta(p_1^2,p_2^2,p_3^2]^{1/2}}C(z_1,z_2,z_3)\ . \tag{13}$$

Corresponding, Eq. (5) reads

$$A(w_1,w_2,w_3;u_1,u_2,u_3)=\int_0^\infty dp_3^2\frac{1}{p_3^2+u_3^2}\int_0^\infty dp_2^2\frac{1}{p_2^2+u_2^2}\int_0^\infty dp_1^2\frac{1}{p_1^2+u_1^2}\frac{1}{[\Delta(p_1^2,p_2^2,p_3^2)]^{1/2}}C(z_1,z_2,z_3)\ . \tag{14}$$

We further introduce the functions

$$\begin{aligned}T(w_1,w_2,w_3,p_2^2,p_3^2)&\\ \equiv\int_0^\infty dp_1^2&\frac{1}{p_1^2+u_1^2}\frac{[\Delta(-u_1^2,p_2^2,p_3^2)]^{1/2}}{[\Delta(p_1^2,p_2^2,p_3^2)]^{1/2}}\\&\times C(z_1,z_2,z_3)\ ,\end{aligned} \tag{15}$$

$$\begin{aligned}Q(w_1,w_2,w_3,p_3^2)&\\ \equiv\int_0^\infty dp_2^2&\frac{1}{p_2^2+u_2^2}\frac{[\Delta(-u_1^2,-u_2^2,p_3^3)]^{1/2}}{[\Delta(-u_1^2,p_2^2,p_3^3)]^{1/2}}\\&\times T(w_1,w_2,w_3,p_2^2,p_3^2)\ ,\end{aligned} \tag{16}$$

$$\begin{aligned}P(w_1,w_2,w_3,u_1,u_2,u_3)&\\ \equiv\int_0^\infty dp_3^2&\frac{1}{p_3^2+u_3^2}\frac{[\Delta(-u_1^2,-u_2^2,-u_3^2)]^{1/2}}{[\Delta(-u_1^2,-u_2^2,p_3^2)]^{1/2}}\\&\times Q(w_1,w_2,w_3,p_3^2)\ ,\end{aligned} \tag{17}$$

where, for the sake of brevity only, the variables u_i are not explicitly written among the arguments of some of the above functions. Equation (14) then becomes

$$\begin{aligned}A(w_1,w_2,w_3;u_1,u_2,u_3)=&\frac{1}{[\Delta(-u_1^2,-u_2^2,-u_3^2)]^{1/2}}\\&\times P(w_1,w_2,w_3;u_1,u_2,u_3)\ .\end{aligned} \tag{18}$$

We will now show that the above way of rewriting the integrals is indeed of help for obtaining a convenient expression for the derivatives with respect to the variables w_i of the function $P(w_1,w_2,w_3;u_1,u_2,u_3)$. Quite generally, let

$$S(a,x)\equiv s_0+s_1(x-b)+\tfrac{1}{2}s_2(x-b)^2 \tag{19}$$

be a second-order polynomial in the variable x, with the coefficients depending on some unspecified parameter a, so that $s_i=s_i(a)$, $i=0,1,2$, and consider the integral

$$K(a)\equiv\int_{x_1}^{x_2}dx\frac{1}{x-b}\frac{\sqrt{S(a,b)}}{\sqrt{S(a,x)}}H(a,x)\ , \tag{20}$$

where the otherwise unspecified function $H(a,x)$ depends on both a and x, while x_1, x_2, and b are independent of a. Thanks to the presence of the factor $\sqrt{S(a,b)}$ in the numerator of Eq. (20), one finds the following formula for the a derivative of $K(a)$:

$$\begin{aligned}\frac{\partial}{\partial a}K(a)=&\int_{x_1}^{x_2}dx\frac{1}{x-b}\frac{\sqrt{S(a,b)}}{\sqrt{S(a,x)}}\frac{\partial}{\partial a}H(a,x)\\&+\frac{1}{s_1^2-2s_0s_2}\frac{1}{\sqrt{S(a,b)}}\int_{x_1}^{x_2}dx\frac{1}{\sqrt{S(a,x)}}\left[-\frac{1}{2}\left[\frac{\partial s_0}{\partial a}s_1s_2-2s_0\frac{\partial s_1}{\partial a}s_2+s_0s_1\frac{\partial s_2}{\partial a}\right](x-b)\right.\\&\left.+\left[\frac{\partial s_0}{\partial a}(s_0s_2-s_1^2)+s_0\frac{\partial s_1}{\partial a}s_1-s_0^2\frac{\partial s_2}{\partial a}\right]\right]\\&\times\left[\delta(x-x_2)-\delta(x-x_1)-\frac{\partial}{\partial x}\right]H(a,x)\ .\end{aligned} \tag{21}$$

Its derivation, which is elementary, is reported in Appendix B for the convenience of the reader: its usefulness relies on the fact that it expresses the a derivative of $K(a)$ in terms of quantities which can be evaluated without explicitly carrying out the original integral, namely the end points of the function $H(a,x)$, given by to the two Dirac δ functions $\delta(x-x_i)$ in Eq. (21), and an integral involving the x derivative of $H(a,x)$.

Equation (21) can be used for obtaining the w_i derivatives of $P(w_1,w_2,w_3;u_1,u_2,u_3)$ [Eq. (17)], with p_3^2, $(p_3^2+u_3^2)$, and $Q(w_1,w_2,w_3,p_3^2)$ in the role of x, $(x-a)$, and of the unspecified function $H(a,x)$, while $\Delta(-u_1^2,-u_2^2,p_3^2)$ is the second-order polynomial in p_3^2 corresponding to $S(a,x)$. A closer inspection of the definition of $Q(w_1,w_2,w_3,p_3^2)$ shows that the end-point values actually vanish, so that the required w_i derivatives of $P(w_1,w_2,w_3,u_1,u_2,u_3)$ are expressed as the integral on p_3^2 of a combination of rational functions of p_3^2 times the corresponding w_i and p_3^2 derivatives of $Q(w_1,w_2,w_3,p_3^2)$.

Equation (21) can be used again for evaluating the derivatives of $Q(w_1,w_2,w_3,p_3^2)$ because $\Delta(-u_1^2,p_2^2,p_3^2)$, which appears on the right-hand-side (rhs) of Eq. (16), is also a second-order polynomial in p_2^2. As in the previous case the end-point contributions are found to vanish and the required w_i and p_3^2 derivatives of $Q(w_1,w_2,w_3,p_3^2)$ are expressed in terms of the various derivatives of $T(w_1,w_2,w_3,p_2^2,p_3^2)$.

The process can be iterated once more, so that all the w_i and p_i^2 derivatives of $C(z_1,z_2,z_3)$ are eventually needed. $C(z_1,z_2,z_3)$ depends on the w_i and the p_i^2 only through the three variables z_i [Eq. (4)], it is in fact sufficient to evaluate its three z_i derivatives. The derivatives with respect to z_1 and z_2 can also be worked out by means of formula (21) because $\delta(z_1,z_2,z)$, as already observed, is a second-order polynomial in z [the change of sign in the argument of the square root in the numerator of Eq. (10) is an overall constant factor which does not affect the applicability of the formula]. The case of the z_3 derivative is slightly different—its easiest derivation is perhaps through Eq. (37), which will be introduced below—but the result is similar and explicitly exhibits the expected symmetry of $C(z_1,z_2,z_3)$ for the exchange of the arguments.

When carrying out the above procedure, the factor $(s_1^2-2s_0s_2)$ appearing in the denominator of Eq. (21) takes the value $4(z_1^2-1)(z_2^2-1)$, while the "unspecified function" on the rhs of the definition of $C(z_1,z_2,z_3)$ [Eq. (10)], is in fact the explicitly known logarithm of Eq. (10). Its derivative, a fraction, contains, among others, terms in $1/\sqrt{\delta(z_1,z_2,z)}$, which get multiplied by the same square-root factor appearing in Eq. (21) to generate the denominator $1/\delta(z_1,z_2,z)$. After some fully straightforward albeit lengthy algebra, that denominator is found to disappear; the z integration is then elementary and the explicit analytic values of the required z_i derivative are rather simple. One finds, for instance,

$$\frac{\partial C(z_1,z_2,z_3)}{\partial z_1}=\frac{2}{\sqrt{\delta(z_1,z_2,z_3)}}\left[\frac{z_1z_2-z_3}{z_1^2-1}\ln\left[\frac{z_2+1}{z_2-1}\right]+\frac{z_1z_3-z_2}{z_1^2-1}\ln\left[\frac{z_3+1}{z_3-1}\right]-\ln\left[\frac{z_1+1}{z_1-1}\right]\right] . \tag{22}$$

Due to the already recalled symmetry of $C(z_1,z_2,z_3)$ in its arguments, it is not necessary to write explicitly the derivatives with respect to z_2 and z_3.

Once the derivatives of $C(z_1,z_2,z_3)$ are evaluated, one can proceed backward to evaluate the derivatives of $T(w_1,w_2,w_3,p_2^2,p_3^2)$, which were seen to be an integral over p_1^2 of the derivatives of $C(z_1,z_2,z_3)$ times suitable rational factors. At this stage, to simplify the calculation, we put $u_1=0$ in the denominator $(p_1^2+u_1^2)$ of Eq. (15). When Eqs. (4) and (12) are used for eliminating the z_i, everything is expressed in terms of the p_i^2 and w_i, and the denominator $1/\Delta(p_1^2,p_2^2,p_3^2)$ appears in the same way that $1/\delta(z_1,z_2,z)$ appeared in the previous case. After a very lengthy algebraic manipulation, that denominator also disappears (such a result is always expected in this kind of calculations, although a satisfactory formal proof of this fact is missing; the elimination of the denominator provides in practice one of the most important guidelines in the organization of the whole calculation). One is eventually left with a relatively simple expression, say about 100 terms, or less, for each of the derivatives. That expression generally has the form of a ratio of polynomials in the integration variable p_1^2 as well as in the other variables, times the three logarithms appearing in Eq. (22). More explicitly, one finds that an essential role is played by the three polynomials of second order in the arguments p^2,q^2,w^2,

$$\begin{aligned}&R_2(p_1^2,p_2^2,-w_3^2)\ ,\\ &R_2(p_2^2,p_3^2,-w_1^2)\ ,\\ &R_2(p_3^2,p_1^2,-w_2^2)\ ,\end{aligned} \tag{23}$$

where

$$R_2(p^2,q^2,-w^2)\equiv p^2+q^4+w^4-2p^2q^2+2w^2p^2+2w^2q^2\ . \tag{24}$$

Remarkably, the actual value of the factor $(s_1^2-2s_0s_2)$ appearing in Eq. (21) is in this case $R_2(w_1^2,w_2^2,w_3^2)R_2(p_2^2,p_3^2,-w_1^2)$.

All the p_1^2 integrals consist of an algebraic factor, whose possible denominators are $1/p_1^2$, which corresponds to $1/(p_1^2+u_1^2)$ of Eq. (15) at $u_1=0$, $1/R_2(p_1^2,p_2^2,-w_3^2)$, and $1/R_2(p_3^2,p_1^2,-w_2^2)$, times one of the logarithms of Eq. (22). A closer inspection shows that, in general, any p integral involving a factor $1/R_2(p^2,q^2,-w^2)$ can be conveniently written in terms of the four basic combinations

$$dp^2\frac{wq}{R_2(p^2,q^2,-w^2)},\quad dp^2\frac{(p^2-q^2+w^2)}{R_2(p^2,q^2,-w^2)},$$
$$dp\frac{w(p^2+q^2+w^2)}{R_2(p^2,q^2,-w^2)},\quad dp\frac{q(p^2-q^2-w^2)}{R_2(p^2,q^2,-w^2)}. \tag{25}$$

When that is done, one obtains a limited number of p_1^2 integrals such as

$$\int_0^\infty dp_1^2\frac{p_3w_2}{R_2(p_3^2,p_1^2,-w_2^2)}\ln\left[\frac{z_3+1}{z_3-1}\right],$$
$$\int_0^\infty dp_1^2\frac{p_1^2-p_2^2+w_3^2}{R_2(p_3^2,p_1^2,-w_2^2)}\ln\left[\frac{z_2+1}{z_2-1}\right]. \tag{26}$$

Terms in $\ln[(z_1+1)/(z_1-1)]$ also exist; as this logarithm does not depend on p_1, those terms can be integrated at once; the integrals that occur are

$$\int_0^\infty dp\frac{p^2}{R_2(p^2,q^2,-w^2)}=\frac{\pi}{4w},$$
$$\int_0^\infty dp\frac{1}{R_2(p^2,q^2,-w^2)}=\frac{\pi}{4w}\frac{1}{q^2+w^2}. \tag{27}$$

For continuation of the calculation it is not necessary to evaluate explicitly the other p_1^2 integrals, but it is in fact convenient to keep them in the form of Eq. (26), giving them *ad hoc* names, or just "protecting" them with suitable brackets in the subsequent steps. To summarize, each of the 50–100 terms occurring in the expressions of the derivatives of $T(w_1,w_2,w_3,p_2^2,p_3^2)$ with respect to any of its five arguments is therefore the product of one of the above p_1^2 integrals times a rational fraction in the five variables p_2^2, p_3^2, and w_i, times the overall factor $1/[\Delta(0,p_2^2,p_3^2)]^{1/2}$, generated by use of Eq. (21) for determining the derivatives of $T(w_1,w_2,w_3,p_2^2,p_3^2)$ [Eq. (15)].

With the so-obtained expression for the derivatives of $T(w_1,w_2,w_3,p_2^2,p_3^2)$ we can again use Eq. (21) to obtain the derivatives of $Q(w_1,w_2,w_3,p_3^2)$ [Eq. (16)], at $u_2=0$. The pattern is the same, the denominator $1/\Delta(0,p_2^2,p_3^2)$ is generated, but actually disappears following some algebra, all the p_2 integrals involving $R_2(p_2^2,p_3^2,-w_1^2)$ can be written in one of the four forms of Eq. (25), the explicit integration in p_2 is neither necessary nor convenient, and an overall denominator $1/[\Delta(0,0,p_3^2)]^{1/2}$ appears.

With one more iteration of the algorithm one obtains the three w_i derivatives of $P(w_1,w_2,w_3,0,0,0)$. The denominator $1/\Delta(0,0,p_3^2)$ is generated, but found to disappear, while everything is multiplied by the simple overall factor $1/\sqrt{\Delta(0,0,0)}=1/(w_1w_2w_3)$. The derivatives consist of a limited number (a couple of dozens) of integrals such as

$$\int_0^\infty dp_3\frac{w_1}{p_3^2+w_1^2}\int_0^\infty dp_2\frac{p_3(p_2^2-p_3^2-w_1^2)}{R_2(p_2^2,p_3^2,-w_1^2)}\times\int_0^\infty dp_1^2\frac{p_1^2-p_2^2+w_3^2}{R_2(p_1^2,p_2^2,-w_3^2)}\ln\left[\frac{z_2+1}{z_2-1}\right]=\tfrac{1}{2}\pi^3\ln\left[\frac{w_1+w_2+w_3}{3w_1+w_2+w_3}\right], \tag{28}$$

$$\int_0^\infty dp_3^2\left[\frac{1}{p_3^2+w_1^2}-\frac{1}{p_3^2}\right]\int_0^\infty dp_2^2\frac{p_3w_1}{R_2(p_2^2,p_3^2,-w_1^2)}\times\int_0^\infty dp_1^2\frac{p_1^2-p_3^2+w_2^2}{R_2(p_3^2,p_1^2,-w_2^2)}\ln\left[\frac{z_3+1}{z_3-1}\right]=\pi^3\ln\left[\frac{w_1+w_2+w_3}{3w_1+w_2+w_3}\right]. \tag{29}$$

All the appearing triple integrals are in general equal to a factor of π^3 times a logarithm whose arguments are linear combinations of the w_i with simple integer coefficients, such as $(w_1+3w_2+w_3)$, $(2w_1+w_3)$, (w_2+w_3), etc. To establish the above results, one can differentiate the integral in p_3 with respect to one of arguments w_i by using formulas which are the extension of Eq. (21) to the present case (two of them are reported in Appendix B), so obtaining end-point values and derivative with respect to w_i and p_3 of the p_3 integrand, which is an integral in p_2. By repeated use of the same formulas, one can propagate the derivatives through the subsequent p_2 and p_1 integrations, until only the derivatives of the logarithm are needed. In doing so one finds that the p_1, p_2, and p_3 integrations are elementary [ironically, only the two integrals of Eq. (27) occur], and the required w_i derivative of the triple integral over p_3,p_2,p_1 is found to be equal to π^3 times simple rational denominators in w_i. The rhs of Eqs. (28) and (29) can then be obtained by quadrature. The otherwise arbitrary additive constant of the quadrature is fixed by checking that the left-hand-side (lhs) and rhs coincide for some special set of values of the w_i. The lhs and rhs and Eqs. (28) and (29), for instance, both vanish at $w_2=\infty$. Collecting results, one finally obtains

$$\frac{\partial}{\partial w_1}P(w_1,w_2,w_3,0,0,0)=32\pi^3\left\{\frac{1}{w_1+w_2-w_3}\ln\left[\frac{w_1+w_2}{w_3}\right]-\frac{1}{w_1-w_2+w_3}\ln\left[\frac{w_2+w_3}{w_1}\right]+\frac{1}{w_1-w_2+w_3}\ln\left[\frac{w_3+w_1}{w_2}\right]-\frac{1}{w_1+w_2+w_3}\left[\ln\left[\frac{w_1+w_2}{w_3}\right]+\ln\left[\frac{w_2+w_3}{w_1}\right]+\ln\left[\frac{w_3+w_1}{w_2}\right]\right]\right\}, \tag{30}$$

and similar formulas for the other derivatives, which are not written explicitly due to the symmetry for exchange of the w_i.

From inspection, one sees that one can easily evaluate the integral Eq. (2), at $u_i=0$ and in the limit $w_3 \gg w_1, w_2$, by performing the change of variable $\mathbf{r}_3 \to \mathbf{r}$, $\mathbf{r}=w_3\mathbf{r}_3$, and then approximating $|\mathbf{r}_1-\mathbf{r}_3| \simeq r_1$, $|\mathbf{r}_2-\mathbf{r}_3| \simeq r_2$. In that limit the integration is elementary, giving the result

$$A(w_1,w_2,w_3,0,0,0) \simeq \frac{64\pi^3}{w_1 w_2 w_3^2}\left[w_1 \ln\left[\frac{w_1+w_2}{w_1}\right]+w_2 \ln\left[\frac{w_1+w_2}{w_2}\right]\right], \quad w_3 \gg w_1, w_2 . \tag{31}$$

We can at last integrate Eq. (30) by quadrature in w_1, fixing the otherwise undetermined additive constant by comparison with Eq. (31) at large w_3. The result is

$$P(w_1,w_2,w_3,0,0,0)=32\pi^3 D(w_1,w_2,w_3) , \tag{32}$$

where

$$\begin{aligned} D(w_1,w_2,w_3) \equiv {} & \ln\left[\frac{w_1+w_2}{w_3}\right]\ln\left[\frac{w_1+w_2+w_3}{w_1+w_2}\right]-\mathrm{Li}_2\left[-\frac{w_3}{w_1+w_2}\right]-\mathrm{Li}_2\left[1-\frac{w_3}{w_1+w_2}\right] \\ & +\ln\left[\frac{w_2+w_3}{w_1}\right]\ln\left[\frac{w_1+w_2+w_3}{w_1+w_3}\right]-\mathrm{Li}_2\left[-\frac{w_2}{w_1+w_3}\right]-\mathrm{Li}_2\left[1-\frac{w_2}{w_1+w_3}\right] \\ & +\ln\left[\frac{w_3+w_1}{w_2}\right]\ln\left[\frac{w_1+w_2+w_3}{w_2+w_3}\right]-\mathrm{Li}_2\left[-\frac{w_1}{w_2+w_3}\right]-\mathrm{Li}_2\left[1-\frac{w_1}{w_2+w_3}\right] . \end{aligned} \tag{33}$$

The function $\mathrm{Li}_2(x)$ appearing in Eq. (33) is the Euler dilogarithm, whose definition and main properties are recalled in Appendix A for the convenience of the reader; it suffices to repeat once more here that it can be numerically evaluated as quickly and accurately as the logarithm.

According to Eqs. (2), (12), and (18) one can also write

$$A(w_1,w_2,w_3,0,0,0)=\frac{1}{w_1 w_2 w_3} P(w_1,w_2,w_3,0,0,0) ,$$

i.e.,

$$\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \frac{e^{-w_1 r_1}}{r_1}\frac{e^{-w_2 r_2}}{r_2}\frac{e^{-w_3 r_3}}{r_3}\frac{1}{|\mathbf{r}_2-\mathbf{r}_3|}\frac{1}{|\mathbf{r}_3-\mathbf{r}_1|}\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}=\frac{32\pi^3}{w_1 w_2 w_3} D(w_1,w_2,w_3) . \tag{34}$$

III. EXTENSION TO RELATED INTEGRALS

In order to proceed from Eq. (34) towards the integral Eq. (1), let us differentiate Eq. (2) twice with respect to u_1 and then set $u_1=0$ for all i; in so doing we obtain

$$\left.\frac{\partial^2}{\partial u_1^2} A(w_1,w_2,w_3,u_1,u_2,u_3)\right|_{u_i=0}=\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \frac{e^{-w_1 r_1}}{r_1}\frac{e^{-w_2 r_2}}{r_2} e^{-w_3 r_3}|\mathbf{r}_2-\mathbf{r}_3|\frac{1}{|\mathbf{r}_3-\mathbf{r}_1|}\frac{1}{|\mathbf{r}_1-r_2|} . \tag{35}$$

According to Eq. (14), for finite u_i one also has

$$\frac{\partial^2}{\partial u_1^2} A(w_1,w_2,w_3,u_1,u_2,u_3)=\int_0^\infty dp_3^2 \frac{1}{p_3^2+u_3^2}\int_0^\infty dp_2^2 \frac{1}{p_2^2+u_2^2}\int_0^\infty dp_1^2 \frac{6u_1^2-2p_1^2}{(p_1^2+u_1^2)^3}\frac{1}{[\Delta(p_1^2,p_2^2,p_3^2)]^{1/2}} C(z_1,z_2,z_3) . \tag{36}$$

To evaluate such an integral, let us observe that if $S(x)$ is, in the notation of Eqs. (19) and (20) (but dropping the dependence on the parameters a, which play no role here), a second-order polynomial in x, the following "integration-by-parts" formula holds:

$$\int_{x_1}^{x_2} dx \frac{1}{(x-b)^n} \frac{1}{\sqrt{S(x)}} H(x)$$

$$= -\frac{1}{n-1}\frac{1}{S(b)}\int_{x_1}^{x_2} dx \left[\frac{1}{2\sqrt{S(x)}} \left[\frac{2n-3}{(x-b)^{n-1}} s_1 + \frac{n-2}{(x-b)^{n-2}} s_2 \right] + \frac{\sqrt{S(x)}}{(x-b)^{n-1}} \left[\delta(x-x_2) - \delta(x-x_1) - \frac{\partial}{\partial x} \right] \right] H(x) . \tag{37}$$

Equation (37) can be used to express the p_1^2 integral of Eq. (36) in terms of the integral with a single inverse power of $(p_1^2+u_1^2)$, essentially equivalent to Eq. (15), plus terms involving the derivatives of $C(z_1,z_2,z_3)$, which are explicitly known and are given in Eq. (22), plus end-point values which are easy to obtain (in the considered case they actually vanish). After the integration by parts the $u_1 \to 0$ limit is trivial. Setting also $u_2=u_3=0$, one immediately identifies a term proportional to $D(w_1,w_2,w_3)$, plus a number of terms which, after some by-now-standard algebra, can be brought in the form of the integrals already encountered in the w_i derivatives of $D(w_1,w_2,w_3)$, such as those listed in Eqs. (28) and (29). The result reads

$$\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \frac{e^{-w_1 r_1}}{r_1}\frac{e^{-w_2 r_2}}{r_2}\frac{e^{-w_3 r_3}}{r_3}\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\frac{1}{|\mathbf{r}_3-\mathbf{r}_1|}|\mathbf{r}_2-\mathbf{r}_3|$$

$$= \frac{64\pi^3}{w_2^2 w_3^2}\left[\frac{w_2^2+w_3^2-w_1^2}{2w_1w_2w_3} D(w_1,w_2,w_3) - \left[\frac{1}{w_1+w_2} + \frac{1}{w_1+w_3} \right] + \frac{w_1-w_2}{w_1w_2}\ln\left[\frac{w_1+w_2}{w_3}\right] + \frac{w_1-w_3}{w_1w_3}\ln\left[\frac{w_2+w_3}{w_1}\right] + \frac{w_2-w_3}{w_2w_3}\ln\left[\frac{w_3+w_1}{w_2}\right] \right] . \tag{38}$$

The whole procedure can be repeated for the variable u_3, which multiplies $|\mathbf{r}_1-\mathbf{r}_2|$ in the exponential of Eq. (2) to obtain the formula

$$\left.\frac{\partial^2}{\partial u_3^2}\frac{\partial^2}{\partial u_1^2} A(w_1,w_2,w_3,u_1,u_2,u_3)\right|_{u_i=0}$$

$$= \int_0^\infty dp_3^2 \frac{6u_3^2-2p_3^2}{(p_3^2+u_3^2)^3}\int_0^\infty dp_2^2 \frac{1}{p_2^2+u_2^2}\int_0^\infty dp_1^2 \frac{6u_1^2-2p_1^2}{(p_1^2+u_1^2)^3}\frac{1}{[\Delta(p_1^2,p_2^2,p_3^2)]^{1/2}} C(z_1,z_2,z_3) . \tag{39}$$

After integrating by parts over u_1 and u_3, the $u_i=0$ case is trivial and the result reads

$$\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \frac{e^{-w_1 r_1}}{r_1}\frac{e^{-w_2 r_2}}{r_2}\frac{e^{-w_3 r_3}}{r_3}|\mathbf{r}_1-\mathbf{r}_2|\frac{1}{|\mathbf{r}_3-\mathbf{r}_1|}|\mathbf{r}_2-\mathbf{r}_3|$$

$$= \frac{64\pi^3}{w_1^3 w_2^5 w_3^3}\Bigg[\tfrac{1}{2}[w_2^2(2w_1^2+w_2^2+2w_3^2)-3(w_1^2-w_3^2)^2]D(w_1,w_2,w_3)$$
$$+w_1[(w_3-w_2)w_2^2+3w_3(w_1^2+w_3^2)+3w_2(w_1^2-w_3^2)]\ln\left[\frac{w_2+w_3}{w_1}\right]$$
$$+w_3[(w_1-w_2)w_2^2+3w_1(w_1^2+w_3^2)-3w_2(w_1^2-w_3^2)]\ln\left[\frac{w_1+w_2}{w_3}\right]$$
$$+w_2(w_1+w_3)[3(w_1-w_3)^2-w_2^2]\ln\left[\frac{w_3+w_1}{w_2}\right]$$
$$+2w_1w_3\left[w_2^3\frac{w_1^2+3w_1w_3+w_3^2}{(w_1+w_3)^3} - w_2\frac{2w_1^2+w_1w_3+2w_3^2}{w_1+w_3} + \frac{w_1^3}{w_1+w_2} + \frac{w_3^3}{w_2+w_3} - w_1^2+w_2^2-w_3^2\right]\Bigg] . \tag{40}$$

We can now turn to the evaluation of the integral Eq. (1), which is the main purpose of this paper. We have obviously

$$Z(w_1,w_2,w_3) = -\left.\frac{\partial}{\partial w_1}\frac{\partial}{\partial w_2}\frac{\partial}{\partial w_3}\frac{\partial^2}{\partial u_3^2}\frac{\partial^2}{\partial u_1^2} A(w_1,w_2,w_3,u_1,u_2,u_3)\right|_{u_i=0} . \tag{41}$$

As Eqs. (39) and (40) are exact in all the w_i, to obtain the value of the desired integral in closed analytic form it is sufficient to differentiate Eq. (40) three times with respect to w_1, w_2, and w_3, and then change the overall sign. The derivatives of $D(w_1,w_2,w_3)$ are already known [see Eq. (30)], so that the actual differentiation of Eq. (40) is completely straightforward, especially when an algebraic program is used. As matter of fact, it was much easier to perform the derivatives than to properly retype the terms obtained to exhibit the obvious properties of symmetry for the exchange of w_1 with w_3 and of regularity at $w_3=w_1+w_2$, etc. The result can be written as

$$\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 e^{-w_1 r_1} e^{-w_2 r_2} e^{-w_3 r_3} |\mathbf{r}_1-\mathbf{r}_2| \frac{1}{|\mathbf{r}_3-\mathbf{r}_1|} |\mathbf{r}_2-\mathbf{r}_3|$$

$$\begin{aligned}
&= \frac{64\pi^3}{w_1^4 w_2^6 w_3^4} \Bigg[\tfrac{3}{2}[3w_2^4+6(w_1^2+w_3^2)w_2^2+5(3w_1^4+2w_1^2w_3^2+3w_3^4)]D(w_1,w_2,w_3) \\
&\quad + 8w_1^2 w_2^3 w_3^2 \left[\frac{\ln_2[(w_1+w_2)/w_3]}{(w_1+w_2-w_3)^3} - \frac{\ln_2[(w_2+w_3)/w_1]}{(w_1-w_2-w_3)^3} \right. \\
&\qquad \left. - \frac{\ln_2[(w_1+w_3)/w_2]}{(w_1-w_2+w_3)^3} - \frac{\mathrm{Sln}(w_1,w_2,w_3)}{(w_1+w_2+w_3)^3} \right] \\
&\quad + 12 w_1 w_2^2 w_3 (w_1^2+w_3^2) \left[\frac{\ln_1[(w_1+w_2)/w_3]}{(w_1+w_2-w_3)^2} + \frac{\ln_1[(w_2+w_3)/w_1]}{(w_1-w_2-w_3)^2} \right. \\
&\qquad \left. - \frac{\ln_1[(w_1+w_3)/w_2]}{(w_1-w_2+w_3)^2} + \frac{\mathrm{Sln}(w_1,w_2,w_3)}{(w_1+w_2+w_3)^2} \right] \\
&\quad + 12 w_2 [(w_1^2+w_3^2)(w_1+w_3)^2 - 3w_1^2 w_3^2] \left[\frac{\ln[(w_1+w_2)/w_3]}{w_1+w_2-w_3} - \frac{\ln[(w_2+w_3)/w_1]}{w_1-w_2-w_3} \right] \\
&\quad - 12 w_2 [(w_1^2+w_3^2)(w_1-w_3)^2 - 3w_1^2 w_3^2] \left[\frac{\ln[(w_1+w_3)/w_2]}{(w_1-w_2+w_3)^2} + \frac{\mathrm{Sln}(w_1,w_2,w_3)}{(w_1+w_2+w_3)} \right] \\
&\quad + 3w_3 [3(w_1-w_2)w_2^2 - (9w_1^2+7w_3^2)w_2 - 15(w_1^2+w_3^2)w_1] \ln \left[\frac{w_1+w_2}{w_3} \right] \\
&\quad + 3w_1 [3(w_3-w_2)w_2^2 - (7w_1^2+9w_3^2)w_2 - 15(w_1^2+w_3^2)w_3] \ln \left[\frac{w_2+w_3}{w_1} \right] \\
&\quad - 3w_2 [3(w_1+w_3)w_2^2 + 7w_1^3 + 9w_1^2 w_3 + 9 w_1 w_3^2 + 7w_3^3] \ln \left[\frac{w_3+w_1}{w_2} \right] \\
&\quad - 2(2w_1^2 - 9w_1w_3 + 2w_3^2)w_2^2 + 80 w_1 w_3 (w_1^2+w_3^2) + 2(8w_1^3 + 13 w_1^2 w_3 + 13 w_1 w_3^2 + 8 w_3^3) w_2 \\
&\quad + 8 \frac{w_1 w_2^2 w_3}{(w_1+w_2+w_3)^2} (w_1^2 + w_1 w_3 + w_3^2) - 4 \frac{w_2}{w_1+w_2+w_3} (4w_1^4 + 3w_1^3 w_3 + 5 w_1^2 w_3^2 + 3 w_1 w_3^3 + 4 w_3^4) \\
&\quad + 48 \frac{w_1^3 w_2^3 w_3^3}{(w_1+w_3)^5} + 24 \frac{w_1^2 w_2 w_3^2}{(w_1+w_3)^3} (w_2^2 + 2 w_1 w_3) + 8 \frac{w_1 w_2 w_3}{w_1+w_3} (3w_2^2 - 2 w_1 w_3) \\
&\quad - 8 w_1 w_3 \left[\frac{w_1^5}{(w_1+w_2)^3} + \frac{w_3^5}{(w_2+w_3)^3} \right] + 48 w_1 w_3 \left[\frac{w_1^4}{(w_1+w_2)^2} + \frac{w_3^4}{(w_2+w_3)^2} \right] \\
&\quad - 120 w_1 w_3 \left[\frac{w_1^3}{w_1+w_2} + \frac{w_3^3}{w_2+w_3} \right] \Bigg] . \qquad (42)
\end{aligned}$$

For ease of typing, we have introduced in Eq. (40) the quantities

$$\mathrm{Sln}(x,y,z)\equiv\ln\left[\frac{x+y}{z}\right]+\ln\left[\frac{x+z}{y}\right]+\ln\left[\frac{y+z}{x}\right],$$

$$\ln_1(x)\equiv\ln(x)-(x-1),$$

$$\ln_2(x)\equiv\ln(x)-(x-1)+\tfrac{1}{2}(x-1)^2 .$$

Equation (40) looks, and perhaps is, somewhat cumbersome, but in fact its structure is remarkably simple. It involves only the dilogarithmic combination $D(w_1,w_2,w_3)$ defined in Eq. (33), the three logarithms $\ln[(w_1+w_2)/w_3]$, $\ln[(w_1+w_3)/w_2]$, $\ln[(w_2+w_3)/w_1]$, and simple rational functions of the w_i. Furthermore, it is ready for the actual numerical evaluation, being in particular regular (as expected, of course) at, say, $w_1+w_2=w_3$, because the numerators of all the terms with $1/(w_1+w_2-w_3)^n$ vanish as $(w_1+w_2-w_3)^n$ (the same is true for the other two denominators without definite sign).

It is clear from the derivation why Eq. (42) is larger than Eqs. (40), (38), and the really compact Eq. (34). It is also clear that similar formulas can be obtained, when needed, for all the related three electron-correlation integrals with higher positive powers of the r_i and $|\mathbf{r}_i-\mathbf{r}_j|$ in the numerator, so that the algorithm presented in this paper is by no means restricted to s-wave functions only.

IV. COMPARISON WITH PREVIOUS WORK

After the completion of this work, the author discovered the existence of the work of Fromm and Hill [4], where the analytic evaluation of three-electron integrals was also worked out; the result of Ref. [4] is in fact more general, as it provides a formula valid for any value of the parameters u_i, not just at the point $u_i=0$ (notation of this paper). In the common region of applicability, the results are in perfect numerical agreement. In the terminology of Ref. [4], at the auxiliary reference point (ARP) $w_1=w_2=w_3=1, u_1=u_2=u_3=0$, the numerical values of Eqs. (34), (38), and (40) are $4.382\,174\,441\,144\times10^2$, $1.204\,780\,633\,933\times10^3$, and $8.504\,405\,304\,091\times10^3$, coinciding with the entries (000 000,000 200,000 220) of Table III of Ref. [4], while at the same ARP for Eq. (42) we find $9.155\,447\,160\,887\times10^4=2^{10}\pi^3\times2.883\,566\,595\,319$, to be compared with 2.883 566 595, as quoted in Ref. [5].

The approach of Ref. [4] and of the present paper is the same, i.e., Fourier transform for the auxiliary integral Eq. (2), called the generating function in Ref. [4]. Reference [4], however, differs strongly in the technique followed for performing the quadruple definite integral corresponding to Eq. (14); rather than using the "differentiate and integrate" algorithm of this paper, the first integration corresponding to Eq. (9) is performed by brute force by means of Eq. (4.34) of Ref. [4]. The result is [see the remarks after Eq. (9) of this paper] a combination of dilogarithmic functions of complicated arguments, whose subsequent integration on the three momenta is then ingeniously carried out in Ref. [4] by contour integration. As a consequence of the original brute-force integration, the key result, Eq. (2.1) of Ref. [4] and following formulas, is obtained in a form somewhat discouraging to the reader, as it contains many dilogarithms of complicated and complex (i.e., not real) arguments, exhibiting a variety of spurious singularities which cancel out in the final result, and whose actual numerical evaluation requires among the other subtleties a careful preliminary branch tracking. That contrasts with the plainness of Eq. (33) and those thereafter of this paper, where the results are expressed as a combination of real functions of real variables, whose numerical evaluation is immediate, in the whole range of variability of the arguments w_i.

Without underestimating the complications inherent in the much more general $u_i\neq0$ case, it is likely that also Eq. (2.1) of Ref. [4], after a major rewriting effort, can be recast in the form of a simpler expression, and of much greater practical use, in which the compensating singularities do not appear at all. Once expressed in that way, the result of Ref. [4] could receive the acknowledgment that it deserves and produce the expected impact in high-precision correlation calculations.

V. CONCLUSIONS

The use of Eq. (42) as well as of the related formulas for the three-electron correlation integrals with higher positive powers of the r_i and $|\mathbf{r}_i-\mathbf{r}_j|$ in the numerator is expected to speed up considerably the computational time required for the proper accounting of two-electron correlation effects in atoms, thus making high-precision calculations easier. It is being investigated whether and how the techniques introduced here can be of use for the analytic evaluation of atomic integrals with many-electron-correlation effects or of two-electron-correlation effects in *ab initio* calculations of simple molecules.

ACKNOWLEDGMENTS

The author wants to thank G. Bendazzoli and F. Bernardi for focusing his interest on this problem, S. Turrini who kindly provided him with direct numerical checks of the key formulas and M. Veltman for the assistance in the use of the algebra manipulating program SCHOONSCHIP.

APPENDIX A

The Euler dilogarithm $\mathrm{Li}_2(y)$, sometimes also called the Spence function, appears naturally when integrating a logarithm multiplied by a rational expression, in the same way that logarithms appear when integrating rational expressions. It is defined by

$$\mathrm{Li}_2(y)\equiv-\int_0^1 dt\frac{1}{t}\ln(1-yt)=-\int_0^y dt\frac{1}{t}\ln(1-t) . \qquad \text{(A1)}$$

It is real for real $y\leq1$ and develops an imaginary part for real $y>1$. From Eq. (A1) one has the power-series expansion

$$\mathrm{Li}_2(y)=\sum_{m=1}^{\infty}\frac{y^m}{m^2}\ , \tag{A2}$$

which converges for $y\le 1$, $\mathrm{Li}_2(0)=0$, and the values at $y=1$,

$$\mathrm{Li}_2(1)=-\int_0^1 dt\frac{1}{t}\ln(1-t)=\zeta(2)\ , \tag{A3}$$

where $\zeta(p)\equiv\sum_{m=1}^{\infty}1/m^p$ is the Riemann ζ function of argument p. From the definition, one has also

$$\frac{d}{dy}\mathrm{Li}_2(y)=-\frac{1}{y}\ln(1-y)\ . \tag{A4}$$

By elementary use of the above equations one can easily obtain a number of relations between dilogarithms of related arguments. One has, for instance,

$$\tfrac{1}{2}\mathrm{Li}_2(y^2)=\mathrm{Li}_2(y)+\mathrm{Li}_2(-y)\ . \tag{A5}$$

The relation holds at $y=0$, while the derivatives on the lhs and the rhs are equal for any y; therefore Eq. (A5) is true for any value of y. From (A5) at $y=-1$ one obtains

$$\int_0^1 dt\frac{1}{t}\ln(1+t)=-\mathrm{Li}_2(-1)=\tfrac{1}{2}\zeta(2)\ . \tag{A6}$$

By the same technique one can also obtain identities between dilogarithms whose arguments are related by the transformations $y\to 1/y$, $y\to(1-y)$, and combinations thereof. All the identities can best be established by checking their validity at some convenient particular value of y and then differentiating with respect to y, thereby obtaining an identity between logarithms whose validity is trivial to ascertain. One finds, for real $y>0$,

$$\mathrm{Li}_2(y)=-\mathrm{Li}_2(1-y)-\ln y\,\ln(1-y)+\zeta(2)\ , \tag{A7}$$

$$\mathrm{Li}_2(-y)=-\mathrm{Li}_2\left[-\frac{1}{y}\right]-\tfrac{1}{2}\ln^2 y-\zeta(2)\ , \tag{A8}$$

By analytic continuation of Eq. (A8) to $y=-1$, as $\ln^2(-1)=-\pi^2$ one derives the known relation $\zeta(2)=\pi^2/6$.

With the above formulas, it is quite easy to evaluate numerically $\mathrm{Li}_2(y)$; for small y one can directly use the expansion (A2). More systematically, one can use the proper combination of Eqs. (A7) and (A8) to express the required value of $\mathrm{Li}_2(x)$ in terms of a dilogarithm whose argument x is in the range $-1<x<\frac{1}{2}$; in that interval the dilogarithm is analytic and can be evaluated by a quickly convergent power expansion (see Ref. [3] for an implementation of the method).

APPENDIX B

We sketch here a proof of Eq. (21). When differentiating $K(a)$ [Eq. (20)] with respect to a, one obtains, on the rhs, three terms, corresponding to (i) the derivative of the function $H(a,x)$, (ii) the derivative of $\sqrt{S(a,b)}$ in the numerator, and (iii) the derivative of $\sqrt{S(a,x)}$ in the denominator. For the third term, with the definition of $S(a,x)$ [Eq. (19)] one has obviously

$$\frac{\partial}{\partial a}\frac{1}{\sqrt{S(a,x)}}=-\frac{1}{2}\frac{1}{\sqrt{S(a,x)}}\frac{1}{S(a,x)}\times\left[\frac{\partial s_0}{\partial a}+\frac{\partial s_1}{\partial a}(x-b)+\frac{1}{2}\frac{\partial s_0}{\partial a}(x-b)^2\right]\ .$$

Only in the term with $\partial s_0/\partial a$ the denominator $1/(x-b)$ appearing in Eq. (20) is still present; to process it one can use the algebraic identity

$$\frac{1}{S(a,x)}\frac{1}{x-b}=\frac{1}{S(a,b)}\left[\frac{1}{x-b}-\frac{s_1+\frac{1}{2}s_2(x-b)}{S(a,x)}\right]\ ,$$

and the first term on the rhs is found to cancel out exactly with the contribution (ii) above. One can then integrate by parts the remaining terms

$$\frac{dx}{[\sqrt{S(a,x)}]^3},\quad \frac{dx\,(x-b)}{[\sqrt{S(a,x)}]^3}\ ,$$

and then collect results until Eq. (21) is obtained.

By a similar approach one can deal with the integrals involving the factors of Eq. (25). As the analog of Eq. (21) one finds, for instance, for any function $F(p,q,w)$,

$$\begin{aligned}\frac{\partial}{\partial q}\int_{p_1}^{p_2}dp^2\frac{wq}{R_2(p^2,q^2,-w^2)}F(p,q,w)&=\int_{p_1}^{p_2}dp^2\frac{wq}{R_2(p^2,q^2,-w^2)}\frac{\partial F(p,q,w)}{\partial q}\\&-\int_{p_1}^{p_2}dp^2\frac{wq}{R_2(p^2,q^2,-w^2)}\frac{p^2+q^2+w^2}{2q^2}\left[\delta(p-p_2)-\delta(p-p_1)-\frac{\partial}{\partial p}\right]F(p,q,w)\ ,\end{aligned} \tag{B1}$$

$$\begin{aligned}\frac{\partial}{\partial w}\int_{p_1}^{p_2}dp^2\frac{wq}{R_2(p^2,q^2,-w^2)}F(p,q,w)&=\int_{p_1}^{p_2}dp^2\frac{wq}{R_2(p^2,q^2,-w^2)}\frac{\partial F(p,q,w)}{\partial w}\\&-\int_{p_1}^{p_2}dp^2\frac{wq}{R_2(p^2,q^2,-w^2)}\frac{p^2-q^2-w^2}{2w^2}\left[\delta(p-p_2)-\delta(p-p_1)-\frac{\partial}{\partial p}\right]F(p,q,w)\ .\end{aligned} \tag{B2}$$

Similar formulas hold for all the other terms listed in Eq. (25).

[1] M. J. Levine, E. Remiddi, and R. Roskies, in *Quantum Electrodynamics,* edited by T. Kinoshita (World Scientific, Singapore, 1990), pp. 162–321, and references therein.

[2] H. Strubbe, Comput. Phys. Commun. **8**, 1 (1974); **18**, 1 (1979); M. Veltman, SCHOONSCHIP, A program for Symbol Handling (unpublished).

[3] K. S. Kölbig, J. A. Mignaco, and E. Remiddi, BIT **10**, 38 (1970).

[4] D. M. Fromm and R. N. Hill, Phys. Rev. A **36**, 1013 (1987).

[5] W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).