The Evaluation of Two-Centre Molecular Integrals Involving One-Electron Green's Functions

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The numerical evaluation of certain two-centre molecular integrals involving one-electron Green's functions is considered. Considerable improvement is realized over earlier calculations when semi-analytic methods are employed using Fourier transforms to reduce the order of the multiple quadratures. The resulting triple integrals are evaluated using improved polar grids which yield almost machine accuracy on utilizing Gaussian quadrature prescriptions. For illustration, integrals arising from two alternative variational functionals are evaluated and the corresponding energy curves compared for the H_2^+ ion, thus providing an assessment of the validity of the Born-Oppenheimer separation embodied in one of the functionals.

1. Introduction

In a previous paper, Hall, Hyslop, and Rees [1] proposed a variation principle for molecular energies involving the use of Green's functions. Two alternative functionals were introduced, the simpler of which was derived using the usual Born-Oppenheimer approximation. This functional was applied to the calculation of an upper bound for the ground state energy of the hydrogen molecular ion H_2^+. The six-dimensional Green's function integrals involved were evaluated by using semi-analytical techniques employing two-centre elliptic co-ordinates together with a Fourier transform representation of the one-electron Green's function. By this means, the singularities associated with the potential energy and with the Green's function were effectively removed and the integrals were reduced to, at most, triple quadratures. The resulting triple integrals were then evaluated using a basic Gauss-Legendre product formula (Davis and Rabinowitz [2]) with a 5^3 point grid. The regions over which the integrations were to be carried out were finite ellipsoids and the suggested routine was seriously in error when the size of these volumes increased beyond a certain limit. Obviously, modification of the integration procedure is necessary to allow for formulae of the Gauss-Laguerre type to be used, particularly when the trial functions employed are to be defined over all space. This modification is one of the themes of the present paper.

Again, it is of interest to extend these semi-analytical ideas to cover the case of the alternative functional suggested in [1], so that a direct comparison is made

possible and the validity of the Born-Oppenheimer approximation assessed accurately in this particular case.

Furthermore, the direct numerical evaluation of the integrals involved in both functionals has been considered by Hyslop [3]. The Green's function singularity was removed by a subtraction technique and reductions in computing time were realized by employing an empirically determined extrapolation formula of the Richardson type. Once again, the limitations on the accuracy produced by this method were such that the approximate energies obtained from both variational functions were indistinguishable. In the present work, the possibility of improving these results is investigated.

The integrals involved in this particular application are considered in some detail, since they are typical of the class of integral which arises in one-electron Green's function calculations and, indeed, the techniques described are very widely applicable to molecular integrals in general.

2. The Variational Functionals and Formulation of the Integrals

On using the scaling techniques described in [1], the variational functional as derived using the Born-Oppenheimer approximation may be written as

$$\kappa = I/J = \langle \omega V | G | V \omega \rangle / \langle \omega | V | \omega \rangle . \tag{1}$$

In this equation $\omega(\varrho)$ is the trial function of the scaled variable ϱ ($\varrho = \kappa r$) and G is the operator corresponding to the scaled one-electron Green's function

$$G(\varrho_1, \varrho_2) = -\exp(-\varrho_{12})/(2\pi\varrho_{12}) \tag{2}$$

with $\varrho_{12} = |\varrho_1 - \varrho_2|$.

In the case of the hydrogen molecular ion, H_2^+, the electronic potential energy $V(\varrho)$ is given by

$$V(\varrho) = -(1/\varrho_a + 1/\varrho_b) \tag{3}$$

where ϱ_a and ϱ_b are the distances between the electron and the protons A and B whose separation is $P = \kappa R$ (all distances being scaled).

The approximate electronic energy corresponding to the functional (1) is

$$E = -\tfrac{1}{2}\kappa^2 \tag{4}$$

yielding the total energy of the molecule as

$$W = -\frac{1}{2}\kappa^2 + \frac{1}{R} \tag{5}$$

assuming the usual Born-Oppenheimer separation.

The alternative functional is written as

$$\kappa' = I'/J' = \langle \omega V' | G | V' \omega \rangle / \langle \omega | V' | \omega \rangle \tag{6}$$

in which V' is the total scaled potential energy according to

$$V' = -(1/\varrho_a' + 1/\varrho_b') + 1/P' \tag{7}$$

in which all distances have been subjected to the scaling factor κ' and the corresponding total energy is $-\kappa'^2/2$.

Values of κ are then obtained as functions of the independent variable $P = \kappa R$ from Eq. (1) with corresponding internuclear separation P/κ. Similarly, κ' is given as a function of $P' = \kappa'R$ from Eq. (6) at separation P'/κ' and so energy curves may be obtained and compared.

It is natural to express the above integrals in terms of the two-centre elliptic coordinates (λ, μ, ϕ) where

$$\lambda = (r_a + r_b)/R, \qquad \mu = (r_a - r_b)/R \tag{8}$$

with the usual notation, ϕ being the azimuthal angle about the internuclear axis. To illustrate the integration techniques, the simple united atom approximation of the earlier work, namely

$$\omega(\varrho) = \exp(-c\lambda) \tag{9}$$

is again utilized, the function being regarded as already scaled, since it involves only ratios of distances. As noted in [3], the normalization integrals J and J' are immediate and the analytical results are quoted in the earlier work.

The main integrals I and I' may be conveniently expressed in the form

$$I = -\tfrac{1}{4}P^4 \int \varrho_{12}^{-1}\exp(-\varrho_{12})Q(\lambda_1, \lambda_2)d\tau \tag{10a}$$

and

$$I' = -\tfrac{1}{4}P'^4 \int \varrho_{12}^{-1}\exp(-\varrho_{12})Q'(\lambda_1, \lambda_2)d\tau \tag{10b}$$

where, for abbreviation purposes,

$$Q(\lambda_1, \lambda_2)d\tau \equiv \exp[-c(\lambda_1 + \lambda_2)]\lambda_1\lambda_2 d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\phi \tag{11a}$$

and

$$\begin{aligned}Q'(\lambda_1, \lambda_2)d\tau \equiv \exp[-c(\lambda_1 + \lambda_2)][\lambda_1 - \tfrac{1}{4}(\lambda_1^2 - \mu_1^2)] \\ \cdot [\lambda_2 - \tfrac{1}{4}(\lambda_2^2 - \mu_2^2)]d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\phi \end{aligned} \tag{11b}$$

with $1 \leqq \lambda < \infty$, $-1 \leqq \mu \leqq 1$ and $0 \leqq \phi \leqq 2\pi$.

The scaled distance ϱ_{12} is given by

$$\begin{aligned}4\varrho_{12}^2/P^2 = (\lambda_1^2 - 1)(1 - \mu_1^2) + (\lambda_2^2 - 1)(1 - \mu_2^2) + (\lambda_1\mu_1 - \lambda_2\mu_2)^2 \\ - 2[(\lambda_1^2 - 1)(1 - \mu_1^2)(\lambda_2^2 - 1)(1 - \mu_2^2)]^{1/2}\cos\phi \end{aligned} \tag{12}$$

in Eq. (10a), whilst in (10b) P is replaced by P' in this expression. The angle ϕ represents the difference in azimuthal angles $(\phi_1 - \phi_2)$.

3. Direct Numerical Evaluation of the Integrals

The basic prescription for the numerical evaluation of the integrals (10a) and (10b) is a five-dimensional Gaussian product formula of the type discussed by Davis and Rabinowitz [2] or by Stroud and Secrest [4], full details of the method adopted being presented in [3]. As pointed out in [3], the main difficulty in the

evaluation of these integrals is the wellknown one associated with the presence of the ϱ_{12}^{-1} singularity and a subtraction technique was proposed to deal with this. The method involved the numerical evaluation of the integral

$$S_1 = \tfrac{1}{4} P^4 \int \varrho_{12}^{-1} [1 - \exp(-\varrho_{12})] Q(\lambda_1, \lambda_2) d\tau \tag{13}$$

the integrand having been smoothed by the removal of the singularity. It was then necessary to evaluate analytically the subsidiary integral

$$A_1 = \tfrac{1}{4} P^4 \int \varrho_{12}^{-1} Q(\lambda_1, \lambda_2) d\tau \tag{14}$$

and its treatment was described in [3]. The approximate value of I was then given by I_1 where

$$I_1 = S_1 - A_1 . \tag{15}$$

This subtraction technique produced a considerable improvement in convergence. Hence, in the present work, the possibility of producing further smoothing of the integrand by extracting additional terms in the Taylor series for $\exp(-\varrho_{12})$ is considered. Thus, the integrals

$$S_2 = \tfrac{1}{4} P^4 \int \varrho_{12}^{-1} [1 - \varrho_{12} - \exp(-\varrho_{12})] Q(\lambda_1, \lambda_2) d\tau \tag{16}$$

and

$$A_2 = \tfrac{1}{4} P^4 \int Q(\lambda_1, \lambda_2) d\tau \tag{17}$$

are introduced and correspond to the approximate I value of

$$I_2 = S_2 - A_1 + A_2 . \tag{18}$$

At the next stage, we consider

$$S_3 = \tfrac{1}{4} P^4 \int \varrho_{12}^{-1} [1 - \varrho_{12} + \tfrac{1}{2} \varrho_{12}^2 - \exp(-\varrho_{12})] Q(\lambda_1, \lambda_2) d\tau \tag{19}$$

and

$$A_3 = \tfrac{1}{4} P^4 \int \varrho_{12} Q(\lambda_1, \lambda_2) d\tau \tag{20}$$

with

$$I_3 = S_3 - A_1 + A_2 - \tfrac{1}{2} A_3 \tag{21}$$

and so on.

It will be noted that if the implied numerical integration of A_i contained within the evaluation of S_i is exact, then no improvement is made in convergence in going from S_{i-1} to S_i ($i = 2, 3, \ldots$) and consequently $I_i = I_{i-1}$. This is indeed the case when i is even, for it is clearly seen from Eq. (12) that, when even powers of ϱ_{12} are involved, exact values of the analytic integrals A_i could be obtained from the N^5-point Gaussian numerical integration grid. The required condition would be $N \geq 2i - 3$ for $i = 2, 4, 6, \ldots$. Hence, for instance, $I_2 = I_1$. Therefore, only significant improvement in convergence rates can be made by investigating I_i where i is odd. In practical terms, the integrals $A_2, A_4, A_6, \ldots$ do not improve the con-

vergence of the numerical evaluation of S_i and, indeed, are effectively ignored. Thus, for example, I_3 and S_3 are taken in practice to be

$$S_3 = \tfrac{1}{4}P^4 \int \varrho_{12}^{-1}[1 + \tfrac{1}{2}\varrho_{12}^2 - \exp(-\varrho_{12})]Q(\lambda_1, \lambda_2)d\tau \tag{22}$$

and

$$I_3 = S_3 - A_1 - \tfrac{1}{2}A_3 \tag{23}$$

in contrast with the recommendations of Eq. (19) and (21).

The analytical evaluation of the auxiliary integrals A_i is effected here by using the Fourier transform techniques described in Section 4. In the earlier work [3], A_1 only was required and the Neumann expansion of ϱ_{12}^{-1} (Harris and Michels [5]) was utilized on that occasion.

Similar techniques are applied to the evaluation of I'.

As an example of the results obtained, comparison is made between I_1 and I_3 for the particular values of the parameters $P = 3.0$ and $c = 1.3$. The results are presented in the following table, the exact value of I being obtained using the semi-analytic methods described later. (Exact value $= -3.28693$).

N	I_1	I_3
4	−3.21395	−3.29611
5	−3.23753	−3.29214
6	−3.25212	−3.28940
7	−3.26144	−3.28817
8	−3.26755	−3.28755

3.1. The Use of Shanks' Non-Linear Transformations to Accelerate Convergence

On denoting the value of I_3 given by using an N^5 grid by T_N, it may be observed that whilst some improvement over the I_1 results is achieved, the sequence $\{T_N\}$ is converging only slowly towards the exact value of I.

The Shanks technique [6] involves the transformation of the sequence $\{T_N\}$, $N = 0, 1, 2, \ldots$ into the sequence $\{B_{j,N}\}$ $N = j, j+1, \ldots$ by means of the operators e_j according to the relationship

$$\{B_{j,N}\} = e_j\{T_N\}, \quad j = 1, 2, \ldots . \tag{24}$$

The general term in $\{B_{j,N}\}$ may be written as the ratio of two determinants of order $(j+1)$. Details of the transformations together with restrictions imposed and conditions to be satisfied are given in Shanks' paper. The most frequently used transformation is e_1 which produces the simple form

$$B_{1,N} = (T_{N+1}T_{N-1} - T_n^2)(T_{N+1} + T_{N-1} - 2T_N)^{-1} \tag{25}$$

which is, of course, the familiar Aitken δ^2 extrapolation procedure. It was essentially this result which was used in [3] to produce empirically an acceleration technique. Here, the use of the more general Shanks' transformations is considered systematically. It is worth while pointing out that transformations of this type have been employed recently by various authors [7–9], in quadrature investigations.

Representative results are presented in the following table for the case $P = 3.0$ and $c = 1.3$. (Exact value $= -3.28693$).

N	T_N	$e_1\{T_N\}$	$e_1^2\{T_N\}$	$e_1^3\{T_N\}$	$e_2\{T_N\}$
2	-2.75942				
3	-3.26436	-3.29824			
4	-3.29611	-3.29258	-3.30716		
5	-3.29214	-3.28333	-3.28603	-3.28691	-3.28723
6	-3.28940	-3.28715	-3.28695		-3.28694
7	-3.28817	-3.28694			
8	-3.28755				

The results seem to indicate that the subtraction of the further two terms in the expansion of $\exp(-\varrho_{12})$ yields an increase in accuracy of between 1 and 2 significant figures in the evaluation of I. Thus, the application of Shanks' acceleration technique produces 5-figure accuracy, provided values of N as large as $N = 8$ are tolerated.

Similar remarks apply to the evaluation of I' and it is concluded that, in practice, the number of function evaluations required may still be prohibitively large, even when smoothing of the integrand is effected by subtraction techniques and acceleration procedures are employed. Consequently, attention is now given to the alternative method involving the extension of the semi-analytical Fourier transform prescriptions.

4. Fourier Transform Techniques

The use of Fourier transforms described here is analogous to the convolution methods suggested by Prosser and Blanchard [10] and by Geller [11] for the calculation of certain two-centre integrals and is also mentioned in the review paper of Harris and Michels [5].

Thus, when integrals of the form

$$\int f_1^*(\varrho_1) f_2(\varrho_2) f_3(\varrho_1 - \varrho_2) d\varrho_1 d\varrho_2 \tag{26}$$

are considered, separation of the variables ϱ_1 and ϱ_2 is achieved by introducing the Fourier representation

$$f_3(\varrho_1 - \varrho_2) = (8\pi^3)^{-1} \int F_3(s) \exp[is \cdot (\varrho_1 - \varrho_2)] ds, \tag{27}$$

where

$$F_3(s) = \int f_3(p)\exp(-is \cdot \varrho)d\varrho .$$ (28)

Consequently, the integral may be expressed as

$$\int f_1^*(\varrho_1)f_2(\varrho_2)f_3(\varrho_1 - \varrho_2)d\varrho_1 d\varrho_2 = (8\pi^3)^{-1} \int F_1^*(s)F_2(s)F_3(s)ds$$ (29)

where

$$F_1(s) = \int f_1(\varrho)\exp(-is \cdot \varrho)d\varrho$$ (30)

and

$$F_2(s) = \int f_2(\varrho)\exp(-is \cdot \varrho)d\varrho .$$ (31)

The basic relation (29) was used in [1] to reduce the I evaluation to a triple quadrature in the worst cases considered. However, it is, of course, a very general result and in the present work it is also applied by way of illustration to the calculation of the auxiliary integrals A_1, A_2 and A_3 and also the previous work is extended to cover the alternative integral I'.

4.1. Evaluation of the Auxiliary Integrals $A_1, A_2, A_3, \ldots$

Previously, Hyslop [3] evaluated the integral

$$A_1 = (2\pi)^{-1} \int \omega^*(\varrho_1)V(\varrho_1)\varrho_{12}^{-1}V(\varrho_2)\omega(\varrho_2)d\varrho_1 d\varrho_2$$ (32)

by using the Neumann expansion of ϱ_{12}^{-1} in terms of two-centre coordinates and the earlier results are useful for checking purposes.

In the present paper, Fourier representations for ϱ_{12}^{n-2} may be obtained for $n = 1, 3, 5, \ldots$ corresponding to $A_1, A_3, A_{5}, \ldots$ by means of the formal result

$$(2\pi)^{-1} \int \varrho^{n-2}\exp(-is \cdot \varrho)d\varrho = 2(n-1)! \quad (-1)^{(n-1)/2}s^{-(n+1)} \quad (n=1,3,5,\ldots) .$$ (33)

The integrals A_n may therefore be expressed as

$$A_n = (2\pi)^{-1} \int \omega^*(\varrho_1)V(\varrho_1)\varrho_{12}^{n-2}V(\varrho_2)\omega(\varrho_2)d\varrho_1 d\varrho_2$$ (34)

$$= 2(n-1)!(-1)^{(n-1)/2}(8\pi^3)^{-1} \int |F(s)|^2 s^{-(n+1)}ds ,$$ (35)

where

$$F(s) = \int \omega(\varrho)V(\varrho)\exp(-is \cdot \varrho)d\varrho .$$ (36)

This two-centre Fourier transform with $\omega(\varrho)$ and $V(\varrho)$ given by Eq. (9) and (3) respectively is easily reduced to the form

$$F(s) = -(4\pi P/s) \int_u^\infty \exp(-c\lambda)\sin(sP\xi/2)d\xi$$ (37)

in which

$$\lambda = (\xi^2 + 1 - u^2)^{1/2}$$ (38)

and

$$u = \hat{s} \cdot \hat{R} ,$$ (39)

R being the vector $\overrightarrow{AB}$. The details of the transformation, which involves the use of eliptical coordinates, are presented in [1]. Similar two-centre transforms have been considered by Laurenzi [12].

Substitution into Eq. (35) and change of the order of integration followed by contour integration over the variable s yields the expression

$$A_n = (8\pi P^{n+2})(2^n n)^{-1} \int_0^1 \int_u^\infty \int_u^\eta \exp[-c(\lambda + \lambda_1)][(\xi + \eta)^n - (\eta - \xi)^n] d\xi d\eta du \qquad (40)$$

with

$$\lambda_1 = (\eta^2 + 1 - u^2)^{1/2} \qquad (41)$$

and $n = 1, 3, 5, \ldots$.

Analytical evaluation is now possible and elementary analysis shows that A_n may be expressed in terms of the family of integrals $I_n(\alpha)$ defined by

$$I_n(\alpha) = \int_1^\infty \lambda^n \exp(-\alpha\lambda) \log[(\lambda + 1)/(\lambda - 1)] d\lambda \qquad (42)$$

with $n = 0, 1, 2, 3, \ldots$. Analytical expressions for $L_n(\alpha)$ are readily written down by successive differentiations with respect to α of the basic result

$$L_0(\alpha) = \alpha^{-1}[(\gamma + \log 2\alpha)\exp(-\alpha) + \exp(\alpha)E_1(2\alpha)] \qquad (43)$$

(cf. Gradshteyn and Ryzhik [13, pp. 573–574]).

In this formula $\gamma = 0.5772\ldots$ is Euler's constant and $E_1(z)$ is the exponential integral

$$E_1(z) = \int_1^\infty t^{-1} \exp(-zt) dt \qquad (44)$$

as defined by Abramowitz and Stegun [14, p. 231].

Analytical expressions for A_1 and A_3 are easily obtained in this way, but the expressions are somewhat cumbersome and need not be reproduced here, since the derivation is entirely straightforward.

Note also that the Fourier representation (33) is *not* available for even values of n, so that $A_2, A_4, \ldots$ cannot be evaluated using the above techniques. However, since even powers of ϱ_{12} only are involved, it is immediately obvious from Eq. (12) that the integrals required may be expressed in terms of the standard molecular integrals

$$\int_1^\infty \lambda^n \exp(-\alpha\lambda) d\lambda \quad \text{and} \quad \int_{-1}^{+1} \mu^n \exp(-\alpha\mu) d\mu \qquad (45)$$

(Harris and Michels [5]). The particularly simple result for A_2, which is used in the acceleration technique for evaluating I according to Eq. (21), is readily shown to be

$$A_2 = 2\pi (P/c)^4 (1+c)^2 \exp(-2c). \qquad (46)$$

In practice, of course, as pointed out in Section 3, the integrals $A_2, A_4, A_6, \ldots$ do not improve the convergence of the numerical evaluation of S_n and, indeed, are effectively ignored.

4.2. Analytical Reduction of the Integral I

The Green's function $G(\varrho_1, \varrho_2)$ of Eq. (2) is replaced by its Fourier representation

$$G(\varrho_1, \varrho_2) = -(4\pi^3)^{-1} \int \exp[-is \cdot (\varrho_1 - \varrho_2)](s^2 + 1)^{-1} ds \qquad (47)$$

and, proceeding as in the derivation of Eq. (35), we obtain

$$I = \int \int \omega^*(\varrho_1) V(\varrho_1) G(\varrho_1, \varrho_2) V(\varrho_2) \omega(\varrho_2) d\varrho_1 d\varrho_2$$

$$= -(4\pi^3)^{-1} \int |F(s)|^2 (s^2 + 1)^{-1} ds \qquad (48)$$

where $F(s)$ is given by Eq. (37).

This result is then processed in the same manner as above and the expression

$$I = -16\pi P^2 \int_0^1 \int_u^\infty \int_u^\eta \exp(-c\lambda - c\lambda_1 - P\eta/2) \sinh(P\xi/2) d\xi d\eta du \qquad (49)$$

is obtained, which is analogous to Eq. (40). This is, of course, the form obtained in the earlier work [1].

Further analytical progress is not possible here and a new triple numerical integration procedure is suggested in Section 3, which represents a distinct improvement on the method suggested in Ref. [1] for this integral.

4.3. Analytical Reduction of the Integral I'

The Fourier techniques are extended here to deal with the integral I' defined in Eq. (6) by

$$I' = \int \omega^*(\varrho_1) [V(\varrho_1) + 1/P'] G(\varrho_1, \varrho_2) [V(\varrho_2) + 1/P'] \omega(\varrho_2) d\varrho_1 d\varrho_2 \qquad (50)$$

which is transformed to

$$I' = -(4\pi^3)^{-1} \int |F'(s)|^2 (s^2 + 1)^{-1} ds . \qquad (51)$$

In this result $F'(s)$ denotes the Fourier transform

$$F'(s) = \int \omega(\varrho) [V(\varrho) + 1/P'] \exp(-is \cdot \varrho) d\varrho . \qquad (52)$$

This two-centre transform is processed in a similar manner to $F(s)$ and it is easily shown that the result may be expressed in the form

$$F'(s) = (\pi P'/s) \int_u^\infty \exp(-c\lambda)[(C_1 + C_3/s^2)\sin\beta s + (C_2/s)\cos\beta s] d\xi \qquad (53)$$

with

$$\beta = \xi P'/2 ,$$

$$C_1(\xi) = [\lambda(\xi^2 - u^2) - 4\xi^2]/\xi^2 ,$$

$$C_2(\xi) = -2[\lambda^2(3\xi^2 - 1) + 1 - u^2]/(\lambda P' \xi^3) ,$$

$$C_3(\xi) = -2C_2/(P'\xi) ,$$

and

$$\lambda = (\xi^2 + 1 - u^2)^{1/2} .$$

Analysis similar to that carried out earlier enables I' to be written as

$$I' = -\pi P'^2 \int_0^1 \int_u^\infty \int_u^\eta \exp[-c(\lambda+\lambda_1)] \sum_{i=1}^3 \sum_{j=1}^3 C_i(\eta)C_j(\xi)T_{ij}d\xi d\eta du \qquad (54)$$

with, again,

$$\lambda_1 = (\eta^2 + 1 - u^2)^{1/2} .$$

The coefficients T_{ij} which arise on evaluating principal valued contour integrals over the variable s in Eq. (51) are conveniently expressed in the form of a matrix as

$$\begin{bmatrix} S & -C+1 & -S+\beta \\ S & -C-\alpha & -S-\alpha\beta \\ -S+\beta & C-\frac{1}{2}(\alpha^2+\beta^2)-1 & S-\frac{1}{6}\beta^3-\frac{1}{2}\alpha^2\beta-\beta \end{bmatrix}$$

with

$$C = \exp(-\alpha)\cosh\beta ,$$
$$S = \exp(-\alpha)\sinh\beta ,$$

where

$$\alpha = P'\eta/2 \quad \text{and} \quad \beta = P'\xi/2 \quad (\alpha > \beta) .$$

5. Numerical Evaluation of the Analytically Reduced Integrals I and I'

By means of the Fourier Transform technique described above, the ϱ_1 and ϱ_2 coordinates are separated and the ϱ_{12}^{-1} singularity removed. Furthermore, the integrals have been reduced from five-dimensional to three-dimensional quadratures.

The evaluation of these integrals is accomplished by sub-dividing the region and integrating over each subregion by means of combinations of the standard Gaussian Quadrature formulae (Stroud and Secrest [4]):
(a) N-point Gauss-Legendre

$$\int_a^b f(x)dx = \frac{1}{2}(b-a)\sum_{i=1}^N A_P(i)f[\frac{1}{2}(b-a)+\frac{1}{2}(b-a)z_P(i)] , \qquad (56)$$

(b) N-point Gauss-Laguerre

$$\int_a^\infty g(x)dx = \gamma^{-1}\sum_{i=1}^N A_L(i)\exp[z_L(i)]g[z_L(i)/\gamma+a] \qquad (57)$$

where $g(x) \sim \exp(-\gamma x)$ for large values of x.

The coefficients $A_P(i)$, $z_P(i)$, $A_L(i)$, $z_L(i)$ are extensively tabulated for various values of N by Stroud and Secrest.

The integrals I and I' both take the general form

$$T(P, c) = \int_0^1 \int_u^\infty \int_u^\eta B(\xi, \eta, u, P, c)d\xi d\eta du \qquad (58)$$

where B denotes the integrand of Eq. (49) or (54).

The integration over the variable u is effected by means of Eq. (56) and the results may be expressed in the form

$$T(P, c) = \int_0^1 V(u, P, c) = \frac{1}{2}\sum_{i=1}^N A_P(i)V(u_i, P, c) \qquad (59)$$

where

$$u_i = \tfrac{1}{2}[1 + z_P(i)] \, .$$

It now remains to evaluate the set of N double integrals defined by

$$V(u_i, P, c) = \int_{u_i}^{\infty} \int_{u_i}^{\eta} B(\xi, \eta, u_i, P, c) d\xi d\eta \, . \tag{60}$$

For the evaluation of these integrals, a two dimensional polar grid is proposed, based on the coordinates (r, θ) defined by

$$\eta = u_i + r\cos\theta, \qquad \xi = u_i + r\sin\theta \tag{61}$$

with $0 \leqq r < \infty$ and $0 \leqq \theta \leqq \pi/4$.

It is considered that this polar grid is more convenient than a rectangular grid of the type used in [1], particularly when infinite regions are considered.

The infinite range of integration is now conveniently divided into finite annular segments of the form shown in Fig. 1, and infinite annular segments as shows in Fig. 2.
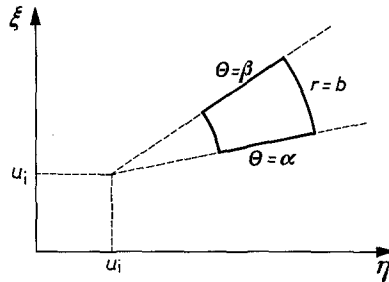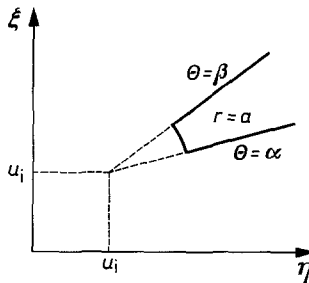

Fig. 1

Fig. 2

A pattern of annular segments covering the region of integration is chosen to reduce the number of points used in the numerical quadrature. The function B is relatively large near the apex of the region, and it is desirable to concentrate points in this vicinity.

To achieve this, the range of r is first subdivided, thus forming one infinite and several finite annular segments. The θ range was also split where necessary, and in each of the resulting finite annular regions R_l, the number of points for the r integrations is taken as M_{1l}, and for the θ integrations as M_{2l}.

In the present work, for a given finite region R_l, M_{1l}, and M_{2l} are taken to be M, so that the M-point Gauss Legendre rule (56) can be used for both the r and θ integrations. The contribution to V, given in Eq. (60), from such a region (see Fig. 1) may be written as

$$\tfrac{1}{4}(\beta-\alpha)(b-a)\sum_{j=1}^{M}\sum_{k=1}^{M}A_P(j)A_P(k)B(\xi_{ijk},\eta_{ijk},u_i,P,c)r_j \tag{62}$$

where

$$r_j=\tfrac{1}{2}(b+a)+\tfrac{1}{2}(b-a)z_P(j)\,,$$

$$\theta_k=\tfrac{1}{2}(\beta+\alpha)+\tfrac{1}{2}(\beta-\alpha)z_P(k)\,,$$

$$\eta_{ijk}=u_i+r_j\cos\theta_k\,,$$

$$\xi_{ijk}=u_i+r_j\sin\theta_k\,.$$

The less stable-Gauss-Laguerre rule (57) need now only be used for the r integration in the outlying infinite annular segments, whose contribution is relatively small. The Gauss-Legendre rule is still applicable to the θ integration. It is now necessary to ascertain the behaviour of B as $r\to\infty$ along a radius vector defined by $\theta=\text{constant}=\theta'$, in order to fix the value of γ which appears in Eq. (57). It may be readily shown that

$$B\sim\exp(-\gamma r)$$

where

$$\gamma=(c+\tfrac{1}{2}P)\cos\theta'+(c-\tfrac{1}{2}P)\sin\theta'\,.$$

Hence the contribution to V from a typical infinite region (see Fig. 2) may be written as

$$\tfrac{1}{2}(\beta-\alpha)\sum_{j=1}^{M}\sum_{k=1}^{M}A_P(k)A_L(j)\exp(z_L(j))B(\xi_{ijk},\eta_{ijk},u_i,P,c)r_{jk}/\gamma_k \tag{63}$$

where

$$\theta_k=\tfrac{1}{2}(\alpha+\beta)+\tfrac{1}{2}(\alpha-\beta)z_P(k)\,,$$

$$\gamma_k=(c+\tfrac{1}{2}P)\cos\theta_k+(c-\tfrac{1}{2}P)\sin\theta_k\,,$$

$$r_{jk}=z_L(j)/\gamma_k+a\,,$$

$$\xi_{ijk}=u_i+r_{jk}\cos\theta_k\,,$$

$$\eta_{ijk}=u_i+r_{jk}\sin\theta_k\,.$$

6. Results Arising from the Semi-Analytic Methods

The alternative treatment of the integrals I and I', as presented in Section 4 and 5, represents a considerable increase in speed and accuracy of computation over the direct methods described earlier. An accuracy of 9 significant figures is obtained using approximately 1300 integration points for I, and about 1800 for I'.

6.1. Processing of the Functionals κ and κ'

The relevant formulae required to convert the numerical values yielded by this method into meaningful physical quantities are presented in Section 2.

For a pre-determined value of P, the total energy W given by Eq. (5) was minimized over all values of the variational parameter c, in order to give a "best" upper bound to E_0, at that particular value of P. In practice the entirely equivalent operation of maximizing $\kappa(P, c)$ over c was performed, giving $\kappa_{opt}(P)$. This yielded the energy curve

$$W(R) = -\tfrac{1}{2}[\kappa_{opt}(P)]^2 + \kappa_{opt}(P)/P \tag{64}$$

the value of R corresponding to $W(R)$ being given by $R = P/\kappa_{opt}(P)$.

Processing of $\kappa'(P', c)$ was similar giving

$$W(R) = -\tfrac{1}{2}[\kappa'_{opt}(P')]^2 \tag{65}$$

at $R = P'/\kappa'_{opt}(P')$.

The equilibrium separation R_0 is obtained by minimizing $W(R)$ or $W'(R)$, giving W_0 and W'_0 as upper bounds to the total equilibrium ground state energy of the molecule.

The one dimensional optimization required to calculate the energy curves was performed using a simple quadratic fit method. The evaluation of the equilibrium separation R_0 and the energies W_0 and W'_0 required a two-dimensional

Table 1. Values of the energies given by the functional $\kappa = I/J$

P	R	c_{opt}	κ_{opt}	$E = -\tfrac{1}{2}[\kappa_{opt}]^2$	$W = E + 1/R$
1.0	0.54102896	0.47988	1.84832990	-1.70816172	0.14016819
1.5	0.86012085	0.70664	1.74394099	-1.52066508	-0.35803776
2.0	1.21625599	0.92871	1.64439067	-1.35201034	-0.52981501
2.5	1.60983262	1.14787	1.55295648	-1.20583691	-0.58465432
3.0	2.04058200	1.36525	1.47016881	-1.08069816	-0.59064189
3.5	2.50795050	1.58161	1.39556183	-0.97379642	-0.57506446
4.0	3.01127135	1.79746	1.32834260	-0.88224703	-0.55016138
4.5	3.54984899	2.01316	1.26765956	-0.80348038	-0.52177825
5.0	4.12300165	2.22892	1.21270871	-0.73533121	-0.49278946
6.0	5.37048506	2.66138	1.11721752	-0.62408749	-0.43788457
8.0	8.25477962	3.53206	0.96913550	-0.46961181	-0.34846987
[a] 2.83652	1.89568	1.29432	1.49630	-1.11946	-0.59194851

[a] Optimum of $W = -\tfrac{1}{2}[\kappa(P, c)]^2 + 1/R$ over all values of P and c.

optimization procedure. In this case a standard subroutine based on the method of Powell [15] was selected.

6.2. Numerical Results

The energy approximations and the corresponding values of the parameters P, R, c are presented in Tables 1 and 2. As demonstrated by the tables, the value of R at which we are tabulating is not known until the calculation of κ or κ' is complete. Comparison of results is, therefore, most conveniently made graphically, although accurate numerical values are presented for reference purposes, so that the accuracy of any alternative molecular integration scheme which is developed may be assessed.

Figure 3 illustrates the energy curves given by the method. W and W' are in fact indistinguishable to this scale, and are both represented by (1). The curve (2) is constructed from the exact values of the energies, as tabulated by Wind [16]. As anticipated, the approximation to the exact curve given by the functionals is very good in the united atom limit as R becomes small.

Figure 4 is drawn to a larger scale, and clearly demonstrates the separation of the curves representing W and W'. The calculation of W' does not assume the Born-Oppenheimer separation, and therefore, yields a better (lower) upper bound to the exact energy curve.

Table 2. Values of the energies given by the functional $\kappa' = I'/J'$

P'	R	c_{opt}	κ'_{opt}	$E' = W' - I/R$	$W' = -\frac{1}{2}\left[\kappa'_{opt}\right]^2$
1.25	1.21392422	0.90935	1.02971831	-1.35393455	-0.53015990
1.50	1.40831882	1.02703	1.06509974	-1.27728521	-0.56721872
1.75	1.61602104	1.14259	1.08290669	-1.20514728	-0.58634345
2.00	1.83607371	1.25794	1.08928089	-1.13790687	-0.59326643
2.50	2.31083693	1.48874	1.08186911	-1.01795322	-0.58520957
3.00	2.82915405	1.71992	1.06038764	-0.91567353	-0.56221098
3.50	3.38873325	1.95143	1.03283432	-0.82846888	-0.53337336
4.00	3.98781895	2.18328	1.00305456	-0.75382287	-0.50305923
4.50	4.62497359	2.41549	0.97297853	-0.68956106	-0.47334361
5.00	5.29898262	2.64810	0.94357735	-0.63388458	-0.44516911
6.00	6.75352787	3.11455	0.88842456	-0.54271986	-0.39464910
8.00	10.0669068	4.05257	0.79468303	-0.41509594	-0.31576056
[a] 2.07422	1.90368	1.29217	1.08958	1.11890	-0.59359666

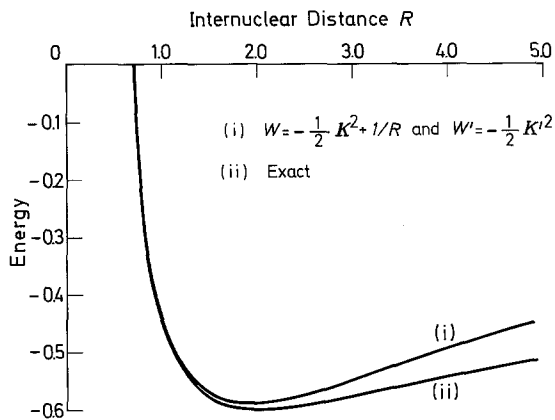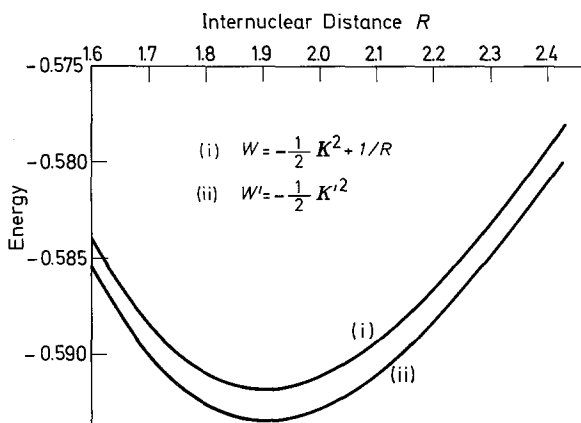[a] Optimum of $W' = -\frac{1}{2}[\kappa'(P', c)]^2$ over all values of P' and c.

Internuclear Distance R

Fig. 3. Total energy curves for H_2^+

Internuclear Distance R

Fig. 4. Total energy curves plotted about their minima

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