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A Six-Dimensional Quadrature Procedure*

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An account is given of the use of Gaussian quadrature product formulae in the evaluation of certain six-dimensional, two-centre integrals involving one-electron Green's functions. These integrals occur in a new molecular variational principle recently proposed by Hall, Hyslop and Rees [1] from which an approximate energy may be derived which can be shown to be at least as good as that obtained from the Rayleigh-Ritz principle. Reductions in computing time are realized by removing certain singularities using a subtraction technique and also by using an empirically determined Richardson-type extrapolation formula.

Key words: Gaussian quadrature – Green's functions – Singularities

1. Introduction

In a recent paper Hall, Hyslop and Rees [1] proposed a variation principle for molecular energies and applied it to the calculation of an upper bound for the ground state energy of the H_2^+ molecule. The six-dimensional Green's function integrals involved were evaluated by employing a semi-analytical technique in which a Fourier transform representation of the Green's function enabled the integrals to be reduced to a single quadrature in the simplest cases considered and to a triple quadrature in more complicated cases. However, generalization of this method is not straightforward and indeed as pointed out in [1], some of the additional integrals required in an alternative functional cannot be evaluated by the techniques employed on the original functional.

The functional contained in the original principle was derived using the usual Born-Oppenheimer approximation that the nuclear and electronic coordinates could be completely separated, whereas the alternative functional proposed did not assume this separation. Since a direct comparison of these functionals is of interest and also since an integration routine which is more readily generalized is necessary the possibility of direct numerical evaluation of the integrals is considered.

2. Formulation of the Integrals

On introducing a class $\psi(x)$ of scaled trial functions, where the scaled variables are denoted by x with $x = kr$ when the electronic energy is given by

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$E = -k^2/2$, the functional used in [1] may be written as

$$k = \iint \psi^*(\boldsymbol{x}_1)\, V(\boldsymbol{x}_1)\, G(\boldsymbol{x}_1, \boldsymbol{x}_2)\, V(\boldsymbol{x}_2)\, \psi(\boldsymbol{x}_2)\, d\boldsymbol{x}_1 d\boldsymbol{x}_2 / \int \psi^*(\boldsymbol{x})\, V(\boldsymbol{x})\, \psi(\boldsymbol{x})\, d\boldsymbol{x}\,. \tag{1}$$

$G(\boldsymbol{x}_1, \boldsymbol{x}_2) = -\exp(-x_{12})/(2\pi x_{12})$ is the scaled Green's function with $x_{12} = |\boldsymbol{x}_1 - \boldsymbol{x}_2|$ and $V(\boldsymbol{x})$ is the scaled electronic potential energy corresponding to

$$V(r) = -(1/r_a + 1/r_b) \tag{2}$$

where r_a and r_b are the distances between the electron and protons a and b, whose separation is R. The total energy is then given by

$$W = -k^2/2 + 1/R \tag{3}$$

The alternative functional may be written as

$$k' = \iint \psi^*(\boldsymbol{x}_1)\, V'(\boldsymbol{x}_1)\, G(\boldsymbol{x}_1, \boldsymbol{x}_2)\, V'(\boldsymbol{x}_2)\, \psi(\boldsymbol{x}_2)\, d\boldsymbol{x}_1 d\boldsymbol{x}_2 / \int \psi^*(\boldsymbol{x})\, V'(\boldsymbol{x})\, \psi(\boldsymbol{x})\, d\boldsymbol{x} \tag{4}$$

in which $V'(\boldsymbol{x})$ is the scaled total potential energy corresponding to

$$V'(r) = -(1/r_a + 1/r_b) + 1/R \tag{5}$$

and the total energy corresponding to this functional is

$$W' = -k'^2/2 \tag{6}$$

The values of k are then obtained as functions of the independent variable $\varrho = kR$ from equation (1) with corresponding internuclear separation ϱ/k. Correspondingly k' is given as a function of $\varrho' = k'R$ by equation (4) at the internuclear separation ϱ'/k' and hence energy curves may be obtained and compared.

Two centre elliptic coordinates (λ, μ, ϕ) are used where

$$\lambda = (r_a + r_b)/R\,, \qquad \mu = (r_a - r_b)/R \tag{7}$$

and ϕ is the azimuthal angle about the internuclear axis. By way of illustration the trial function used is the simple united atom approximation

$$\psi(\boldsymbol{x}) = \exp(-c\lambda) \tag{8}$$

where c is a variable parameter. This function may be regarded as being already scaled since it involves only the ratio of distances.

On writing the functionals k and k' as I/J and I'/J' respectively it is easily seen that the normalization integrals J and J' are given by

$$J(\varrho, c) = -\tfrac{1}{2}\pi\, (\varrho/c)^2 (1 + 2c) \exp(-2c) \tag{9a}$$

and

$$J'(\varrho', c) = -\tfrac{1}{24}\pi\, (\varrho^2/c^3)\, (20c^2 + 6c - 3) \exp(-2c) \tag{9b}$$

and that the main integrals I and I' may be written as

$$I = -\tfrac{1}{4}\varrho^4 \int x_{12}^{-1} \exp(-x_{12}) \exp[-c(\lambda_1 + \lambda_2)]\, \lambda_1 \lambda_2\, d\lambda_1\, d\lambda_2\, d\mu_1\, d\mu_2\, d\phi \tag{10a}$$

and

$$\begin{aligned} I' = -\tfrac{1}{4}\varrho'^4 \int x_{12}^{-1} \exp(-x_{12}) \exp[-c(\lambda_1 + \lambda_2)]\, [\lambda_1 - (\lambda_1^2 - \mu_1^2)/4] \\ \cdot [\lambda_2 - (\lambda_2^2 - \mu_2^2)/4]\, d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\phi \end{aligned} \tag{10b}$$

The scaled distance x_{12} is given by

$$\begin{aligned}4x_{12}^2/\varrho^2 = {} & (\lambda_1^2-1)(1-\mu_1^2)+(\lambda_2^2-1)(1-\mu_2^2)+(\lambda_1\mu_1-\lambda_2\mu_2)^2 \\ & -2\left[(\lambda_1^2-1)(1-\mu_1^2)(\lambda_2^2-1)(1-\mu_2^2)\right]^{1/2}\cos\phi\end{aligned} \tag{11}$$

where $\phi=\phi_1-\phi_2$ is the difference in azimuthal angles.

In the I' integral, therefore, ϱ is replaced by ϱ' and the $\lambda_1\lambda_2$ term in I is replaced by

$$[\lambda_1-(\lambda_1^2-\mu_1^2)/4]\,[\lambda_2-(\lambda_2^2-\mu_2^2)/4] \tag{12}$$

3. Numerical Integration Procedure

The formula used for the integrations is a five-dimensional Gaussian product formula of the type given by Stroud and Secrest [2]. For the μ integrations the basic result is

$$\int_{-1}^{+1} f(\mu)\,d\mu=\sum_{i=1}^{N} A_\varrho(i)\,f[x_\varrho(i)] \tag{13}$$

where $x_\varrho(i)$ is the i^{th} grid-point and $A_\varrho(i)$ the corresponding weight for N-point Gauss-Legendre quadrature. In the case of the λ integrations the result is

$$\int_{1}^{\infty} f(\lambda)\exp(-c\lambda)\,d\lambda=c^{-1}\exp(-c)\sum_{i=1}^{N} A_L(i)\,f[1+x_L(i)/c] \tag{14}$$

in which $x_L(i)$ and $A_L(i)$ are the grid-points and weights for N-point Gauss-Laguerre quadrature. The quantities $x_\varrho(i)$, $A_\varrho(i)$, $x_L(i)$ and $A_L(i)$ are extensively tabulated by Stroud and Secrest. The azimuthal integration is carried out by means of the Chebyshev-type result

$$\int_{0}^{2\pi} f(\cos\phi)\,d\phi=\frac{2\pi}{N}\sum_{i=1}^{N} f\left\{\cos\left[\frac{(2i-1)\pi}{2N}\right]\right\} \tag{15}$$

which is also referred to by Kopal [3] as the N-point Gauss-Mehler quadrature formula.

The main difficulty associated with the use of Gaussian quadrature formulae in the evaluation of molecular integrals of the type I or I' is the extremely slow convergence with increasing N because of the x_{12}^{-1} singularity. Extensive numerical tests were carried out using the technique of Boys and Rajagopal [3] for the removal of the singularity, but, even when various modifications were used, the convergence was still found to be exceedingly slow. It is proposed therefore to consider numerically the integrals S and S' rather than I and I' where

$$S=\tfrac{1}{4}\varrho^4\int x_{12}^{-1}\,[1-\exp(-x_{12})]\exp[-c(\lambda_1+\lambda_2)]\,\lambda_1\lambda_2\,d\lambda_1\,d\lambda_2\,d\mu_1\,d\mu_2\,d\phi \tag{16}$$

with a similar expression for S' with ϱ replaced by ϱ' and $\lambda_1\lambda_2$ replaced by (12). The singularity of $x_{12}=0$ is now removable and numerical tests confirm that a considerable improvement in convergence is realized when an N^5-point Gaussian formula is used.

It is necessary then to evaluate the complementary integral

$$A = \tfrac{1}{4}\varrho^4 \int x_{12}^{-1} \exp[-c(\lambda_1 + \lambda_2)]\, \lambda_1 \lambda_2 d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\phi \tag{17}$$

with a corresponding expression for A', using (12). These integrals may be treated analytically using the Neumann expression of x_{12}^{-1} in terms of (λ, μ, ϕ) as quoted, for example, by Harris and Michels [4]. The analysis is similar to that used by Sugiura [5] in his classical evaluation of the Heitler-London hydrogen molecule integrals and analytical expressions for A and A' are readily obtained in terms of the subsiduary integrals

$$L_n(c) = \int_1^\infty \lambda^n \exp(-c\lambda) \log(\lambda + 1)/(\lambda - 1)\, d\lambda, \tag{18}$$

n ranging from 0 to 4. The values of $L_n(c)$ are obtained by successive differentiations of the result

$$L_0(c) = c^{-1}[(\gamma + \log 2c)\exp(-c) + \exp(c) E_1(2c)] \tag{19}$$

where $\gamma = 0.577215\ldots$ is Euler's constant and $E_1(z)$ is the exponential integral

$$E_1(z) = \int_1^\infty t^{-1} \exp(-zt)\, dt \tag{20}$$

as defined by Abramowitz and Stegun [6].

The integrals I and I' are then given by subtraction to be $I = S - A$ and
$I' = S' - A'$ (21)
once S and S' have been evaluated numerically and A and A' evaluated analytically.

4. Improvement in Convergence

Denoting the value of S obtained from the N^5-point Gauss formula by S_N, numerical tests indicate that the convergence of the required $\{S_N\}$ is rapidly approaching geometric, so that the Aitken δ^2-extrapolation procedure may be used to speed up the process, Noble [7]. In fact, using a combination of the Richardson and Aitken extrapolation techniques as outlined in [7] it appears that a formula of the form

$$S \simeq S_{N+1} - a(S_N - S_{N+1}) \tag{22}$$

is valid for large N, certainly for N greater than 8.

In order to reduce the value of N an empirical formula of the form

$$S \simeq b[S_5 - a(S_4 - S_5)] \tag{23}$$

was investigated and extensive numerical tests indicated that an optimum value for the constant a could be found which was such that the correction factor b was extremely slowly varying with ϱ and the corresponding value of c in the region of its optimum value, as prescribed by section 5. Some representative values demonstrating the validity of this formula are shown in the following table for both S and S'.

Table 1. Variation of the correction factor b in the extrapolation formula

ϱ	c	S integrals $a=0.8$	S' integrals $a=0.9$
1.0	0.48	0.99843	0.99777
2.0	0.93	0.99876	0.99891
3.0	1.36	0.99882	0.99902
4.0	1.80	0.99880	0.99902
5.0	2.23	0.99869	0.99896
6.0	2.67	0.99854	0.99887

Further numerical tests on extrapolation formula (23) indicate that both S and S' may be obtained to an accuracy of better than 3 parts in 10^4 for values of ϱ (or ϱ') greater than 1.0 with a maximum value of $N=5$, that is, 3125 Gauss-points for the five-dimensional integrals. For $\varrho \leqq 1.0$, it is necessary to increase N, but in this case since the united atom limit is being rapidly approached, the resulting electronic energy values are very close to the exact results, of Dalgarno and Poots [8]. Indeed, in this region the behaviour of the total potential energy curve is dominated by the $1/R$ nuclear repulsion term.

5. Optimization Routine

The technique is similar to that used in [1]. Thus, for a given ϱ the functional k is optimized with respect to the parameter c according to

$$(\partial k/\partial c)_\varrho = 0 \tag{24}$$

using a simple one-dimensional research routine based on extrapolation formula (23) coupled with analytical evaluation of A and A'. Various checks on accuracy are carried out involving increases in the number of Gauss points. This yields optimum values k_{opt} and c_{opt} with corresponding R values given by ϱ/k_{opt} and W given by

$$W_{\text{opt}}(\varrho) = -k_{\text{opt}}^2/2 + 1/R \tag{25}$$

Similarly the functional k' is optimized according to

$$(\partial k'/\partial c)_{\varrho'} = 0 \tag{26}$$

and yields k'_{opt}, c_{opt} and correspondingly $R' = \varrho'/k'_{\text{opt}}$ and

$$W'_{\text{opt}}(R') = -k'^2_{\text{opt}}/2 \tag{27}$$

The equilibrium separation Ro is obtained by optimizing $W(\varrho, c)$ or $W'(\varrho', c)$ as in [1] using the direct search routine of Rosenbrock [9], making use once again of the empirical extrapolation formula (23) to reduce computing time.

6. Discussion

The main limitation on accuracy is the numerical evaluation of the six-dimensional integrals S and S'. The use of the empirically determined extrapolation formula enables a maximum error of 3×10^{-4} to be realized with a total of 3125 Gauss-points in the determination of these integrals. Cancellation effects in evaluating $(S-A)$ and $(S'-A')$ and also between $-k^2/2$ and $1/R$ may increase the error to a maximum of 3×10^{-3} in the total energies. The energy curves $E(R)$ and $E'(R')$ and $W(R)$ and $W'(R')$ are found to be indistinguishable to this accuracy and it is concluded that the Born-Oppenheimer separation in the functionals is valid within the limits of the accuracy of the present calculations. As an illustration, the optimum values of $W=-0.590$ at $R=1.912$ as compared with $W'=-0.593$ at $R'=1.909$ may be quoted and compared with the exact result of -0.603 at 2.00.

References

1. Hall, G. G., Hyslop, J., Rees, D.: Intern. J. Quantum Chem. **4**, 5 (1970)
2. Stroud, A. H., Secrest, D.: Gaussian quadrature formulas. Englewood Cliffs, New Jersey: Prentice-Hall, 1966
3. Boys, S. F., Rajagopal, P.: Adv. Quantum Chem. **2**, 1 (1965)
4. Harris, F. E., Michels, H. H.: Adv. Chem. Phy. **13**, 205 (1967)
5. Sugiura, Y.: Z. Physik **45**, 484 (1927)
6. Abramowitz, M., Stegun, I. A.: Handbook of mathematical functions. New York: Dover Publications (1965)
7. Noble, B.: Numerical methods. Edinburgh: Oliver and Boyd (1964)
8. Dalgarno, A., Poots, G.: Proc. Phys. Soc. (London) A **67**, 343 (1954)
9. Rosenbrock, H. H.: Computer Journal **3**, 175 (1960)

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