ON THE EVALUATION OF THREE-CENTRE HELLMANN-FEYNMAN FORCE INTEGRALS INVOLVING SLATER-TYPE ATOMIC ORBITALS

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(Communicated by S. Basu, F.N.A.)

(*Received 18 December 1970*)

A combination of analytical and semi-numerical methods is suggested for the accurate evaluation of three-centre Hellmann-Feynman force integrals occurring in some studies of molecular systems. The analytical method combines the expansion techniques of Coulson (1937) and Bader (1962) while the semi-numerical method employs a double-zeta expansion (Barnett 1963). Explicit analytical expressions are listed for all required non-vanishing integrals involving up to $2s$ and $2p$ Slater-type atomic orbitals.

Introduction

In the last ten years considerable interest has been aroused in the chemical applications of the Hellmann-Feynman theorem (Hellmann 1937; Feynman 1939). This theorem states that if ψ is an exact (unnormalized) eigenfunction of a Hamiltonian H and E is the corresponding energy eigenvalue, then if λ is any parameter on which H or ψ depends

$$\frac{\partial E}{\partial \lambda} \langle \psi | \psi \rangle = \left\langle \psi \left| \frac{\partial H}{\partial \lambda} \right| \psi \right\rangle \quad \ldots \quad (1)$$

In other words, for a normalized wave function, the first derivative of the energy with respect to a parameter is equal to the expectation value of the corresponding first derivative of the Hamiltonian. A proof of this theorem has been given by Berlin (1951) as well as by Hirschfelder and Coulson (1962). Depending on the physical nature of the parameter λ (e.g. it may be an internuclear distance, a semi-empirical parameter in an approximate theory, a nuclear charge, a nuclear coordinate and so on), one can obtain much valuable information about variations in the energy of a molecular system with the help of the above theorem.

If λ is taken as the x-coordinate, say, of the pth nucleus in a molecule, then, in the framework of the adiabatic approximation, the Hellmann-Feynman theorem leads (Feynman 1939) to the following expression for the x-component, F_{px}, of the force acting on the pth nucleus

$$F_{px} = Z_p \left[\sum_{q \neq p} \frac{Z_q}{R_{pq}^2} \frac{\partial R_{pq}}{\partial x_p} - \int \rho(\underset{\sim}{r}) \frac{x_p}{r_p^3} d\tau \right] \quad \ldots \quad (2)$$

where Z_p is the nuclear charge of p, R_{pq} an internuclear distance and $\rho(\underset{\sim}{r})$ is the total one-electron density at the point $\underset{\sim}{r}$. The integration in (2) is to be done in the one-electron space. Equation (2) has seen interesting applications in recent years, for example, in viewing molecular shapes and chemical binding in terms of the forces on nuclei (Berlin 1951; Bader and Jones 1961, 1963; Bader *et al.* 1967; Coulson and Deb 1971).

It may be remarked here that the Hellmann-Feynman theorem is valid for exact wave functions, genuine self-consistent-field wave functions and certain other wave functions (Goddard 1968) which are not of Hartree-Fock type. But in practical applications of the theorem, employing present-day wave functions, the validity of the theorem with such approximate functions is tacitly assumed even though equation (2) has been found to be rather sensitive to small inaccuracies in the wave function.

If one chooses a single-determinantal wave function, then

$$\rho(\underset{\sim}{r}) = \sum_i \eta_i \phi_i^2(\underset{\sim}{r}) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

where ϕ_i is the ith MO (real) with occupation number η_i. If ϕ_i is a conventional poly-centre LCAO-MO, then the calculation of the electron-nuclear component of the net force in equation (2) involves the evaluation of one-centre integrals $<x_\mu | f_\mu | x'_\mu>$, two-centre integrals $<x_\mu | f_\mu | x'_\nu>$ and $<x_\nu | f_\mu | x'_\nu>$, and the three-centre integrals $<x_\mu | f_\kappa | x'_\nu>$, where x_μ is an AO centred on μ and f_κ is a force operator; the prime in x'_ν indicates that this AO may have a functional form different from the AO x_μ. The analytical expressions for many one- and two-centre integrals have been listed by Coulson (1942) as well as by Bader and Jones (1961). In this paper we are concerned with only the three-centre integrals.

Summary of Different Methods

In general, there are four techniques for reducing the three-centre integrals into single-centre ones. None of these, however, is completely satisfactory. These are: (i) expanding the force operator f_κ and the AO x'_ν about the centre μ, the former in terms of Gegenbauer polynomials (Magnus and Oberhettinger 1954) and the latter in terms of Legendre polynomials and modified Bessel functions (Watson 1958); (ii) expanding both the AO's, x_μ and x'_ν, about the centre κ of the force operator (double-zeta technique, Barnett 1963); (iii) transforming two of the distances, r_μ, r_κ and r_ν, in terms of the third distance, bond length and bond angle (*see* Bader and Jones 1963); and (iv) the use of spheroidal coordinates based on the centres μ and ν, with f_κ being a directional derivative of the Neumann expansion of $1/r_\kappa$ (*see* Appendix for details). Of these, (i) and (iv) are purely analytical methods for evaluating these integrals and involve no other approximation besides truncating an infinite series. The second method is a semi-numerical one where the integrals of products of modified Bessel functions $I_{m+1/2}(z)$ and $K_{m+1/2}(z)$ are obtained numerically, and also involves terminating an infinite series. The third method is one of straightforward numerical integration up to a prescribed accuracy and is less efficient, computationally, than the analytical methods. We would like to suggest that for evaluating a three-centre force integral one may choose either (i) or (ii) depending on whether the integral, expressed as an infinite sum, converges or not. In general, (i) leads to convergence, although slowly, if the centres κ and ν are equidistant from the centre of expansion μ. Where this is not satisfied (i) results in non-convergence and one then may resort to (ii) which has a faster rate of convergence; for (i) convergence of the infinite sum also depends on the orbital exponent of x_μ, a higher exponent resulting in faster convergence. However, whenever convergent (i) provides a rapid method for computing such integrals, involving very little additional labour for several other values of the valence angle involved; this is not so with the numerical and the semi-numerical methods.

The Analytical and Semi-numerical Methods

Fig. 1 depicts the coordinate system employed in these calculations. The integrals may be evaluated by choosing two of the cartesian axes to lie in

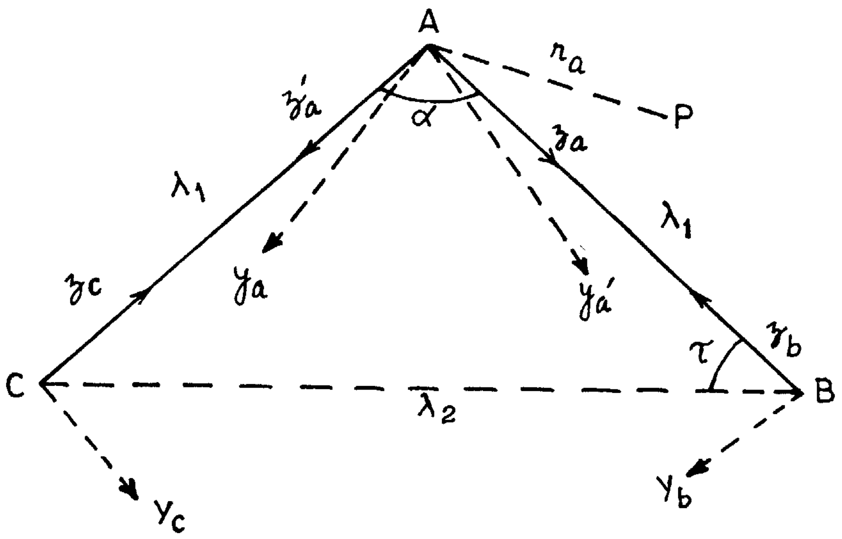

Fig. 1. Coordinate system for the evaluation of three-centre force integrals. The x-axes are perpendicular to the plane of the paper, and $\lambda_1 < \lambda_2$.

the plane containing the three centres involved. For this purpose the AO's and force vectors may be transformed, if necessary, by rotation to appropriate basis sets. The analytical method of evaluating $<x_\mu | f_\kappa | x'_\nu>$ consists of the following main steps:

(1) expanding the radial function of x'_ν about the centre μ, as an infinite sum, in terms of Legendre functions and modified Bessel functions of first and second kinds, $I_{m+1/2}(z)$ and $K_{m+1/2}(z)$, respectively (Coulson 1937; Barnett and Coulson 1951);

(2) expanding f_κ, as another infinite sum, about the centre μ in terms of products of Gegenbauer polynomials and certain radial functions (Bader 1962);

(3) reduction of the double infinite sum to a single one by invoking the addition theorem for Legendre functions (*see* Magnus and Oberhettinger 1954).

Final simplifications are achieved with the help of various recurrence and orthogonality relations of the functions involved. A somewhat similar procedure is followed with the semi-numerical method except that the step (2) is to be replaced by a similar step like (1), since the centre of expansion for both the AO's is now that of the force operator f_κ. We refrain here from providing an illustrative example for the above procedures since both Coulson (1937) and Bader (1962) have illustrated their individual techniques with simple representative examples. Therefore, we shall list in the next section only the explicit analytical expressions for the integrals obtained by combining these two techniques without indicating the tedious but simple algebra involved in deriving them.

The number of convergents to be taken for an infinite sum in an actual calculation depends on the prescribed accuracy. In order to obtain a value with four significant figures 20 convergents (sometimes less for method (ii)) usually suffice. For a test integral $\left\langle h_c \left| \frac{y_b}{r_b^3} \right| 1s_a \right\rangle$ (*see* Fig. 1), where h_c and $1s_a$ indicate Slater-type hydrogen and central atom $1s$ orbitals respectively, the two procedures gave computed values agreeing up to the fourth significant figure. The agreement is expected to improve when one chooses a finer quadrature grid for the numerical integration in method (ii).

A word is needed about the use of a Mulliken-type approximation

$$x_\mu x_\nu \simeq \tfrac{1}{2} S_{\mu\nu}(x_\mu^2 + x_\nu^2) \qquad \text{.. .. .. ..} \quad (4)$$

which apparently might be applied to evaluate these three-centre integrals. Bader and Jones (1963) have used (4) to calculate the integral $\left\langle h_b \left| \frac{z_a''}{r_a^3} \right| h_c \right\rangle$ (*see* Fig. 1, z_a'' bisects $\angle BAC$). In Table I we compare the values, obtained by using (4), of this and another integral with the corresponding values obtained in the present calculations. We notice that for both the integrals the difference between the approximate and the accurate value—

which is quite appreciable—decreases as the three centres approach a linear configuration. This is presumably because of the fact that the approximation (4), in effect, distributes the overlap density on to the separate atoms. In classical language, this amounts to expressing the force vector directed to the centre of overlap density $x_\mu x_\nu$ as the resultant of two vectors directed to the two centres μ and ν; obviously this becomes more and more valid as the centres κ, μ and ν tend to linearity. For further discussion regarding approximation (4) we refer to Newton *et al.* (1966), Dahl and Ballhausen (1968) and Doggett and McKendrick (1968).

TABLE I

The accuracy of Mulliken-type approximation (4)
H-atom exponent = 1·0; A-atom exponent = 2·275;
λ_1 = 1·8101 a.u., z_a'' bisects $\angle BAC$ (Fig. 1)

Integral	$\left\langle h_c \left\| \frac{z_b}{r_b^3} \right\| 2s_a \right\rangle$		$\left\langle h_b \left\| \frac{z_a''}{r_a^3} \right\| h_c \right\rangle$	
Valence angle α in deg.	Approximate	Accurate	Approximate	Accurate
90	0·05950	0·1048	0·06714	0·09855
100	0·05880	0·09944	0·05441	0·08513
105	0·05847	0·09706	0·04878	0·07874
110	0·05816	0·09487	0·04360	0·07255
120	0·05761	0·09103	0·03954	0·06073
180	0·05615	0·08105	0	0

MASTER FORMULAE

In this section we list explicit analytical expressions for all required non-vanishing integrals involving up to 2*s* and 2*p* STO's with exponents ζ_i. In cases where a scale factor has been employed to satisfy the virial theorem (Kaldor and Shavitt 1966) the orbital exponents and bond lengths are to be multiplied and divided, respectively, by this factor. Most of the quantities written below, viz. p_m, q_m, A_m, B_m, C_m, etc., together with their recurrence relations have been defined by Coulson* (1937) while $P_m(\cos\alpha)$, $P_m^1(\cos\alpha)$ are the Legendre and associated Legendre functions respectively. In order to avoid the accumulation of round-off errors the basic functions A_m and B_m are to be built up *in decreasing order* of *m* by using sum-type recurrence relations instead of difference-type. For this purpose, A_m for a highest required

* Coulson's (1937) relation, $\rho^2 A_n F_{n-1} + A_{n-1} F_n = 2e^{-2c\rho}$, should read

$$\rho^2 A_{n-1} F_n + A_n F_{n-1} = 2e^{-2c\rho}. \quad \quad (5)$$

m may be computed, from which the corresponding B_m may be evaluated by using an asymptotic formula (Coulson 1937). For $m = 24$ this procedure results in a B_0 accurate up to the tenth significant figure.*

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* For computing A_m for the highest m one should use, for the modified Bessel function $I_{m+1/2}(z)$, the formula

$$I_{m+1/2}(z) = \left(\frac{2z}{\pi}\right)^{1/2} 2^m \sum_{j=0}^{\infty} \frac{(m+j)\,!}{j\,!\,(2m+2j+1)\,!} z^{m+2j} \quad \ldots \quad (6)$$

The alternative closed formula,

$$I_{m+1/2}(z) = \frac{1}{(2\pi z)^{1/2}}\left[e^z \sum_{j=0}^{m} \frac{(-1)^j(m+j)\,!}{j\,!\,(m-j)\,!\,2z^j} + (-1)^{m+1} e^{-z} \sum_{j=0}^{m} \frac{(m+j)\,!}{j\,!\,(m-j)\,!\,2z^j}\right] \quad \ldots \quad (7)$$

which is mathematically equivalent to (6), was found to be unsuitable for computational purposes.

From Fig. 1 we notice that

$$\left.\begin{aligned} z_c &= \lambda_1 - z'_a \\ &= \lambda_1 - z_a \cos\alpha - y_a \sin\alpha \\ y_c &= y'_a \\ &= z_a \sin\alpha - y_a \cos\alpha \end{aligned}\right\} \quad \ldots \quad (8)$$

There are eight integrals (*see* later) which could not be simplified like the others according to method (i). We, therefore, give their expressions according to method (ii); limitations of space prevent us from giving similar expressions for other integrals. The various integrals $P_1(m)$, $Q_1(m)$, $R_1(m)$, etc., may be computed numerically since they can be expressed as sums of integrals involving products of functions $I_{m+1/2}(z)$ and $K_{m+1/2}(z)$.

Let $\Lambda = \zeta_c\lambda_1$, $\mu = \zeta_a/\zeta_c$, $\lambda_1 < \lambda_2$. One then replaces R and a in Coulson's (1937) quantities by Λ and μ respectively. To reduce the final integral expressions to relatively simple forms we first define the following quantities:

(A) $c_m = F_{m-1}C_{m+1} - F_mC_{m+2}$; $\quad d_m = F_{m-1}D_{m+1} - F_mD_{m+2}$;

$e_m = F_{m-1}E_{m+1} - F_mE_{m+2}$; $\quad g_m = A_mG_{m-1} - A_{m+1}G_m$;

$h_m = A_mH_{m-2} - A_{m+1}H_{m-1}$; $\quad i_m = F_{m-1}I_m - F_mI_{m+1}$;

$k_m = F_{m-1}K_{m+1} - F_mK_{m+2}$; $\quad l_m = F_{m-1}L_{m+1} - F_mL_{m+2}$;

$m_m = A_mM_{m-3} - A_{m+1}M_{m-2}$; $\quad n_m = A_mN_{m-4} - A_{m+1}N_{m-3}$;

$o_m = A_mO_{m-5} - A_{m+1}O_{m-4}$; $\quad s_m = A_mS_m - A_{m+1}S_{m+1}$;

$t_m = A_mT_m - A_{m+1}T_{m+1}$.

$$\text{(B)}\quad c'_m = F_m C_{m+1} - \frac{2(m+1)}{2m+1} F_{m+1} C_{m+2};$$

$$d'_m = F_m D_{m+1} - \frac{2(m+1)}{2m+1} F_{m+1} D_{m+2};$$

$$e'_m = F_m E_{m+1} - \frac{2(m+1)}{2m+1} F_{m+1} E_{m+2};$$

$$e''_m = F_m E_{m+1} - \frac{2m}{2m+1} F_{m-1} E_m;$$

$$g'_m = A_m G_m - \frac{2m}{2m+1} A_{m-1} G_{m-1};$$

$$g''_m = A_m G_m - \frac{2(m+1)}{2m+1} A_{m+1} G_{m-1};$$

$$h'_m = A_m H_{m-1} - \frac{2m}{2m+1} A_{m-1} H_{m-2};$$

$$h''_m = A_m H_{m-1} - \frac{2(m+1)}{2m+1} A_{m+1} H_m;$$

$$i'_m = F_m I_m - \frac{2m}{2m+1} F_{m-1} I_{m-1}; \qquad i''_m = F_m I_m - \frac{2(m+1)}{2m+1} F_{m+1} I_{m+1};$$

$$k'_m = F_m K_{m+1} - \frac{2m}{2m+1} F_{m-1} K_m; \qquad l'_m = F_m L_{m+1} - \frac{2m}{2m+1} F_{m-1} L_m;$$

$$m'_m = A_m M_{m-2} - \frac{2(m+1)}{2m+1} A_{m+1} M_{m-1}; \qquad m''_m = A_m M_{m-2} - \frac{2m}{2m+1} A_{m-1} M_{m-3};$$

$$n'_m = A_m N_{m-3} - \frac{2(m+1)}{2m+1} A_{m+1} N_{m-2}; \qquad o'_m = A_m O_{m-4} - \frac{2(m+1)}{2m+1} A_{m+1} O_{m-3};$$

$$s'_m = A_m S_{m+1} - \frac{2m}{2m+1} A_{m-1} S_m; \qquad t'_m = A_m T_{m+1} - \frac{2m}{2m+1} A_{m-1} T_m,$$

where

$$I_m = (2\pi)^{1/2} P_{m+9/2,\, m+1/2}, \qquad I_m = D_{m+3} + (2m+3) D_{m+2};$$

$$K_m = (2\pi)^{1/2} P_{m+9/2,\, m-1/2}, \qquad K_m = E_{m+2} + (2m+1) E_{m+1};$$

$$L_m = (2\pi)^{1/2} P_{m+11/2,\, m-1/2}, \qquad L_m = I_{m+1} + (2m+1) I_m;$$

$$O_m = \left(\frac{2}{\pi}\right)^{1/2} Q_{m+1/2,\, m+9/2}, \qquad O_m = M_m + (2m+7) M_{m+1};$$

$$S_m = \left(\frac{2}{\pi}\right)^{1/2} Q_{m+3/2,\, m-1/2}, \qquad S_{m+1} = \frac{1}{2m+1}(G_{m+1} - S_m),$$

$$S_1 = \left(\frac{1}{2\Lambda^2} - \frac{\mu+1}{2\Lambda}\right) e^{-(\mu+1)\Lambda} + \tfrac{1}{2}(\mu+1)^2 G_0;$$

$$T_m = \left(\frac{2}{\pi}\right)^{1/2} Q_{m+1/2,\, m-1/2}, \qquad T_{m+1} = \frac{1}{2m+1}(H_m - T_m),$$

$$T_1 = \frac{e^{-(\mu+1)\Lambda}}{\Lambda} - (\mu+1) G_0 \ \text{[Coulson (1937)]}$$

The various non-vanishing three-centre force integrals may now be expressed as the following infinite sums:

Let

$$\frac{y_b}{r_b^3} \equiv f_b, \quad \frac{z_b}{r_b^3} \equiv g_b, \quad \frac{x_b}{r_b^3} \equiv \pi_b.$$

(1) $< 1s_c | f_b | 1s_a >$

$$= 2\zeta_c^2 \mu^{3/2} \frac{e^{\mu\Lambda}}{\Lambda^2} \sum_{m=0}^{\infty} P_m^1(\cos\alpha)[c_m + \Lambda g_m]$$

(2) $< 1s_c | g_b | 1s_a >$

$$= 4\left(\frac{\zeta_c^3 \zeta_a^3}{\lambda_1 \lambda_2}\right)^{1/2} \sum_{m=0}^{\infty} [(m+1)\, P_{m+1}(\cos\tau)\{P_1(m) + Q_1(m) + R_1(m)\}$$
$$+ m\, P_{m-1}(\cos\tau)\{P_2(m) + Q_2(m) + R_2(m)\}]$$

where

$$P_1(m) = \int_0^{\lambda_1} \frac{1}{r}\, p_m^{<}(\zeta_a, r;\ \lambda_1) p_{m+1}^{<}(\zeta_c, r;\ \lambda_2)\, dr,$$

$$Q_1(m) = \int_{\lambda_1}^{\lambda_2} \frac{1}{r}\, p_m^{>}(\zeta_a, r;\ \lambda_1) p_{m+1}^{<}(\zeta_c, r;\ \lambda_2)\, dr,$$

$$R_1(m) = \int_{\lambda_2}^{\infty} \frac{1}{r}\, p_m^{>}(\zeta_a, r;\ \lambda_1) p_{m+1}^{>}(\zeta_c, r;\ \lambda_2)\, dr.$$

$P_2(m)$, $Q_2(m)$, $R_2(m)$ are obtained by replacing p_{m+1} in $P_1(m)$, $Q_1(m)$, $R_1(m)$, respectively, by p_{m-1}; $<$ and $>$ indicate whether r is less or greater, respectively, than the bond length argument (λ_1 or λ_2) of p_k.

(3) $< 1s_c | f_b | 2s_a >$

$$= \tfrac{2}{3}\, \zeta_c^2 (3\mu^5)^{1/2} \frac{e^{\mu\Lambda}}{\Lambda^2} \sum_{m=0}^{\infty} P_m^1(\cos\alpha)[d_m + \Lambda h_m]$$

(4) $< 1s_c | g_b | 2s_a >$

$$= 4\left(\frac{\zeta_c^3 \zeta_a^5}{3\lambda_1 \lambda_2}\right)^{1/2} \sum_{m=0}^{\infty} [(m+1) P_{m+1}(\cos\tau)\{P_3(m) + Q_3(m) + R_3(m)\}$$
$$+ m\, P_{m-1}(\cos\tau)\{P_4(m) + Q_4(m) + R_4(m)\}]$$

where $P_3(m)$, $R_4(m)$ are obtained by replacing p_m in $P_1(m)$, $R_2(m)$, respectively, with q_m.

(5) $< 1s_c | f_b | 2pz_a >$

$$= 2\zeta_c^2 \mu^{5/2} \frac{e^{\mu\Lambda}}{\Lambda^3} \sum_{m=0}^{\infty} P_m^1(\cos\alpha)\left[\frac{m+2}{2m+3}(e_m + \Lambda^3 g_m) + \frac{m-1}{2m-1}(\Lambda m_m + \Lambda^2 c_m)\right]$$

(6) $< 1s_c | g_b | 2pz_a >$

$$= 4\left(\frac{\zeta_c^3 \zeta_a^5}{\lambda_1 \lambda_2}\right)^{1/2} (\lambda_1 I_1 - I_2)$$

where I_1 is given by the infinite sum of integral (2) above and

$$I_2 = \sum_{m=0}^{\infty} \left[\frac{(m+1)(m+2)}{2m+3} P_{m+2}(\cos\tau)\{P_5(m) + Q_5(m) + R_5(m)\}\right.$$
$$+ \frac{4m^3 + 6m^2 - 1}{(2m-1)(2m+3)} P_m(\cos\tau)\{P_6(m) + Q_6(m) + R_6(m)\}$$
$$\left. + \frac{m(m-1)}{2m-1} P_{m-2}(\cos\tau)\{P_7(m) + Q_7(m) + R_7(m)\}\right]$$

where

$$P_5(m) = \int_0^{\lambda_1} p_m^{<}(\zeta_a, r;\ \lambda_1) p_{m+2}^{<}(\zeta_c, r;\ \lambda_2)\, dr,$$

$$Q_5(m) = \int_{\lambda_1}^{\lambda_2} p_m^{>}(\zeta_a, r;\ \lambda_1) p_{m+2}^{<}(\zeta_c, r;\ \lambda_2)\, dr,$$

$$R_5(m) = \int_{\lambda_2}^{\infty} p_m^{>}(\zeta_a, r;\ \lambda_1) p_{m+2}^{>}(\zeta_c, r;\ \lambda_2)\, dr,$$

and $P_6(m)$, $P_7(m)$, $Q_6(m)$, $Q_7(m)$, etc., are obtained by replacing p_{m+2} in the corresponding above quantities by p_m and p_{m-2}.

(7) $<1s_c|f_b|2py_a> = <1s_c|\pi_b|2px_a>$

$$= \zeta_c{}^2\mu^{5/2}\frac{e^{\mu\wedge}}{\wedge^3}\sum_{m=0}^{\infty} P_m(\cos\alpha)\left[\frac{(m+1)(m+2)}{2m+3}(e_m+\wedge^3 g_m) - \frac{m(m-1)}{2m-1}(\wedge m_m + \wedge^2 c_m)\right]$$

(8) $<1s_c|g_b|2py_a>$

$$= 2\zeta_c{}^2\mu^{5/2}\frac{e^{\mu\wedge}}{\wedge^3}\sum_{m=0}^{\infty} P_m{}^1(\cos\alpha)\left[\frac{m}{2m-1}(\wedge m_m + \wedge^2 c_m) - \frac{m+2}{2m+3}(e_m + \wedge^3 g_m)\right]$$

(9) $<2s_c|f_b|1s_a>$

$$= \tfrac{2}{3}\zeta_c{}^2(3\mu^3)^{1/2}\frac{e^{\mu\wedge}}{\wedge^2}\sum_{m=0}^{\infty} P_m{}^1(\cos\alpha)\left[e''_m + \wedge m'_m + \wedge^2 c'_m + \wedge^3 g_m\right]$$

(10) $<2s_c|g_b|1s_a>$

$$= 4\left(\frac{\zeta_c{}^5\zeta_a{}^3}{3\lambda_1\lambda_2}\right)^{1/2}\sum_{m=0}^{\infty}[(m+1)P_{m+1}(\cos\tau)\{P_8(m)+Q_8(m)+R_8(m)\}$$
$$+m\,P_{m-1}(\cos\tau)\{P_9(m)+Q_9(m)+R_9(m)\}]$$

where $P_8(m)$, $Q_9(m)$, etc., are obtained by replacing p_{m+1} in $P_1(m)$, p_{m-1} in $Q_2(m)$, etc., by q_{m+1} and q_{m-1} respectively.

(11) $<2s_c|f_b|2s_a>$

$$= \tfrac{2}{3}\zeta_c{}^2\mu^{5/2}\frac{e^{\mu\wedge}}{\wedge^2}\sum_{m=0}^{\infty} P_m{}^1(\cos\alpha)[i'_m + \wedge n'_m + \wedge^2 d'_m + \wedge^3 h'_m]$$

(12) $<2s_c|g_b|2s_a>$

$$= \tfrac{4}{3}\left(\frac{\zeta_c{}^5\zeta_a{}^5}{\lambda_1\lambda_2}\right)^{1/2}\sum_{m=0}^{\infty}[(m+1)P_{m+1}(\cos\tau)\{P_{10}(m)+Q_{10}(m)+R_{10}(m)\}$$
$$+m\,P_{m-1}(\cos\tau)\{P_{11}(m)+Q_{11}(m)+R_{11}(m)\}]$$

where $P_{10}(m)$, $Q_{11}(m)$, etc., are obtained by replacing p_{m+1} in $P_3(m)$, p_{m-1} in $Q_4(m)$, etc., by q_{m+1} and q_{m-1} respectively.

(13) $<2s_c|f_b|2pz_a>$

$$= \tfrac{2}{3}\zeta_c{}^2(3\mu^5)^{1/2}\frac{e^{\mu\wedge}}{\wedge^3}\sum_{m=0}^{\infty} P_m{}^1(\cos\alpha)\left[\frac{m+2}{2m+3}(k'_m + \wedge^2 e'_m + \wedge^3 m'_m + \wedge^5 g'_m)\right.$$
$$\left. + \frac{m-1}{2m-1}(\wedge o'_m + \wedge^2 e''_m + \wedge^3 m''_m + \wedge^4 c'_m)\right]$$

(14) $<2s_c|g_b|2pz_a> = 4\left(\frac{\zeta_c^5\zeta_a^5}{3\lambda_1\lambda_2}\right)^{1/2}(\lambda_1 I_3 - I_4)$

where I_3 is given by the infinite sum in integral (10) and

$$I_4 = \sum_{m=0}^{\infty}\left[\frac{(m+1)(m+2)}{2m+3}P_{m+2}(\cos\tau)\{P_{12}(m)+Q_{12}(m)+R_{12}(m)\}\right.$$
$$+\frac{4m^3+6m^2-1}{(2m-1)(2m+3)}P_m(\cos\tau)\{P_{13}(m)+Q_{13}(m)+R_{13}(m)\}$$
$$\left.+\frac{m(m-1)}{2m-1}P_{m-2}(\cos\tau)\{P_{14}(m)+Q_{14}(m)+R_{14}(m)\}\right]$$

where

$$P_{12}(m) = \int_0^{\lambda_1} p_m^<(\zeta_a, r;\ \lambda_1)q_{m+2}^<(\zeta_c, r;\ \lambda_2)\, dr,$$

$$Q_{12}(m) = \int_{\lambda_1}^{\lambda_2} p_m^>(\zeta_a, r;\ \lambda_1)q_{m+2}^<(\zeta_c, r;\ \lambda_2)\, dr,$$

$$R_{12}(m) = \int_{\lambda_2}^{\infty} p_m^>(\zeta_a, r;\ \lambda_1)q_{m+2}^>(\zeta_c, r;\ \lambda_2)\, dr$$

and $P_{13}(m)$, $Q_{14}(m)$, etc., are obtained by replacing q_{m+2} in the above corresponding quantities by q_m and q_{m-2} respectively.

(15) $<2s_c|f_b|2py_a> = <2s_c|\pi_b|2px_a>$

$$= \tfrac{1}{3}\zeta_c^2(3\mu^5)^{1/2}\frac{e^{\mu\Lambda}}{\Lambda^3}\sum_{m=0}^{\infty}P_m(\cos\alpha)\left[\frac{(m+1)(m+2)}{2m+3}(k'_m+\Lambda^2e'_m+\Lambda^3m'_m+\Lambda^5g'_m)\right.$$
$$\left.-\frac{m(m-1)}{2m-1}(\Lambda o'_m+\Lambda^2e''_m+\Lambda^3m''_m+\Lambda^4c'_m)\right]$$

(16) $<2s_c|g_b|2py_a>$

$$= \tfrac{2}{3}\zeta_c^2(3\mu^5)^{1/2}\frac{e^{\mu\Lambda}}{\Lambda^3}\sum_{m=0}^{\infty}P_m^1(\cos\alpha)\left[\frac{m}{2m-1}(\Lambda o'_m+\Lambda^2e''_m+\Lambda^3m''_m+\Lambda^4c'_m)\right.$$
$$\left.-\frac{m+2}{2m+3}(k'_m+\Lambda^2e'_m+\Lambda^3m'_m+\Lambda^5g'_m)\right]$$

(17) $<2pz_c|f_b|1s_a>$

$$= \Lambda<1s_c^{(2)}|f_b|1s_a> - \cos\alpha<1s_c^{(2)}|f_b|2pz_a^{(1)}> - \sin\alpha<1s_c^{(2)}|f_b|2py_a^{(1)}>$$

The forms of all these three integrals have been given above; we note that for the last two integrals $\mu^{5/2}$ is now replaced by $\mu^{3/2}$. The superscript (1) indicates that the exponent ζ_a is that of $1s_a$ while (2) indicates ζ_c to be that of a $2p$ AO.

(18) $<2pz_c|g_b|1s_a>$

$$= \Lambda<1s_c^{(2)}|g_b|1s_a> - \cos\alpha<1s_c^{(2)}|g_b|2pz_a^{(1)}> - \sin\alpha<1s_c^{(2)}|g_b|2py_a^{(1)}>$$

(19) $<2py_c|f_b|1s_a> = \sin\alpha<1s_c^{(2)}|f_b|2pz_a^{(1)}> - \cos\alpha<1s_c^{(2)}|f_b|2py_a^{(1)}>$

(20) $<2py_c|g_b|1s_a> = \sin\alpha<1s_c^{(2)}|g_b|2pz_a^{(1)}> - \cos\alpha<1s_c^{(2)}|g_b|2py_a^{(1)}>$

(21) $<2pz_c|f_b|2s_a>$

$$= \Lambda<1s_c^{(2)}|f_b|2s_a> - \cos\alpha<1s_c^{(2)}|f_b|r_a\,2pz_a^{(2)}> - \sin\alpha<1s_c^{(2)}|f_b|r_a\,2py_a^{(2)}>$$

where $2pz_a^{(2)}$, $2py_a^{(2)}$ indicate the normalizing constant for the $2s_a$ AO. The form of the first integral has been given previously and

$$<1s_c^{(2)}|f_b|r_a\,2pz_a^{(2)}>$$

$$=\frac{2}{\sqrt{3}}\zeta_c^2\mu^{5/2}\frac{e^{\mu\Lambda}}{\Lambda^3}\sum_{m=0}^{\infty}P_m^1(\cos\alpha)\left[\frac{m+2}{2m+3}(i_m+\Lambda^3h_m)+\frac{m-1}{2m-1}(\Lambda n_m+\Lambda^2d_m)\right],$$

$$<1s_c^{(2)}|f_b|r_a\,2py_a^{(2)}>$$

$$=\frac{1}{\sqrt{3}}\zeta_c^2\mu^{5/2}\frac{e^{\mu\Lambda}}{\Lambda^3}\sum_{m=0}^{\infty}P_m(\cos\alpha)\left[\frac{(m+1)(m+2)}{2m+3}(i_m+\Lambda^3h_m)-\frac{m(m-1)}{2m-1}(\Lambda n_m+\Lambda^2d_m)\right]$$

(22) $<2pz_c|g_b|2s_a>$

$$=\Lambda<1s_c^{(2)}|g_b|2s_a>-\cos\alpha<1s_c^{(2)}|g_b|r_a\,2pz_a^{(2)}>-\sin\alpha<1s_c^{(2)}|g_b|r_a\,2py_a^{(2)}>$$

where the first integral has been expressed before and

$$<1s_c^{(2)}|g_b|r_a\,2pz_a^{(2)}>=4\left(\frac{\zeta_c^5\zeta_a^5}{3\lambda_1\lambda_2}\right)^{1/2}(\lambda_1I_5-I_6)$$

where I_5 is given by the infinite sum in integral (4) and

$$I_6=\sum_{m=0}^{\infty}\left[\frac{(m+1)(m+2)}{2m+3}P_{m+2}(\cos\tau)\{P_{15}(m)+Q_{15}(m)+R_{15}(m)\}\right.$$
$$+\frac{4m^3+6m^2-1}{(2m-1)(2m+3)}P_m(\cos\tau)\{P_{16}(m)+Q_{16}(m)+R_{16}(m)\}$$
$$\left.+\frac{m(m-1)}{2m-1}P_{m-2}(\cos\tau)\{P_{17}(m)+Q_{17}(m)+R_{17}(m)\}\right]$$

where

$$P_{15}(m)=\int_0^{\lambda_1}q_m^<(\zeta_a,r;\lambda_1)p_{m+2}^<(\zeta_c,r;\lambda_2)\,dr,$$

$$Q_{15}(m)=\int_{\lambda_1}^{\lambda_2}q_m^>(\zeta_a,r;\lambda_1)p_{m+2}^<(\zeta_c,r;\lambda_2)\,dr,$$

$$R_{15}(m)=\int_{\lambda_2}^{\infty}q_m^>(\zeta_a,r;\lambda_1)p_{m+2}^>(\zeta_c,r;\lambda_2)\,dr,$$

and $P_{16}(m)$, $R_{17}(m)$, etc., are obtained by replacing p_{m+2} in the corresponding quantities by p_m, p_{m-2}, etc., respectively.

$$<1s_c^{(2)}|g_b|r_a\,2py_a^{(2)}>$$

$$=\tfrac{8}{3}\zeta_c^2(3\mu^5)^{1/2}\frac{e^{\mu\Lambda}}{\Lambda^3}\sum_{m=0}^{\infty}P_m^1(\cos\alpha)\left[\frac{m}{2m-1}(\Lambda n_m+\Lambda^2d_m)-\frac{m+2}{2m+3}(i_m+\Lambda^3h_m)\right]$$

(23) $<2py_c|f_b|2s_a>$

$$=\sin\alpha<1s_c^{(2)}|f_b|r_a\,2pz_a^{(2)}>-\cos\alpha<1s_c^{(2)}|f_b|r_a\,2py_a^{(2)}>$$

(24) $<2py_c|g_b|2s_a>$

$$=\sin\alpha<1s_c^{(2)}|g_b|r_a\,2pz_a^{(2)}>-\cos\alpha<1s_c^{(2)}|g_b|r_a\,2py_a^{(2)}>$$

(25) $<2pz_c|f_b|2pz_a>$

$$=\Lambda<1s_c^{(2)}|f_b|2pz_a>-\cos\alpha<1s_c^{(2)}|f_b|z_a\,2pz_a>-\sin\alpha<1s_c^{(2)}|f_b|y_a\,2pz_a>$$

The first integral on the R.H.S. has been expressed previously.

We have

$$<1s_c^{(2)}|\, f_b|z_a\, 2pz_a>$$

$$= 2\zeta_c^2\mu^{5/2}\frac{e^{\mu\Lambda}}{\Lambda^5}\sum_{m=0}^{\infty} P_m^1(\cos\alpha)\Big[\frac{(m-1)^2}{(2m-1)(2m+3)}(\Lambda^3 n_m+\Lambda^4 d_m)$$

$$+\frac{m-1}{2m-1}(\Lambda^3 e_m+\Lambda^4 m_m)+\frac{(m+1)}{(2m-1)(2m+3)}(\Lambda^2 i_m+\Lambda^5 h_m)$$

$$+\frac{m+2}{2m+3}(\Lambda k_m+\Lambda^6 g_m)-\frac{(m+2)(m+3)}{(2m+3)(2m+5)}(l_m+\Lambda^7 k_m)\Big].$$

$$<1s_c^{(2)}|\, f_b|y_a\, 2pz_a>$$

$$= 2\zeta_c^2\mu^{5/2}\frac{e^{\mu\Lambda}}{\Lambda^4}\sum_{m=0}^{\infty} P_m(\cos\alpha)\Big[\frac{(m+1)(m+2)(m+3)}{(2m+3)(2m+5)}(k_m+\Lambda^5 g_m)$$

$$+\frac{m(m-1)}{(2m-1)(2m+3)}(\Lambda^2 e_m+\Lambda^3 m_m)-\frac{m(m-1)(m-2)}{(2m-1)(2m-3)}(\Lambda o_m+\Lambda^4 c_m)\Big]$$

(26) $<2pz_c|g_b|2pz_a>$

$$= \Lambda<1s_c^{(2)}|g_b|2pz_a>-\cos\alpha<1s_c^{(2)}|g_b|z_a\, 2pz_a>-\sin\alpha<1s_c^{(2)}|g_b|y_a\, 2pz_a>.$$

The first of these three integrals has already been expressed and

$$<1s_c^{(2)}|g_b|z_a\, 2pz_a> = 4\Big(\frac{\zeta_c^5\zeta_a^5}{\lambda_1\lambda_2}\Big)^{1/2}[\lambda_1^2 I_1-2\lambda_1 I_2+I_7]$$

where I_1 and I_2 have been given in (6) and

$$I_7 = \sum_{m=0}^{\infty}\Big[\frac{(m+1)(m+2)(m+3)}{(2m+3)(2m+5)}P_{m+3}(\cos\tau)\{P_{18}(m)+Q_{18}(m)+R_{18}(m)\}$$

$$+\frac{12m^5+56m^4+81m^3+40m^2-9}{(2m-1)(2m+1)(2m+3)(2m+5)}P_{m+1}(\cos\tau)\{P_{19}(m)+Q_{19}(m)+R_{19}(m)\}$$

$$+\frac{3m(m^2-2)}{(2m-3)(2m+3)}P_{m-1}(\cos\tau)\{P_{20}(m)+Q_{20}(m)+R_{20}(m)\}$$

$$+\frac{m(m-1)(m-2)}{(2m-1)(2m-3)}P_{m-3}(\cos\tau)\{P_{21}(m)+Q_{21}(m)+R_{21}(m)\}\Big]$$

where

$$P_{18}(m) = \int_0^{\lambda_1} r\, p_m^<(\zeta_a, r;\ \lambda_1)p_{m+3}^<(\zeta_c, r;\ \lambda_2)\, dr,$$

$$Q_{18}(m) = \int_{\lambda_1}^{\lambda_1} r\, p_m^>(\zeta_a, r;\ \lambda_1)p_{m+3}^<(\zeta_c, r;\ \lambda_2)\, dr,$$

$$R_{18}(m) = \int_{\lambda_2}^{\infty} r\, p_m^>(\zeta_a, r;\ \lambda_1)p_{m+3}^>(\zeta_c, r;\ \lambda_2)\, dr,$$

and $P_{19}(m)$, $Q_{20}(m)$, $R_{21}(m)$, etc., are obtained by replacing p_{m+3} in the corresponding quantities by p_{m+1}, p_{m-1}, p_{m-3}, etc., respectively.

$$<1s_c^{(2)}|g_b|y_a\, 2pz_a>$$

$$= -<1s_c^{(2)}|\, f_b|z_a\, 2pz_a>+2\zeta_c^2\mu^{5/2}\frac{e^{\mu\Lambda}}{\Lambda^5}\sum_{m=0}^{\infty} P_m^1(\cos\alpha)\Big[\frac{m-1}{2m-1}(\Lambda^2 o_m+\Lambda^5 c_m)$$

$$+\frac{m+2}{2m+3}(\Lambda^3 e_m+\Lambda^4 m_m)\Big]$$

(27) $<2py_c|f_b|2pz_a>$

$= \sin\alpha <1s_c^{(2)}|f_b|z_a\,2pz_a> - \cos\alpha <1s_c^{(2)}|f_b|y_a\,2pz_a>$

(28) $<2py_c|g_b|2pz_a>$

$= \sin\alpha <1s_c^{(2)}|g_b|z_a\,2pz_a> - \cos\alpha <1s_c^{(2)}|g_b|y_a\,2pz_a>$

(29) $<2pz_c|f_b|2py_a>$

$= \wedge <1s_c^{(2)}|f_b|2py_a> - \cos\alpha <1s_c^{(2)}|f_b|y_a\,2pz> - \sin\alpha <1s_c^{(2)}|f_b|y_a\,2py_a>.$

The first two integrals on the R.H.S. have been given previously. The third is given by

$$<1s_c^{(2)}|f_b|y_a\,2py_a>$$

$$= \tfrac{3}{2}\zeta_c^2\mu^{5/2}\frac{e^{\mu\wedge}}{\wedge^4}\sum_{m=0}^{\infty} P_m^1(\cos\alpha)\left[\frac{2m(m+1)}{(2m-1)(2m+3)}(\wedge^2 e_m + \wedge^3 m_m) - \frac{(m+2)(m+3)}{(2m+3)(2m+5)}(k_m + \wedge^5 g_m) - \frac{(m-1)(m-2)}{(2m-1)(2m-3)}(\wedge o_m + \wedge^4 c_m)\right]$$

(30) $<2pz_c|g_b|2py_a>$

$= \wedge <1s_c^{(2)}|g_b|2py_a> - \cos\alpha <1s_c^{(2)}|g_b|y_a\,2pz_a> - \sin\alpha <1s_c^{(2)}|g_b|y_a\,2py_a>.$

Only the third integral on the R.H.S. remains to be expressed, -

$$<1s_c^{(2)}|g_b|y_a\,2py_a>$$

$$= \zeta_c^2\mu^{5/2}\frac{e^{\mu\wedge}}{\wedge^4}\sum_{m=0}^{\infty} P_m(\cos\alpha)\left[\frac{2(m+1)(m^2+m-1)}{(2m-1)(2m+3)}(\wedge^2 e_m + \wedge^3 m_m) - \frac{m(m-1)^2}{(2m-1)(2m+3)}(\wedge o_m + \wedge^4 c_m) - \frac{(m+1)(m+2)(m+3)}{(2m+3)(2m+5)}(k_m + \wedge^5 g_m)\right]$$

(31) $<2py_c|f_b|2py_a>$

$= \sin\alpha <1s_c^{(2)}|f_b|y_a\,2pz_a> - \cos\alpha <1s_c^{(2)}|f_b|y_a\,2py_a>$

(32) $<2py_c|g_b|2py_a>$

$= \sin\alpha <1s_c^{(2)}|g_b|y_a\,2pz_a> - \cos\alpha <1s_c^{(2)}|g_b|y_a\,2py_a>$

(33) $<2px_c|f_b|2px_a> = <2px_c|\pi_b|2py_a> = \tfrac{1}{3}<1s_c^{(2)}|f_b|y_a\,2py_a>$

(34) $<2px_c|\pi_b|1s_a>$

$= <1s_c^{(2)}|f_b|2py_a^{(1)}>$, with $\mu^{5/2}$ replaced by $\mu^{3/2}$

(35) $<2px_c|\pi_b|2s_a> = <1s_c^{(2)}|f_b|r_a\,2py_a^{(2)}>$

(36) $<2px_c|\pi_b|2pz_a> = <1s_c^{(2)}|f_b|y_a\,2pz_a>$

(37) $<2pz_c|\pi_b|2px_a>$

$= \wedge <1s_c^{(2)}|f_b|2py_a> - \cos\alpha <1s_c^{(2)}|f_b|y_a\,2pz_a> - \tfrac{1}{3}\sin\alpha <1s_c^{(2)}|f_b|y_a\,2py_a>$

(38) $<2py_c|\pi_b|2px_a>$

$= \sin\alpha <1s_c^{(2)}|f_b|y_a\,2pz_a> - \tfrac{1}{3}\cos\alpha <1s_c^{(2)}|f_b|y_a\,2py_a>.$

Acknowledgements

This work was done during the tenure of a Commonwealth Scholarship at the Mathematical Institute, University of Oxford. I am grateful to Professor C. A. Coulson, F.R.S., for his supervision and many helpful suggestions. I would also like to thank the staff of Oxford University Computing Laboratory for their assistance.

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Appendix

Use of Neumann Expansion for $1/r$: As depicted in Fig. 1, one may use spheroidal coordinates with B and C as foci to obtain a force (f_a) on the third nucleus A. We write

$$f_a = -\text{grad}_a\,(1/r_a) \quad \ldots \quad (\text{A1})$$

where grad_a refers to differentiation with respect to the coordinates of A. Let (ξ_a, η_a, ϕ_a) and (ξ, η, ϕ) represent the spheroidal coordinates of A and any point P respectively. The Neumann expansion for $1/r_a$ is

$$\frac{1}{r_a} = \frac{2}{\lambda_2} \sum_{l=0}^{\infty} \sum_{m=0}^{l} c_{lm} Q_l^m(\xi_>) P_l^m(\xi_<) P_l^m(\eta) P_l^m(\eta_a) \cos m(\phi - \phi_a) \quad \ldots \quad (\text{A2})$$

where

$$c_{lo} = 2l+1\,; \; c_{lm} = (-1)^m\, 2(2l+1)\left[\frac{(l-m)\,!}{(l+m)\,!}\right]^2, \quad m \geqslant 1.$$

$\xi_>$ and $\xi_<$ are the greater and less, respectively, of ξ and ξ_a, and P_l^m, Q_l^m are unnormalized Legendre functions of first and second kinds respectively. Thus, one obtains

$$f_a = -\frac{2}{\lambda_2} \sum_{l=0}^{\infty} \sum_{m=0}^{l} c_{lm}[P_l^m(\xi)P_l^m(\eta) \text{ grad}_a \{Q_l^m(\xi_a)P_l^m(\eta_a) \cos m(\phi-\phi_a)\}$$
$$+Q_l^m(\xi)P_l^m(\eta) \text{ grad}_a \{P_l^m(\xi_a)P_l^m(\eta_a) \cos m(\phi-\phi_a)\}] \quad \text{(A3)}$$

where the first term within the square brackets refers to $\xi < \xi_a$ and the second to $\xi > \xi_a$. Using (A3) one can reduce the original three-centre integral, $<x_b \,|\, f_a \,|\, x_c>$, into an infinite sum of two-centre integrals in spheroidal coordinates. Since the integrals involving $P_l^m(x)$ and $Q_l^m(x)$ die away with increasing l the above infinite sum is expected to converge fairly rapidly.