

On the evaluation of one-centre matrix elements of a modified Coulomb interaction operator

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Abstract. It has been shown that the Fourier transform method can be used to evaluate the one-centre matrix elements of the modified Coulomb operator $(r_{12} + a)^{-1}$ where r_{12} is the interelectronic distance. Four typical integrals of the Coulomb and exchange variety have been explicitly evaluated and their numerical values presented for select values of the parameter a .

Keywords. Coulomb operator ; matrix elements ; Fourier transform method.

1. Introduction

It has been shown recently (Sane *et al* 1979) that the introduction of the 'mean excitation energy' assumption in the Brillouin-Wigner perturbation series, enables exact summation of the infinite series. The resulting expression when applied to the ground state of the helium-like atoms yields the energy shift of the two electron isoelectronic sequence as an expectation value of the operator, $(r_{12} + a)^{-1}$, where $r_{12} (= |\vec{r}_1 - \vec{r}_2|)$ is the inter-electronic distance and a (in atomic units) is the inverse of the mean excitation energy Δ . By treating a as an adjustable parameter, it has been possible to obtain (Jolly *et al* 1980) satisfactory agreement for the ground state energy shifts of ten members of the helium isoelectronic sequence in terms of a single parameter a . It thus appears that the effective Coulomb repulsion operator $(r_{12} + a)^{-1}$ provides a simple prescription for incorporating correlation effects in the framework of an independent particle model.

In order to test this hypothesis further, it is necessary to have a scheme for evaluating matrix elements of the modified Coulomb operator $(r_{12} + a)^{-1}$. This paper is concerned with the computation of the main types of one-centre integrals in the hydrogen orbital basis ; the treatment of two-centre integrals needed for molecular systems shall be discussed elsewhere.

2. Method

There are several well-known methods available for the evaluation of integrals of the type :

$$\langle A(\vec{r}_1) B(\vec{r}_2) | (r_{12} + a)^{-1} | C(\vec{r}_1) D(\vec{r}_2) \rangle, \quad (1)$$

when $a = 0$. For example, if $A = C$ and $B = D$, the integral is proportional to the electrostatic interaction energy of two-charge distributions. It can, therefore, be computed (Pauling and Wilson 1935) by calculating the potential due to one distribution, and then determining the energy of the second distribution in the field of the first. An alternative method that can be used (Margenau and Murphy 1943) when $A \neq B$ and $C \neq D$ introduces r_{12} as an integration variable. A still more general method (Hameka 1967) which does not put any restriction on the nature of the functions consists in expanding r_{12}^{-1} in terms of the Legendre polynomials. However, none of these methods can be used when a is not equal to zero. It turns out that the Fourier transform method, which is also applicable (Hameka 1967) when $a = 0$, is the most convenient one. In what follows, we shall briefly sketch an outline of this method and then apply it to evaluate the main types of one-centre integrals.

The integral in (1) can be written as:

$$I = \int \int f(\vec{r}_1) g(\vec{r}_2) h(r_{12}) d\vec{r}_1 d\vec{r}_2, \quad (2)$$

where the functions f, g and h are readily identifiable. Substituting the definitions given below :

$$p(\vec{r}) = \frac{1}{(2\pi)^3} \int P(\vec{k}) \exp(i\vec{k} \cdot \vec{r}) d\vec{k}, \quad (3a)$$

$$P(\vec{k}) = \int p(\vec{r}) \exp(-i\vec{k} \cdot \vec{r}) d\vec{r}, \quad (3b)$$

$$\text{and } \delta(\vec{k}) = \frac{1}{(2\pi)^3} \int \exp(i\vec{k} \cdot \vec{r}) d\vec{r}. \quad (3c)$$

in equation (2), one gets

$$I = \frac{1}{(2\pi)^9} \int \int \int F(\vec{k}_1) G(\vec{k}_2) H(\vec{k}_3) d\vec{k}_1 d\vec{k}_2 d\vec{k}_3 \\ \times \int \exp[i\vec{r}_1 \cdot (\vec{k}_1 - \vec{k}_3)] d\vec{r}_1 \int \exp[i\vec{r}_2 \cdot (\vec{k}_2 + \vec{k}_3)] d\vec{r}_2 \quad (4)$$

$$= \frac{1}{(2\pi)^3} \int F(\vec{k}) G(-\vec{k}) H(\vec{k}) d\vec{k}. \quad (5)$$

Since we are interested in the matrix elements of the $(r_{12} + a)^{-1}$ operator, we always have

$$h(r_{12}) = (r_{12} + a)^{-1}, \quad (6)$$

and thus

$$\begin{aligned}
 H(\vec{k}) &= \int \frac{1}{r+a} \exp(-i\vec{k} \cdot \vec{r}) d\vec{r} \\
 &= \frac{4\pi}{k} \left[\frac{1}{k} + aU(ka) \right],
 \end{aligned}
 \tag{7}$$

where $U(ka) = \cos ka \operatorname{si}(ka) - \sin ka \operatorname{ci}(ka)$. (7a)

$$\operatorname{si}(x) = - \int_0^{\infty} \frac{\sin t}{t} dt,
 \tag{7b}$$

and $\operatorname{ci}(x) = - \int_0^{\infty} \frac{\cos t}{t} dt$, (7c)

being the well-known sine and cosine integrals (Erdelyi 1954). We shall now discuss the evaluation of I for a few choices of $f(\vec{r})$ and $g(\vec{r})$ using $H(\vec{k})$ given by (7).

3. Evaluation of specific matrix elements

3.1. The Coulomb integral for 1s electrons

The Coulomb-like integral

$$I_{1s,1s} = \langle 1s(\vec{r}_1) 1s(\vec{r}_2) | (r_{12} + a)^{-1} | 1s(\vec{r}_1) 1s(\vec{r}_2) \rangle,
 \tag{8}$$

represents the modified electrostatic repulsion energy of two electrons in the ground state. Here

$$1s(\vec{r}) = \frac{Z^{3/2}}{\pi^{1/2}} \exp(-Zr).
 \tag{9}$$

In the notation of equation (5),

$$\begin{aligned}
 F(\vec{k}) &= G(-\vec{k}) \\
 &= \frac{Z^3}{\pi} \int \exp(-2Zr) \exp(-i\vec{k} \cdot \vec{r}) d\vec{r}, \\
 &= 16Z^4 / (k^2 + 4Z^2)^2,
 \end{aligned}
 \tag{10}$$

Substituting (10), and (7) in (8) one gets:

$$I_{1s,1s} = \frac{5Z}{8} + \frac{512 Z^3 a}{\pi} A_{1s,1s}^e,
 \tag{11}$$

and $A_{1s,1s}^e = \int_0^{\infty} \frac{kdk}{(k^2 + b^2)^4} U(ka)$, (12)

with $b = 2Z$.

To evaluate $A_{1s, 1s}^a$, we note that (Erdelyi 1954)

$$\int_0^{\infty} \frac{ci(yx) \sin xy \cdot x dx}{x^2 + b^2} = -\frac{\pi}{2} \sinh by \operatorname{Ei}(-by), \quad (13a)$$

$$\int_0^{\infty} \frac{si(yx) \cos xy \cdot x dx}{x^2 + b^2} = \frac{\pi}{2} \cosh by \operatorname{Ei}(-by). \quad (13b)$$

It follows therefore that:

$$\begin{aligned} B &\equiv \int_0^{\infty} \frac{U(ka) k dk}{k^2 + b^2} \equiv \pi \exp(ab) \operatorname{Ei}(-ab) \\ &= -\pi \psi(1, 1; ab). \end{aligned} \quad (14)$$

Here $\psi(a, c; x)$ represents the irregular confluent hypergeometric function as in Erdelyi (1954). Clearly :

$$\begin{aligned} A_{1s, 1s}^a &= -\frac{1}{6} \frac{\partial^3 B}{(\partial b^2)^3} = -\frac{\pi a}{16} \left[\frac{3}{b^3} \psi(2, 2; ab) + \frac{6a}{b^4} \psi(3, 3; ab) \right. \\ &\quad \left. + \frac{6a^2}{b^5} \psi(4, 4; ab) \right]. \end{aligned} \quad (15)$$

Combining (15) with (9), we get:

$$\begin{aligned} I_{1s, 1s}^a &= \frac{5z}{8} - \frac{1}{2} a^2 Z^3 [\psi(2, 2; 2za) + 4Za \psi(3, 3; 2za) \\ &\quad + 8Z^2 a^2 \psi(4, 4; 2za)]. \end{aligned} \quad (16)$$

3.2. The coulomb integral for 1s-2s electrons

The following Coulomb integral

$$I_{1s, 2s}^a = \langle 1s(\vec{r}_1) 2s(\vec{r}_2) | (r_{12} + a)^{-1} | 1s(\vec{r}_1) 2s(\vec{r}_2) \rangle \quad (17)$$

represents the modified electrostatic repulsion energy of two electrons which are in the 1s and 2s states respectively. Here

$$2s(\vec{r}) = (Z^3/32\pi)^{1/2} (2 - Zr) \exp(-\frac{1}{2} Zr). \quad (18)$$

The function $F(\vec{k})$ is still given by (10), while $G(-\vec{k})$ is obtained as follows :

$$G(-\vec{k}) = \frac{Z^3}{32\pi} \int \exp(-Zr) \exp(i\vec{k} \cdot \vec{r}) (2 - Zr)^2 d\vec{r}, \quad (19)$$

$$= \frac{Z^4}{(k^2 + Z^2)^2} \left[1 - \frac{3Z^2 - k^2}{k^2 + Z^2} + \frac{3Z^2(Z^2 - k^2)}{(k^2 + Z^2)^2} \right]. \quad (20)$$

Substituting equations (20), (10) and (7) in (17) one gets:

$$I_{1s,2s}^1 = \frac{17z}{81} - \frac{4}{81} az^2 [164\psi(1, 1; az) - 164\psi(1, 1; 2az) - 120aZ\psi(2, 2; az) - 45az\psi(2, 2; 2az) + 72a^2 Z^2\psi(3, 3; az) - 27a^3 Z^3\psi(4, 4; az)]. \quad (21)$$

3.3. The exchange integral for 1s-2s electrons

The following exchange integral

$$I_{1s,2s}^E = \langle 1s(\vec{r}_1) 2s(\vec{r}_2) | (r_{12} + a)^{-1} | 1s(\vec{r}_2) 2s(\vec{r}_1) \rangle, \quad (22)$$

represents the modified exchange energy in the 1s-2s configuration. Using 1s and 2s functions given earlier, the following expression is obtained for $F(\vec{k})$, i.e.

$$F(\vec{k}) = G(-\vec{k}), \\ = \frac{Z^6}{32\pi^2} \int [\exp(-3Zr/2)(2-zr)\exp(i\vec{k}\cdot\vec{r})dr], \quad (23)$$

$$= \frac{64\pi k^2 q}{3(k^2 + q^2)^3}. \quad (24)$$

where $q = 3Z/2$.

Substituting (7) and (24) in (22) yields:

$$I_{1s,2s}^E = \frac{16Z}{729} - \frac{4a^2 Z^3}{243} [3\psi(2, 2; qa) + 6qa\psi(3, 3; qa) + 2q^2 a^2\psi(4, 4; qa) - 16q^3 a^3\psi(5, 5; qa) + 8q^4 a^4\psi(6, 6; qa)]. \quad (25)$$

3.4. The exchange integral for 1s-2p electrons

We now consider a case where one of the functions has angular dependence. The modified exchange energy of the 1s-2p configuration is given by:

$$I_{1s,2p}^E = \langle 1s(\vec{r}_1) 2p(\vec{r}_2) | (r_{12} + a)^{-1} | 1s(\vec{r}_2) 2p(\vec{r}_1) \rangle \quad (26)$$

with $1s(\vec{r})$ given by (9) and

$$2p(\vec{r}) = (Z^3/32\pi)^{1/2} \exp(-Zr/2) Zr \cos \theta. \quad (27)$$

The expression for the function $F(\vec{k})$ for the integral in (26) turns out to be:

$$F(\vec{k}) = -G(-\vec{k}) \\ = \frac{Z^4}{4\pi\sqrt{2}} \int \exp(-i\vec{k}\cdot\vec{r}) \exp(-qr) r \cos \theta d\vec{r} \\ = -\frac{8Z^4 i}{\sqrt{2}} \frac{kq}{(k^2 + q^2)^3}. \quad (28)$$

Table 1. The values of the Coulomb and exchange integrals for $Z = 2$

a	$I_{1s,1s}^C$	$I_{1s,2s}^C$	$I_{1s,2s}^E$	$I_{1s,2p}^E$
0.0	1.2500	0.4197	0.04390	0.03414
0.1	1.0337	0.3913	0.03179	0.02742
0.2	0.9080	0.3698	0.02492	0.02306
0.3	0.8140	0.3518	0.02029	0.01986
0.4	0.7396	0.3363	0.01694	0.01739
0.5	0.6788	0.3226	0.01440	0.01541
0.6	0.6277	0.3103	0.01242	0.01379
0.7	0.5842	0.2992	0.01084	0.01243
0.8	0.5465	0.2889	0.009551	0.01129
0.9	0.5134	0.2796	0.008483	0.01031
1.0	0.4842	0.2709	0.007588	0.009457
1.1	0.4582	0.2628	0.006829	0.008715
1.2	0.4348	0.2552	0.006180	0.008062
1.3	0.4136	0.2482	0.005620	0.007484
1.4	0.3944	0.2415	0.005133	0.006970
1.5	0.3768	0.2353	0.004707	0.006508
1.6	0.3608	0.2294	0.004331	0.006094
1.7	0.3460	0.2238	0.004000	0.005720
1.8	0.3323	0.2185	0.003704	0.005380
1.9	0.3196	0.2135	0.003440	0.005071
2.0	0.3078	0.2087	0.003203	0.004789

Thus after some manipulations, one obtains

$$I_{1s,2p}^E = \frac{112z}{6561} - \frac{4z^3 a^2}{729} [3\psi(2, 2; qa) + 6qa\psi(3, 3; qa) + 6q^2 a^2 \psi(4, 4; qa) - 8q^4 a^4 \psi(6, 6; qa)]. \quad (29)$$

4. Results

A numerical computation of all the one-centre integrals requires evaluation of the irregular confluent hypergeometric function $\psi(a, c; x)$. A special subroutine for doing this has been recently developed (Bhargava *et al* 1980). Utilising this subroutine, the integrals have been computed for various values of the parameter a and the results are given in table 1. The range of a has been restricted to $a \leq 2$ since several estimates (Jolly *et al* 1980) of the mean excitation energy show that a is unlikely to be greater than 2.

References

- Bhargava S C, Raina V and Saxena R P 1980 *Maths. Comput.* (Communicated)
- Erdelyi P 1954 *Integral Transforms* (New York : Mcgraw-Hill) p. 41
- Erdelyi P 1953 *Higher Transcendental Functions* (New York : Mcgraw-Hill) Vol. 1, p. 267
- Hameka H F 1967 *Introduction to Quantum Theory* (New York : Harper and Row) 265 268
- Jolly P, Sane K and Sane K V 1980 *Int. Quant. Chem.* (in press)
- Margenau H and Murphy G M 1943 *The mathematics of physics and chemistry* (Princeton : D Van Nostrand) 382
- Pauling L and Wilson E B 1935 *Introduction of quantum mechanics* (New York : Mcgraw-Hill) p. 446
- Sane K V, Saxena R P and Srivastava P K 1979 *Pramāna* 13 9