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Abstract. We describe a group theoretical method for evaluating hydrogenic two-body radial integrals such as Slater or Marvin integrals. We define a special coupling procedure of the two SO(2, 1) Lie algebras associated with the radial wavefunctions of the two particles. The two-body operators of interest transform like tensor operators of the coupled algebra. The Slater or Marvin integrals can finally be written as a sum of integrals very similar to Slater or Marvin integrals of the simplest possible type, this expansion being very easy to carry out since the coefficients are mainly SO(2, 1) Clebsch–Gordan coefficients (CGC).

1. Introduction

The dynamical (invariance or non-invariance) symmetries of the hydrogen atom have been extensively investigated for a long time (see for example Englefield 1972). However, during many years the impact of these studies on atomic physics remained rather weak. The reason is that the corresponding formalism does not allow us to take advantage of the symmetry properties in the evaluation of the integrals between hydrogenic radial wavefunctions which appear if one utilizes the hydrogenic model as an approximation to the many-electron atom.

   A new approach for dealing with the symmetry properties of the hydrogenic radial wavefunctions was defined by Armstrong (1970, 1971). He introduces an SO(2, 1) Lie algebra acting on the radial wavefunctions only; it appears to be particularly well-adapted to the use of the concept of tensor operator and consequently to the evaluation of radial integrals. However, up to now only one-body integrals have been evaluated by this technique; this is of course an important limitation in the perspective of the study of many-electron atoms. For example, in order to deal with the interelectronic interaction we must be able to evaluate two-body integrals: the Slater integrals (Slater 1929) and, for the internal magnetic interactions, the Marvin integrals (Marvin 1947). Up to now the only group theoretical evaluation of these two-body integrals has been limited to Slater integrals of the type $F^0(nl_1, nl_2)$ (Kumei 1974) (where finite SO(2, 1) transformations were used). The object of this paper is to show that the hydrogenic Slater and Marvin integrals can be calculated in a rather simple and almost quite general way if one uses Armstrong's results and if one defines a convenient coupling procedure for two SO(2, 1) Lie algebras associated with the radial wavefunctions of the two electrons.

2. One-body radial integrals

Armstrong's approach is directly related to the possibility of transforming the hydrogenic radial equation into a factorizable equation of the type B (Infeld and Hull 1951). Then following Miller (1968) the generators of a Lie algebra can be obtained from the ladder operators by introducing a supplementary variable t which has *a priori* no physical meaning. These generators can be written:

$$J_3 = -i\partial_t$$
$$J_\pm = e^{\pm it}[\partial_x \mp b\, e^x \pm (-i\partial_t \pm \tfrac{1}{2})]. \tag{1}$$

They form, with a convenient definition of the scalar product, a realization of the real form SO(2, 1) of the Lie algebra B_1. The basis functions of this realization are

$$\Phi_\nu^\lambda(x, t; b) = e^{i\nu t}\phi_\nu^\lambda(x; b) \tag{2}$$

where the latter functions are solutions of a factorizable equation of the type B:

$$[d^2/dx^2 - b^2\, e^{2x} + 2b\nu\, e^x - (\lambda + \tfrac{1}{2})^2]\phi_\nu^\lambda(x; b) = 0; \tag{3}$$

b is a parameter which characterizes the realization (1), ν is the eigenvalue of J_3 and λ is related to the eigenvalue ω of the Casimir operator of the algebra by $\omega = \lambda(\lambda + 1)$. Furthermore, the normalized solutions of equation (3) are associated, if $b > 0$, with basis functions of bounded-below unitary irreducible representations (UIR) of the type $\uparrow\lambda$ $(\lambda > -\tfrac{1}{2})$, for which the spectrum of J_3 is $\nu = \lambda + 1, \lambda + 2, \ldots$.

The hydrogenic radial equation can be transformed into the form (3) and we can write the radial wavefunctions as

$$R_{nl}(r) = C_{nl}\, e^{x/2}\phi_n^l(x; Z/n) \tag{4}$$

where $x = \ln r$, the constant b of equations (1) can now be identified as $b = Z/n$ and C_{nl} is a normalization constant:

$$C_{nl} = Z(\sqrt{2})n^{-3/2}(2l + 1)^{-1/2}. \tag{5}$$

The tensor operators which are defined as functions of x and t are

$$P_q^K = e^{iqt}\, e^{Kx}. \tag{6}$$

and the integrals of r^k are equal to matrix elements of P^{k+2}. Since the parameter b of equations (1) depends upon n, the Wigner–Eckart theorem can be used directly only for integrals which are diagonal in n. However, for non-diagonal integrals we can obtain a generalization (Crubellier 1974) of the formulae derived in the diagonal case. For this we use the fact that the difference between the generators of two Lie algebras (1) corresponding to different values of the parameter b is a tensor operator with respect to these algebras. The result is very similar to the one obtained by Badawi *et al* (1973), by using the factorization method (type B).

3. Two-body radial integrals

In order to extend these techniques to two-body radial integrals, the simplest procedure would be to use the direct sum of the two single-electron Lie algebras. In this case one has of course to use two independent supplementary variables t_1 and t_2. However it

appears that the interesting two-body integrals do not correspond to tensor operators of this coupled algebra. On the other hand it is possible to use the same t in the two single-electron Lie algebras. In fact it can be shown (Moshinsky 1974, private communication) that t can be interpreted as being the time, in the Schrödinger picture, at least if one considers the pseudo-Coulomb problem which derives from the hydrogenic case by changing r into r/n. Of course if one uses a single t in the two Lie algebras it is no longer possible to form a direct sum, since the two Lie algebras do not commute. However it is possible to define a coupled Lie algebra by

$$J_3 = -i\partial_t \tag{7}$$
$$J_\pm = e^{\pm it}[\partial_{x_1} + \partial_{x_2} \mp b_1 e^{x_1} \mp b_2 e^{x_2} \pm (-i\partial_t \pm 1)]$$

where b_1, x_1 and b_2, x_2 characterize respectively each electron. If we define the scalar product on the space of the functions of x_1, x_2 and t by

$$(\Phi|\Phi') = \int_0^{2\pi} (dt/2\pi) \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \Phi(x_1, x_2, t)^* \Phi'(x_1, x_2, t) e^{\alpha x_1 + \beta x_2} \tag{8}$$

with $\alpha + \beta = 1$, this algebra is a realization (in three variables) of the real Lie algebra, SO(2, 1), which appears to be convenient for the evaluation of hydrogenic two-body radial integrals, in particular for hydrogenic Slater or Marvin integrals.

These integrals are defined by

$$R_{ka}(n_1 l_1, n_2 l_2; n_3 l_3, n_4 l_4)$$
$$= \int_0^{+\infty} dr_1 \int_0^{+\infty} dr_2 R_{n_1 l_1}(r_1) R_{n_2 l_2}(r_2) R_{n_3 l_3}(r_1) R_{n_4 l_4}(r_2) S_{ka} \tag{9}$$

where $S_{ka} = r_<^k / r_>^{k+a}$; $a = 1$ for the Slater integrals and $a = 3$ for the Marvin integrals. By using equations (4), (2) and (8) the general integral (9) can be related to a matrix element by

$$R_{ka}(n_1 l_1, n_2 l_2; n_3 l_3, n_4 l_4)$$
$$= C_{n_1 l_1} C_{n_2 l_2} C_{n_3 l_3} C_{n_4 l_4}$$
$$\times (\Phi_{n_1}^{l_1}(Z/n_1) \Phi_{n_2}^{l_2}(Z/n_2) | e^{i(n_1 + n_2 - n_3 - n_4)t} S'_{ka} | \Phi_{n_3}^{l_3}(Z/n_3) \Phi_{n_4}^{l_4}(Z/n_4)) \tag{10}$$

with $S'_{ka} = e^{kx_<} e^{-(k+1)x_>} e^{(2-\alpha)x_1} e^{(2-\beta)x_2}$.

It is easy to show that the operators $e^{iqt} S'_{ka}$ transform like tensor operators of the coupled Lie algebra (7); the commutation relations of these operators with the generators are exactly those of the P_q^K with $K = 3 - a$, that is:

$$[J_3, e^{iqt} S'_{ka}] = q\, e^{iqt} S'_{ka}$$
$$[J_\pm, e^{iqt} S'_{ka}] = (3 - a \pm q)\, e^{i(q \pm 1)t} S'_{ka}. \tag{11}$$

In order to use this property we must also be able to express the products of single-electron basis functions which appear in the matrix element of equation (10) in terms of basis functions of the coupled algebra. This is easy since the following relation

$$J_\alpha[\Phi_{\nu_1}^{\lambda_1} \Phi_{\nu_2}^{\lambda_2}] = [J_\alpha^1 \Phi_{\nu_1}^{\lambda_1}] \Phi_{\nu_2}^{\lambda_2} + \Phi_{\nu_1}^{\lambda_1}[J_\alpha^2 \Phi_{\nu_2}^{\lambda_2}], \tag{12}$$

holds for the three generators ($\alpha = 3$, $+$ or $-$), even though J_α is not equal to $J_\alpha^1 + J_\alpha^2$. Therefore, if we write as $(\uparrow\lambda_1\nu_1\uparrow\lambda_2\nu_2|\uparrow\lambda\nu)$ the SO(2, 1) CGC involving only bounded-below UIR, the functions defined by

$$\Phi_\nu^{\lambda_1\lambda_2\lambda}(x_1, x_2, t; b_1b_2)$$
$$= \sum_{\nu_1,\nu_2} (\uparrow\lambda_1\nu_1\uparrow\lambda_2\nu_2|\uparrow\lambda\nu)\Phi_{\nu_1}^{\lambda_1}(x_1, t_1; b_1)\Phi_{\nu_2}^{\lambda_2}(x_2, t_2; b_2) \tag{13}$$

are basis functions of the UIR $\uparrow\lambda$ of the coupled algebra. Moreover, if the CGC are orthonormalized we can also write the reciprocal expansion:

$$\Phi_{\nu_1}^{\lambda_1}\lambda_{\nu_2}^{\lambda_2} = \sum_{\lambda,\nu} (\uparrow\lambda_1\nu_1\uparrow\lambda_2\nu_2|\uparrow\lambda\nu)\Phi^{\lambda_1\lambda_2\lambda}_{\ \nu}. \tag{14}$$

If we use this expansion for the bra and ket functions in the matrix element of equation (10), the integral becomes a sum of matrix elements of the type:

$$(\Phi_{n_1+n_2}^{l_1l_1\lambda}(Z/n_1, Z/n_2)|e^{i(n_1+n_2-n_3-n_4)t}S'_{ka}|\Phi_{n_3+n_4}^{l_3l_4\lambda'}(Z/n_3, Z/n_4)). \tag{15}$$

The coupled algebras corresponding to the bra and ket functions are identical only if $n_1 = n_3$ and $n_2 = n_4$ (this is the same difficulty as the one which is encountered for monoelectronic integrals). When these identities are satisfied the Wigner–Eckart theorem can be applied and the matrix element (15) can be written as a product of a ratio of two CGC and of the following particular matrix element:

$$(\Phi_{\lambda+1}^{l_1l_2\lambda}|e^{i(\lambda-\lambda')t}S'_{ka}|\Phi_{\lambda'+1}^{l_3l_4\lambda'}), \tag{16}$$

which contains only 'head' functions, that is basis functions corresponding to the smallest possible eigenvalue of J_3 ($\nu = \lambda+1$) in a given representation $\uparrow\lambda$.

Unfortunately this matrix element is still difficult to evaluate, because the coupled 'head' functions do not have a simple expression. In order to evaluate it we make a second expansion. It can be shown that the coupled 'head' functions can be expressed as a sum of products of uncoupled 'head' functions, the coefficients being essentially SO(2, 1) CGC:

$$\Phi_{\lambda+1}^{l_1l_2\lambda} = \sum (\uparrow l_1\lambda_1+1\uparrow l_2\lambda_2+1|\uparrow\lambda\lambda+1)$$
$$\times \left(\frac{(2l_1+1)(2l_2+1)\Gamma(2\lambda_1+1)\Gamma(2\lambda_2+1)}{(\lambda_1-l_1)!(\lambda_2-l_2)!\Gamma(l_1+\lambda_1+2)\Gamma(l_2+\lambda_2+2)}\right)^{1/2} \Phi_{\lambda_1+1}^{\lambda_1}\Phi_{\lambda_2+1}^{\lambda_2}. \tag{17}$$

Thus we obtain finally only matrix elements of the type:

$$(\Phi_{\lambda_1+1}^{\lambda_1}\Phi_{\lambda_2+1}^{\lambda_2}|e^{i(\lambda_1+\lambda_2-\lambda_3-\lambda_4)t}S'_{ka}|\Phi_{\lambda_3+1}^{\lambda_3}\Phi_{\lambda_4+1}^{\lambda_4}) \tag{18}$$

which are easy to compute because of the very simple form of the functions $\Phi_{\lambda+1}^{\lambda}$:

$$\Phi_{\lambda+1}^{\lambda}(x, t; b) = \Gamma(2\lambda+1)^{-1/2} e^{i(\lambda+1)t} e^{-be^x} e^{x(\lambda+1/2)}. \tag{19}$$

The matrix elements (18) can also be rewritten as integrals in r_1 and r_2 which are (apart from some scale changes in r) very similar to Slater or Marvin integrals of the simplest possible type,

$$R_{ka}(n_1n_1-1, n_2n_2-1; n_3n_3-1, n_4n_4-1), \tag{20}$$

which are easy to compute (see for example Judd 1963). Then finally, having made two expansions (equations (14), (17)), we express the hydrogenic Slater or Marvin integrals as a sum of the very simple integrals of the type (20); the expansions are easy to carry out

because the coefficients are mainly SO(2, 1) CGC (for the computation of these coefficients see for example Holman and Biedenharn 1966, 1968).

It must be noted that for the non-diagonal case (ie $n_1 \neq n_3, n_2 \neq n_4$) it is possible, as for the one-body case, to generalize this type of calculation (Crubellier 1974). This is based on the fact that the difference between the generators of two coupled algebras corresponding to different values of the parameters b_1 and b_2 of equations (7) is a tensor operator with respect to these algebras.

Finally we must also notice that the present group theoretical calculation does not provide a transparent explanation of the various equalities between the Slater integrals which are found in a straightforward numerical computation of these integrals (Butler *et al* 1971). In the present approach these equalities appear to derive from the properties of the integrals of the type (20) which are rather analogous to reduced matrix elements. Up to now these equalities are not explained by the SO(2, 1) symmetry properties of the hydrogenic radial wavefunctions. Some of them have been derived by using the F-type factorization (Savukynas and Čižiunas 1973).

References

Armstrong L Jr 1970 *J. Phys., Paris* **31** Suppl C4–17
—— 1971 *Phys. Rev.* A **3** 1546–50
Badawi M, Bessis N, Bessis G and Hadinger G 1973 *Phys. Rev.* A **8** 727–33
Butler P H, Minchin P E H and Wybourne B G 1971 *Atom. Data* **3** 154–5
Crubellier A 1974 *PhD Thesis* Paris XI Centre d'Orsay
Englefield M J 1972 *Group Theory and the Coulomb Problem* (New York: Wiley)
Holman W J and Biedenharn L C 1966 *Ann. Phys., NY* **39** 1–42
—— 1968 *Ann. Phys., NY* **47** 205–31
Infeld L and Hull T E 1951 *Rev. Mod. Phys.* **23** 21–68
Judd B R 1963 *Operator Techniques in Atomic Spectroscopy* (New York: McGraw-Hill) p 225
Kumei S 1974 *Phys. Rev.* A **9** 2306–11
Marvin H H 1947 *Phys. Rev.* **71** 102–10
Miller W Jr 1968 *Lie Theory and Special Functions* (New York and London: Academic Press)
Savukynas A and Čižiunas 1973 *Lietuv. Fiz. Rink.* **13** 45–50
Slater J C 1929 *Phys. Rev.* **34** 1293–322