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1987 J. Phys. A: Math. Gen. 20 3347

(http://iopscience.iop.org/0305-4470/20/11/037)

J. Phys. A: Math. Gen. **20** (1987) 3347-3352. Printed in the UK

Matrix elements of r^q for quasirelativistic and Dirac hydrogenic wavefunctions†

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Received 16 December 1986

Abstract. Recurrence formulae determining radial matrix elements of r^q between quasi-relativistic hydrogenic wavefunctions are derived. In the diagonal case they are a generalisation of the well known Kramer's relations. The formulae are also transformed to the basis of the Dirac wavefunctions.

1. Introduction

A scalar second-order Schrödinger-like equation which for a single electron in a Coulomb field gives the same energy values as the Dirac equation was derived almost a decade ago by Karwowski and Kłobukowski (1978). In fact it might easily be obtained from much earlier results by Martin and Glauber (1958) and Biedenharn (1962), though the former authors were not aware of this. The scalar hydrogenic equation is a special case of the quasirelativistic (QR) equation of Barthelat *et al* (1980). Relations between the QR theory and the second-order Dirac equation as derived by Biedenharn (1962) were discussed in detail in a recent paper by Karwowski and Kobus (1986) where further references may be found. In particular, very simple formulae expressing the Dirac expectation values in terms of the QR ones have been derived there. On the other hand, the radial hydrogenic QR equation is closely related to its Schrödinger counterpart and, in consequence, methods originally developed in the non-relativistic theory may easily be applied in the QR case.

The hydrogenic radial r^q matrix elements for the non-relativistic case were derived as early as the solutions of the corresponding Schrödinger equation and may be found in many textbooks. In the case of the Dirac wavefunctions the problem is more complicated and attracted some attention recently (see, e.g., Wong and Yeh 1983 and references quoted therein). In the QR case it did not, as yet, receive an adequate treatment. In this paper we derive recurrence formulae which allow the determination of the hydrogenic radial r^q matrix elements between QR wavefunctions. In the diagonal case they correspond to Kramer's relations for the non-relativistic expectation values. The transformation between the QR and the Dirac matrix elements (Karwowski and Kobus 1985, 1986) is applied to obtain a set of useful relations fulfilled by the matrix elements between the Dirac wavefunctions.

† This work has been carried out under research project CPBP. 01.06.

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2. Quasirelativistic radial equation for a hydrogenic atom

The Dirac radial equation for a Coulombic potential in Hartree atomic units can be written as

$$\begin{bmatrix} \mathrm{d}/\mathrm{d}r - k/r & -2/\alpha - \alpha(Z/r + E_{nk}) \\ \alpha(Z/r + E_{nk}) & \mathrm{d}/\mathrm{d}r + k/r \end{bmatrix} \begin{bmatrix} G_{nk} \\ F_{nk} \end{bmatrix} = 0 \tag{1}$$

where G_{nk} and F_{nk} are, respectively, the large and the small components of the wavefunction, E_{nk} is the difference between the total and the rest energy of the electron, Z is the atomic number, α is the fine-structure constant, n is the principal quantum number and k is the quantum number related to the total (j) and orbital (l) angular momentum quantum numbers according to $k = \varepsilon(j + \frac{1}{2}), j = l + \varepsilon/2, \varepsilon = \pm 1$. Equation (1) may be transformed into the second-order form (Karwowski and Kobus 1986)

$$\left[\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{s^2}{r^2} - \frac{2Z(1 + \alpha^2 E_{nk})}{r} - E_{nk}(2 + \alpha^2 E_{nk})\right)\boldsymbol{I} + \frac{1}{r^2}\boldsymbol{M}\right]\begin{bmatrix} G_{nk} \\ F_{nk} \end{bmatrix} = 0 \tag{2}$$

where

$$s = k(1 - \alpha^2 Z^2/k^2)^{1/2} \tag{3}$$

$$\boldsymbol{M} = \begin{bmatrix} -k & -\alpha Z \\ \alpha Z & k \end{bmatrix} \tag{4}$$

and $\boldsymbol{I}$ is the 2×2 unit matrix. Equations (2) may be decoupled by a non-unitary transformation described by the matrix

$$\boldsymbol{A} = c\begin{bmatrix} 1 & -\alpha Z/(k+s) \\ -\alpha Z/(k+s) & 1 \end{bmatrix} \tag{5}$$

where

$$c = (\tilde{n}/Ns)[k(k+s)/2]^{1/2} \tag{6}$$

$$N = (\tilde{n}^2 + \alpha^2 Z^2)^{1/2} \tag{7}$$

and

$$\tilde{n} = n - |k| + |s|. \tag{8}$$

The pair of the decoupled equations is

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \frac{s(s-1)}{\rho^2} - \frac{2Z}{\rho}\right]\Phi_{nk} = 2e_{nk}\Phi_{nk} \qquad k = |k|, -|k| \tag{9}$$

where

$$\rho = r(1 + \alpha^2 E_{nk}) \tag{10}$$

$$e_{nk} = E_{nk}(1 + \alpha^2 E_{nk}/2)/(1 + \alpha^2 E_{nk})^2 \tag{11}$$

and

$$\begin{bmatrix} \Phi_{nk} \\ \Phi_{n-k} \end{bmatrix} = \boldsymbol{A}^{-1}\begin{bmatrix} G_{nk} \\ F_{nk} \end{bmatrix}. \tag{12}$$

Since for bound electron states $E_{nk} = -Z^2/N(N + \tilde{n})$, we have

$$\rho = r\tilde{n}/N \tag{13}$$

and

$$e_{nk} = -Z^2/(2\tilde{n}^2). \tag{14}$$

It is interesting to note that if we define $l^* = |s| - (\varepsilon + 1)/2$ then (9) becomes formally identical with the corresponding Schrödinger equation and its eigenvalues may immediately be written in the form given by (14). Also, in contrast to the first-order Dirac equation, passing to its non-relativistic limit is trivial.

Equations (9) may either be considered as a pair of Dirac second-order equations or as two independent scalar equations. In the former case, the normalisation

$$\langle \Phi_{nk} | \Phi_{nk} \rangle + \langle \Phi_{n-k} | \Phi_{n-k} \rangle = 1 \tag{15}$$

is imposed (this condition is used to derive (6), see Karwowski and Kobus (1986) for details) while in the latter one

$$\langle \Phi^Q_{nk} | \Phi^Q_{nk} \rangle = \langle \Phi^Q_{n-k} | \Phi^Q_{n-k} \rangle = 1. \tag{16}$$

Equation (9), when considered as a scalar equation, is referred to as the quasirelativistic hydrogenic equation and its solutions Φ^Q_{nk}, normalised according to (16), as the quasirelativistic radial wavefunctions.

The resolution of (9) gives (see, e.g., Barthelat *et al* 1980)

$$\Phi^Q_{nk} = \eta r^{\gamma} \, e^{-Zr/N} F(-n+l+1, 2\gamma, 2Zr/N) \tag{17}$$

where

$$\gamma = \begin{cases} s & \text{if } s > 0 \\ -s+1 & \text{if } s < 0 \end{cases} \tag{18}$$

and

$$\eta = \left(\frac{2Z}{N}\right)^{\gamma+1/2} \frac{1}{\Gamma(2\gamma)} \left(\frac{\Gamma(2\gamma+n-l-1)}{2(\gamma+n-l-1)\Gamma(n-l)}\right)^{1/2} \tag{19}$$

is the normalisation constant chosen to fulfil conditions (16).

Applying transformation (5) to the original Dirac equation (1) we get the useful relation (Biedenharn 1962, 1983, Wong and Yeh 1982)

$$\begin{bmatrix} \dfrac{d}{d\rho} - \dfrac{s}{\rho} + \dfrac{Z}{s} & -Z(\tilde{n}^2 - s^2)^{1/2}/s\tilde{n} \\ Z(\tilde{n}^2 - s^2)^{1/2}/s\tilde{n} & \dfrac{d}{d\rho} + \dfrac{s}{\rho} - \dfrac{Z}{s} \end{bmatrix} \begin{bmatrix} \Phi^Q_{nk} \\ \Phi^Q_{n-k} \end{bmatrix} = 0. \tag{20}$$

3. Matrix elements between quasirelativistic wavefunctions

3.1. Expectation values

Let

$$H = -d^2/d\rho^2 + W(\rho) \tag{21}$$

where

$$W(\rho) = s(s-1)/\rho^2 - 2Z/\rho. \tag{22}$$

Then

$$[\rho^{q+1}, H] = q(q+1)\rho^{q-1} + 2(q+1)\rho^{q}\, \mathrm{d}/\mathrm{d}\rho \tag{23}$$

and

$$[\rho^{q}\, \mathrm{d}/\mathrm{d}\rho, H] = q(q-1)\rho^{q-2}\frac{\mathrm{d}}{\mathrm{d}\rho} + 2q\rho^{q-1}\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \rho^{q}\frac{\mathrm{d}W}{\mathrm{d}\rho}. \tag{24}$$

Since

$$\left\langle nk \left| \rho^{q}\frac{\mathrm{d}}{\mathrm{d}\rho} \right| n'k' \right\rangle + \left\langle n'k' \left| \rho^{q}\frac{\mathrm{d}}{\mathrm{d}\rho} \right| nk \right\rangle^{*} = -q\langle nk|\rho^{q-1}|n'k'\rangle \tag{25}$$

where $\langle nk|$ stands for $\langle \Phi^{Q}_{nk}|$, equation (24) gives

$$(q+1)(Z^2/\tilde{n}^2)\langle nk|\rho^{q}|nk\rangle - (2q+1)Z\langle nk|\rho^{q-1}|nk\rangle + \tfrac{1}{4}q[(2s+1)^2 - q^2]\langle nk|\rho^{q-2}|nk\rangle = 0. \tag{26}$$

In the non-relativistic limit $\tilde{n} = n$, $s = k$ and (26) becomes the well known Kramer's relation. (26) may be used to determine all expectation values of ρ^{q} except for $q = -2$. The last value may be derived by direct integration using (17) (see, e.g., Wong and Yeh 1982, Davis 1939).

Matrix elements between Φ^{Q}_{nk} and Φ^{Q}_{n-k} may be obtained from (20). Making use of (25) and (26) we obtain

$$q\langle k|\rho^{q-1}|-k\rangle = Z\frac{(\tilde{n}^2 - s^2)^{1/2}}{s\tilde{n}}[\langle k|\rho^{q}|k\rangle - \langle -k|\rho^{q}|-k\rangle] \tag{27}$$

and

$$\frac{2Z(\tilde{n}^2 - s^2)^{1/2}}{s\tilde{n}}\langle k|\rho^{q}|-k\rangle = \frac{2Z}{s}\langle k|\rho^{q}|k\rangle - (q+2s)\langle k|\rho^{q-1}|k\rangle. \tag{28}$$

Equations (26)-(28) determine in a most simple, recurrent, way all matrix elements of r^{q} between the QR wavefunctions corresponding to the same energy. The explicit formulae for $|q| \leqslant 2$ are as follows:

$$\langle k|r^2|k\rangle = N^2[2 - 6s(s-1) + 10\tilde{n}^2]/(2Z)^2$$

$$\langle k|r|k\rangle = N[3\tilde{n} - s(s-1)/\tilde{n}]/(2Z)$$

$$\langle k|r^{-1}|k\rangle = Z/(N\tilde{n})$$

$$\langle k|r^{-2}|k\rangle = 2|s|(Z/N)^2/[\tilde{n}s(2s-1)]$$

$$\langle k|r^2|-k\rangle = N^2[s^2(6\tilde{n}^2 - s^2 + 1) - \tilde{n}^2(5\tilde{n}^2 - 1)]/[2Z^2\tilde{n}(\tilde{n}^2 - s^2)^{1/2}]$$

$$\langle k|r|-k\rangle = 3N(\tilde{n}^2 - s^2)^{1/2}/(2Z)$$

$$\langle k|-k\rangle = -(\tilde{n}^2 - s^2)^{1/2}/\tilde{n}$$

$$\langle k|r^{-1}|-k\rangle = -Z[(\tilde{n} - |s|)/(\tilde{n} + |s|)]^{1/2}/(N\tilde{n})$$

$$\langle k|r^{-2}|-k\rangle = 0.$$

According to equation (29) of Karwowski and Kobus (1986), the Dirac expectation values may be expressed in terms of the QR ones. Then, after some algebra, we have

$$\langle G_{nk}|\rho^q|G_{nk}\rangle+\langle F_{nk}|\rho^q|F_{nk}\rangle$$
$$=\frac{k\tilde{n}}{2s^2N^2}[(k\tilde{n}+sN)\langle k|\rho^q|k\rangle+(k\tilde{n}-sN)\langle -k|\rho^q|-k\rangle$$
$$-(\alpha Z)^2(\tilde{n}^2-s^2)^{1/2}/(k+s)\langle -k|\rho^q|k\rangle]. \tag{29}$$

3.2. *Off-diagonal matrix elements*

Matrix elements of r^q between the radial QR wavefunctions given by (17) may be determined using the classical method of Gordon (1928). In an explicit form they have been expressed by Wong and Yeh (1982)†. However all these formulations lead to rather complicated equations. Therefore it seems that deriving several simple relations between the matrix elements is of some interest, the more so that all relations between the QR wavefunctions may easily be transformed to the Dirac basis.

Making use of (23), we have

$$(q+1)\left[\left\langle A\left|r^q\frac{\mathrm{d}}{\mathrm{d}r}\right|B\right\rangle-\left\langle B\left|r^q\frac{\mathrm{d}}{\mathrm{d}r}\right|A\right\rangle^*\right]=\langle A|r^{q+1}(W_A-\mathscr{E}_A-W_B+\mathscr{E}_B)|B\rangle \tag{30}$$

where A and B denote two QR wavefunctions

$$W_A(r)=P_A/r^2+Q_A/r \tag{31}$$

$$P_A=s_A(s_A-1) \tag{32}$$

$$Q_A=-2Z\tilde{n}_A/N_A \tag{33}$$

and

$$\mathscr{E}_A=E_A(2+\alpha^2E_A)=-Z^2/N_A^2. \tag{34}$$

After some algebra, from equations (24), (25) and (30), we obtain a general recurrent relation between the QR matrix elements of r^q:

$$(\mathscr{E}_A-\mathscr{E}_B)\langle A|r^{q+1}(\mathscr{E}_A-\mathscr{E}_B-W_A+W_B)|B\rangle+2(q+1)q\langle A|r^{q-1}(\mathscr{E}_A+\mathscr{E}_B-W_A-W_B)|B\rangle$$
$$+(q+1)q(q-1)(q-2)\langle A|r^{q-3}|B\rangle-(q+1)\langle A|r^q[\mathrm{d}(W_A+W_B)/\mathrm{d}r]|B\rangle$$
$$+(q+1)[\langle A|(W_A-W_B)r^q(\mathrm{d}/\mathrm{d}r)|B\rangle$$
$$-\langle B|(W_A-W_B)r^q(\mathrm{d}/\mathrm{d}r)|A\rangle^*]=0. \tag{35}$$

Equation (35) is valid for an arbitrary radial function $W(r)$. In particular, for $A=B$ it is

$$\langle A|r^q(\mathrm{d}W_A/\mathrm{d}r)|A\rangle+2q\langle A|r^{q-1}(W_A-\mathscr{E}_A)|A\rangle=\tfrac{1}{2}q(q-1)(q-2)\langle A|r^{q-3}|A\rangle=0 \tag{36}$$

† Note, however, there is a mistake in this paper. The left-hand side of (3.39) is $S\psi$ rather than ψ. In consequence (3.42) and (3.43) are also in error, the values of the constants being wrong.

giving, for $q=1$, the QR analogue of the non-relativistic virial theorem. Elimination of the terms containing derivatives and substitution of the quantities defined in equations (31)-(33) gives

$$\begin{aligned}\langle A|r^{q-3}q(q+1)\{2(q-1)^2[P_A+P_B-q(q-2)/2]-(P_A-P_B)^2\}\\ +r^{q-2}(2q-1)(q+1)[q(q-1)(Q_A+Q_B)-(P_A-P_B)(Q_A-Q_B)]\\ +r^{q-1}[2q^2(P_A-P_B)(\mathscr{E}_A-\mathscr{E}_B)-(q^2-1)(Q_A-Q_B)^2-2q^2(q^2-1)(\mathscr{E}_A+\mathscr{E}_B)]\\ +r^q(2q+1)(q-1)(\mathscr{E}_A-\mathscr{E}_B)(Q_A-Q_B)\\ -r^{q+1}q(q-1)(\mathscr{E}_A-\mathscr{E}_B)^2|B\rangle=0.\end{aligned} \tag{37}$$

For $q=-1,0,1$ equation (37) leads to the relation

$$(s_A-s_B)(s_A+s_B-1)\langle A|r^{-2}|B\rangle-2Z\left(\frac{\tilde{n}_A}{N_A}-\frac{\tilde{n}_B}{N_B}\right)\langle A|r^{-1}|B\rangle=Z^2\frac{\tilde{n}_A^2-\tilde{n}_B^2}{N_A^2N_B^2}\langle A|B\rangle. \tag{38}$$

In particular, if $\tilde{n}_A=\tilde{n}_B$ and $s_A\neq s_B$ we have

$$\langle nk|r^{-2}|n-k\rangle=0. \tag{39}$$

For the case of $\tilde{n}_A=\tilde{n}_B=\tilde{n}$ and $s_A=-s_B=s$, (37) simplifies to

$$\begin{aligned}(q^2-1)(4s^2-q^2)\langle nk|\rho^{q-2}|n-k\rangle-4Zq(2q+1)\langle nk|\rho^{q-1}|n-k\rangle\\ +(4Z^2/\tilde{n}^2)q(q+1)\langle nk|\rho^q|n-k\rangle=0.\end{aligned} \tag{40}$$

Another set of useful relations results from equation (20). After simple but rather tedious manipulation involving equations (25) and (30) we obtain the off-diagonal counterpart of equation (28):

$$\begin{aligned}\frac{2Z}{s_BN_B}(\tilde{n}_B^2-s_B^2)^{1/2}(q+1)\langle A|r^q|-B\rangle\\ =-(\mathscr{E}_A-\mathscr{E}_B)\langle A|r^{q+1}|B\rangle+\left(\frac{2Z\tilde{n}_B}{s_BN_B}(q+1)+Q_A-Q_B\right)\langle A|r^q|B\rangle\\ -[(q+2s_B)(q+1)-P_A+P_B]\langle A|r^{q-1}|B\rangle\end{aligned} \tag{41}$$

where $|-B\rangle$ stands for the wavefunction defined by the quantum numbers n_B and $-k_B$.

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