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Algebraic solution for the hydrogenic radial Schrödinger equation: matrix elements for arbitrary powers of several r-dependent operators

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Abstract. Recurrence formulae determining radial matrix elements of r^s, $r^s(\ln r)^k$ and $r^s\, \mathrm{d}^n/\mathrm{d}r^n$ between hydrogenic wavefunctions are derived using ladder operators together with the hypervirial theorem. The closed-form expressions are well suited to computing diagonal and off-diagonal matrix elements for any values of the n and l quantum numbers and can easily be programmed on a hand calculator.

1. Introduction

The use of algebraic methods in quantum mechanics has been especially useful in the calculation of the spectrum and the transition matrix elements for certain systems [1–6]. The basic idea of the simplest version of this approach is to generate all the states by successive applications of certain ladder operators which modify the wavefunction quantum numbers in such a way as to cover the whole spectrum. The hypervirial theorem has also been used previously to calculate recurrence relations of matrix elements of different potentials [7–8], but despite its power it was always found necessary to use quantum mechanical sum rules [9] or the Hellmann–Feynman theorem [10] to determine initial matrix elements, and the resulting relationships between diagonal and off-diagonal matrix elements are complicated and often difficult to derive. In this paper, we describe a simple procedure based on the joint use of the hypervirial theorem and of ladder operators to calculate matrix elements of some functions of r between radial hydrogenic wavefunctions of different n and l quantum numbers.

We believe the equations obtained in this paper are, unlike the equations in the literature [11–15], easily handled with no deterioration in the numerical results even for high values of n, l and the power for any matrix element. The present technique has been used before for the harmonic and Morse oscillators, but this is the first time for the hydrogen atom. Our equations can be used to calculate both diagonal and off-diagonal matrix elements, and initial matrix elements may be found from the results given in the appendix.

2. The method

The hydrogen-like radial Schrödinger equation is (in Hartree units)

$$\frac{\mathrm{d}^2 u_{nl}}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2}\, u_{nl} + \frac{2Z}{r}\, u_{nl} = \varepsilon_n u_{nl}. \tag{2.1}$$

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The eigenvalues and eigenvectors, respectively, are

$$\varepsilon_n=\frac{-Z^2}{n^2} \qquad u_{nl}=N_{nl}\rho_n^{l+1}\exp(-\tfrac{1}{2}\rho_n)L_{n-l-1}^{2l+1}(\rho_n) \tag{2.2}$$

where $\rho=2Zr/n$, L_{n-l-1}^{2l+1} is the associated Laguerre polynomial and N_{nl} the normalization constant,

$$N_{nl}=\left(\frac{(n-l-1)!}{2n(n+l)!}\right)^{1/2}. \tag{2.3}$$

The computation of matrix elements $\langle n'l'|\hat{O}(r)|nl\rangle$ between solutions $u_{nl}(r)$ of hydrogen-like Schrödinger equations is of particular interest in quantum physics. In this present work we shall refer specifically to the $\langle u_{n'l'}|r^s|u_{nl}\rangle$, $\langle u_{n'l'}|r^s(\ln r)^k|u_{nl}\rangle$ and $\langle u_{n'l'}|r^s\,\mathrm{d}^n/\mathrm{d}r^n|u_{nl}\rangle$ matrix elements.

2.1. Ladder operators

Considering (2.1) as an F-type factorization problem [2], we can derive the ladder operators which act on the l quantum number ($l\neq 0$):

$$L^+=\frac{n(l+1)}{Z[n^2-(l+1)^2]^{1/2}}\left(\frac{l+1}{r}-\frac{Z}{l+1}-\frac{\mathrm{d}}{\mathrm{d}r}\right) \tag{2.4}$$

$$L^-=\frac{nl}{Z[(n^2-l^2)]^{1/2}}\left(\frac{l}{r}-\frac{Z}{l}+\frac{\mathrm{d}}{\mathrm{d}r}\right). \tag{2.5}$$

The action on the wavefunction u_{nl} is given by $L^+u_{nl}=u_{n,l+1}$ and $L^-u_{nl}=u_{n,l-1}$, being $L^+u_{n,n-1}=0$.

3. Matrix elements between radial hydrogenic wavefunctions

3.1. Calculation of $\langle u_{n'l'}|r^s|u_{nl}\rangle$ matrix elements

Using (2.4) and (2.5) to derive expressions for the r^s and the differential operators in terms of $L^+(l)$ and $L^-(l)$, we obtain the recursion relations

$$\langle r^{s-2}\rangle_{n'l',nl}=\frac{A^+}{2l+1}\langle r^{s-1}\rangle_{n'l',nl+1}+\frac{A^-}{2l+1}\langle r^{s-1}\rangle_{n'l',nl-1}+\frac{Z}{l(l+1)}\langle r^{s-1}\rangle_{n'l',nl} \tag{3.1}$$

$$\begin{aligned}\left\langle r^{s-1}\frac{\mathrm{d}}{\mathrm{d}r}\right\rangle_{n'l',nl}&=\frac{-A^+}{2}\langle r^{s-1}\rangle_{n'l',nl+1}+\frac{A^-}{2}\langle r^{s-1}\rangle_{n'l',nl-1}\\&\quad+\frac{Z}{2l(l+1)}\langle r^{s-1}\rangle_{n'l',nl}+\tfrac{1}{2}\langle r^{s-2}\rangle_{n'l',nl}\end{aligned} \tag{3.2}$$

where

$$A^+=\frac{Z[n^2-(l+1)^2]^{1/2}}{n(l+1)} \qquad \text{and} \qquad A^-=\frac{Z(n^2-l^2)^{1/2}}{nl}. \tag{3.3}$$

Defining H and H' as two hydrogen-like Hamiltonians that belong to the same or distinct hydrogenic atom, we can write

$$\langle n'l'|[H'r^s-r^sH]|nl\rangle=\Delta\varepsilon\langle r^s\rangle_{n'l',nl}. \tag{3.4}$$

Expanding the left side of (3.4),

$$[-\Delta l+s(s-1)]\langle r^{s-2}\rangle_{n'l',nl}+2s\left\langle r^{s-1}\frac{\mathrm{d}}{\mathrm{d}r}\right\rangle_{n'l',nl}+2\Delta Z\langle r^{s-1}\rangle_{n'l',nl}=\Delta\varepsilon\langle r^{s}\rangle_{n'l',nl} \tag{3.5}$$

where $\Delta l=l'(l'+1)-l(l+1)$, $\Delta Z=Z'-Z$ and $\Delta\varepsilon=\varepsilon_{n'}-\varepsilon_n$.

Now, using the ladder operators, (2.4) and (2.5), on $u_{n'l'}$ instead of u_{nl}, we derive two more equations which are analogous to (3.1) and (3.2). Moreover, interchanging $|nl\rangle$ and $|n'l'\rangle$ in (3.4) we obtain another equation, this time analogous to (3.5). In total we have a set of six recursion relations which permit us to eliminate inconvenient matrix elements and then to derive two new expressions that connect powers of the r operator for any value of the n and l quantum numbers,

$$\begin{aligned}\left(Z\frac{s+l'+1}{l(l+1)}-\frac{Z'}{l'+1}\right)\langle r^{s-1}\rangle_{n'l',nl}&+\frac{s-l+l'}{2l+1}A^{+}\langle r^{s-1}\rangle_{n'l',nl+1}\\&+\frac{s+l+l'+1}{2l+1}A^{-}\langle r^{s-1}\rangle_{n'l',nl-1}-A'^{+}\langle r^{s-1}\rangle_{n'l'+1,nl}=0\end{aligned} \tag{3.6}$$

and

$$\begin{aligned}\left(\frac{-Z}{l+1}+Z'\frac{s+l+1}{l'(l'+1)}\right)\langle r^{s-1}\rangle_{n'l',nl}&+\frac{s+l-l'}{2l'+1}A'^{+}\langle r^{s-1}\rangle_{n'l'+1,nl}\\&+\frac{s+l'+l+1}{2l'+1}A'^{-}\langle r^{s-1}\rangle_{n'l'-1,nl}-A^{+}\langle r^{s-1}\rangle_{n'l',nl+1}=0.\end{aligned} \tag{3.7}$$

Using (3.6) and (3.7), we can evaluate all the $\langle n'l'|r^s|nl\rangle$ matrix elements from the initial elements $\langle n'n'-1|r^s|nn-1\rangle$, which can be calculated as shown in the appendix. The strictly diagonal case ($Z=Z'$, $n=n'$ and $l=l'$) can easily be solved by means of the diagonal hypervirial theorem with the operators r^s and $r^s\,\mathrm{d}/\mathrm{d}r$,

$$\langle u_{nl}|[H,r^s]|u_{nl}\rangle=0\qquad\left\langle u_{nl}\left|\left[H,r^s\frac{\mathrm{d}}{\mathrm{d}r}\right]\right|u_{nl}\right\rangle=0. \tag{3.8}$$

Then, from (3.8), following the recursion relation

$$(s-1)[-\tfrac{1}{2}s(s-2)+2l(l+1)]\langle r^{s-3}\rangle_{nl}-2(2s-1)Z\langle r^{s-2}\rangle_{nl}+2s\varepsilon_n\langle r^{s-1}\rangle_{nl}=0 \tag{3.9}$$

which, together with that obtained from the Hellmann–Feynman theorem,

$$\langle r^{-2}\rangle_{nl}=\frac{Z^2}{n^3(l+\frac{1}{2})} \tag{3.10}$$

enables one to calculate the expectation values of all powers of r.

3.2. Calculation of $\langle u_{n'l'}|r^s\,\mathrm{d}^n/\mathrm{d}r^n|u_{nl}\rangle$

From (3.5) we can obtain the matrix elements of the first derivative in terms of those corresponding to the r^s operator, and also derive simply the following known results:

$$\left\langle\frac{\mathrm{d}}{\mathrm{d}r}\right\rangle_{nl}=0\qquad\left\langle r\frac{\mathrm{d}}{\mathrm{d}r}\right\rangle_{nl}=-\tfrac{1}{2}\qquad\langle r^{-2}\rangle_{nl',nl}=0. \tag{3.11}$$

For the nth derivative we must combine (2.4) and (2.5) to obtain the general equation which relates two consecutive derivatives,

$$\left\langle r^s \frac{\mathrm{d}^n}{\mathrm{d}r^n}\right\rangle_{n'l',nl} = -\frac{lA^+}{2l+1}\left\langle r^s \frac{\mathrm{d}^{n-1}}{\mathrm{d}r^{n-1}}\right\rangle_{n'l',nl+1} + \frac{l+1}{2l+1}A^-\left\langle r^s \frac{\mathrm{d}^{n-1}}{\mathrm{d}r^{n-1}}\right\rangle_{n'l',nl-1} + \frac{Z}{l(l+1)}\left\langle r^s \frac{\mathrm{d}^{n-1}}{\mathrm{d}r^{n-1}}\right\rangle_{n'l',nl}. \tag{3.12}$$

To apply this equation, the $\langle r^s\rangle_{n'l',nl-1}$ matrix elements must be known previously.

3.3. Calculation of $\langle u_{n'l'}|r^s(\ln r)^k|u_{nl}\rangle$

As

$$r^s(\ln r)^k = \frac{\partial^k}{\partial s^k} r^s \tag{3.13}$$

successive derivatives of (3.6) and (3.7) yield two separate recursion relations:

$$\begin{aligned}
&+\frac{Zk}{l(l+1)}\langle r^{s-1}(\ln r)^{k-1}\rangle_{n'l',nl} + \left(-\frac{Z'}{l'+1}+\frac{Z(s+l'+1)}{l(l+1)}\right)\langle r^{s-1}(\ln r)^k\rangle_{n'l',nl}\\
&\quad+\frac{A^+k}{2l+1}\langle r^{s-1}(\ln r)^{k-1}\rangle_{n'l',nl+1} + \frac{A^+(s-l+l')}{2l+1}\langle r^{s-1}(\ln r)^k\rangle_{n'l',nl+1}\\
&\quad+\frac{A^-k}{2l+1}\langle r^{s-1}(\ln r)^{k-1}\rangle_{n'l',nl-1} + \frac{A^-(s+l+l'+1)}{2l+1}\langle r^{s-1}(\ln r)^k\rangle_{n'l',nl-1}\\
&\quad-A'^+\langle r^{s-1}(\ln r)^k\rangle_{n'l'+1,nl} = 0
\end{aligned} \tag{3.14}$$

and

$$\begin{aligned}
&\frac{Z'k}{(l'+1)l'}\langle r^{s-1}(\ln r)^{k-1}\rangle_{n'l',nl} - \left(\frac{Z}{l+1}-\frac{Z'(s+l+1)}{l'(l'+1)}\right)\langle r^{s-1}(\ln r)^k\rangle_{n'l',nl}\\
&\quad+\frac{kA'^+}{2l'+1}\langle r^{s-1}(\ln r)^{k-1}\rangle_{n'l'+1,nl} + \frac{A'^+(s+l-l')}{2l'+1}\langle r^{s-1}(\ln r)^k\rangle_{n'l'+1,nl}\\
&\quad+\frac{kA'^-}{2l'+1}\langle r^{s-1}(\ln r)^{k-1}\rangle_{n'l'-1,nl} + \frac{A'^-(s+l+l'+1)}{2l'+1}\langle r^{s-1}(\ln r)^k\rangle_{n'l'-1,nl}\\
&\quad-A^+\langle r^{s-1}(\ln r)^k\rangle_{n'l',nl+1} = 0.
\end{aligned} \tag{3.15}$$

In this case the initial matrix elements $\langle r^{s-1}(\ln r)^k\rangle_{n'n'-1,nn-1}$ can be calculated as shown in (A5) in the appendix.

4. Conclusions

We have derived closed-form expressions for the matrix elements of several r-dependent operators between radial hydrogenic wavefunctions which are valid for any value of the n and l quantum numbers. For the cases of $r^s(\ln r)^k$ and $r^s\,\mathrm{d}^n/\mathrm{d}r^n$ this is the first time that recursion relations to calculate the matrix elements of any value of the power and of the order of the derivative have been published. Our recursion relations work by the following form: we set n and n' and using (A3) and (A4) we calculate the initial matrix element with $l' = n' - 1$ and $l = n - 1$; next from (3.6) and (3.7) (for the r^s case) we could derive matrix elements with $l' = n' - 2, \ldots, 0$ and $l = n - 2, \ldots, 0$. The next step should be started with the same l' value but with $l = n - 2$, and to use again (3.6) and (3.7). Repeating the process, we can obtain all the matrix elements for any value of n, l and s. The same recursive scheme should be used for the other operators. In all cases, our recursion formulae are very easy to handle and, using an appropriate algebraic processor, explicit formulae can be obtained for specific matrix elements.

Appendix

The hydrogenic wavefunctions when $l = n - 1$ have the form

$$u_{n,n-1} = N_{n,n-1}\rho_n^n \exp\left(-\frac{\rho_n}{2}\right) \tag{A1}$$

so, to calculate the matrix elements of r^s, we must solve the integral

$$\langle n'n'-1|r^s|nn-1\rangle = \int_0^\infty \rho_n^n \rho_{n'}^{n'} r^s \exp\left(-\frac{(\rho_n + \rho_{n'})}{2}\right) \mathrm{d}r. \tag{A2}$$

This is carried out by change of variable to $(\rho_n + \rho_{n'})/2 = (Zn + Z'n')/nn'$ and we get a known integral, which permits us to obtain the following result:

$$\langle n'n'-1|r^s|nn-1\rangle = N_{n,n-1}N_{n',n'-1}\frac{(2Z/n)^n(2Z'/n')^{n'}}{[(Zn+Z'n')/nn']^{\nu}}\Gamma(\nu+1) \tag{A3}$$

where $\nu = n + n' + s$.

From (A3) we can derive a most useful relationship,

$$\langle n'n'-1|r^{s+1}|nn-1\rangle = \frac{(n+n'+s+1)nn'}{Zn+Z'n'}\langle n'n'-1|r^s|nn-1\rangle. \tag{A4}$$

Taking the kth derivative with respect to s of (A4), we obtain

$$\langle n'n'-1|r^s(\ln r)^k|nn-1\rangle = \sum_{i=0}^{k-1}\binom{k-i}{i}\psi^{i)}(\nu)\langle n'n'-1|r^s(\ln r)^{k-i-1}|nn-1\rangle \tag{A5}$$

where $\psi^{i)}$ represents the ith derivative of the digamma function ψ [16], with ψ^0 being

$$\psi^0(\nu) = \psi(\nu) - \ln\left(\frac{Zn+Z'n'}{n+n'}\right). \tag{A6}$$

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