

The electron-electron interaction in doubly-excited states of atoms

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Abstract. Doubly-excited states of the isoelectronic sequence of H^- , in which both electrons are in high principal quantum numbers, are examined on the basis of alternative pictures of the correlations between the two electrons. Restricting ourselves to the lowest 1S states with both electrons in principal quantum number n , we parametrise the electron-electron interaction on the basis of these pictures and compare the resulting simple expressions with more elaborate numerical calculations. This provides further understanding of the nature of correlations in such states.

Keywords. Doubly-excited states; angular correlations; radial correlation; O_4 symmetry; high orbital angular momentum.

1. Introduction

This paper is part of a continuing study of electron-electron correlations in high doubly excited states of atoms (Rau 1983 and 1984). Its focus is on alternative parametrisations of the electron-electron interaction $1/r_{12}$ in such states. The emphasis is on the systematics of such doubly-excited states, particularly with increasing excitation that approaches the double ionization limit of the atom.

In these higher reaches of an atomic spectrum, the number of independent particle states that are mixed together by $1/r_{12}$ diverges. Conventional calculations in terms of basis sets that are products of single particle functions lead to parametrisation of $1/r_{12}$ in terms of Slater integrals. When both electrons are in a high principal quantum number n , the number of Slater integrals increases with a proportionality to n^3 , making for formidable numerical complexity of the calculations. For this reason, it seems desirable to get alternative renderings of $1/r_{12}$. These simpler parametrisations are not only useful for computations involving such states but, more importantly, they contribute to our understanding of the nature of electron correlations in such two-electron states.

This paper is divided into two main sections, reflecting the two types of correlations, angular and radial, that prevail in doubly-excited states. Section 2 deals with angular correlations which arise dominantly from mixing of states with the same n . By analysing different pictures of the angular correlation between the electrons, new light is cast on the expressions for $1/r_{12}$ that were previously derived on the basis of group theoretical considerations of the symmetry of this operator. Section 3 deals with the organization of states of different n into a novel kind of Bohr-Rydberg series that describes the pair of electrons as a single tightly-correlated (both angular and radial) entity.

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2. Angular correlations within an n -manifold

For simplicity, we restrict our treatment to the simplest two-electron system, the isoelectronic sequence of H^- , and to states of $^1S^e$ symmetry with both electrons in a principal quantum number n . Mixing of states with different values of n is, of course, important at very high n when the spacing between different hydrogenic n levels becomes very small. But, at least for $n \leq 10$, the main focus of this section, we can set aside this mixing across in n . However, the mixing of different $(n\ell)^2$ states within the n -manifold is important from the start because these states are degenerate in the initial description of independent particle hydrogenic functions. This section concentrates, therefore, on angular correlations represented by the mixing of $(n\ell)^2$ values. The mixing of different n 's which we do not consider here constitutes instead a radial correlation. We return to this in §3.

A model that has proved successful in describing the angular correlations between two electrons in a constant n -manifold treats the $1/r_{12}$ interaction as having the approximate symmetry of an SO_4 group which is based on the total angular momentum, $\mathbf{L} = \ell_1 + \ell_2$, and the difference between Runge-Lenz vectors of the electrons, $\mathbf{B} = \mathbf{b}_1 - \mathbf{b}_2$ (Wulfman 1973; Sinanoglu and Herrick 1975; Crance and Armstrong 1982). These studies have shown that the operator r_{12}^2 for $L = 0$ states can be written on the basis of this symmetry as (Herrick *et al* 1980; Crance and Armstrong 1982)

$$r_{12}^2 = (3n^2/2) [(11i^2/2) + (5n^2/6) + (19/6)], \quad i = 0, 1, \dots, n-1, \quad (1)$$

where i labels the n different 1S eigenvectors in the manifold. The $1/r_{12}$ operator is then simply constructed by taking the inverse square root of (1).

The lowest eigenvector, $i = n-1$, within each n manifold is of particular interest because both experimentally (Buckman *et al* 1983) and theoretically (see a review: Fano 1983) it is the one that is dominantly excited. The expression in (1) reduces in this case to

$$\langle r_{12}^2 \rangle^{(SO_4)} = (n^2/2)(19n^2 - 33n + 26). \quad (2)$$

[We will use atomic units throughout this paper except when specified otherwise.] To understand what this means in terms of angular correlations between the electrons we will examine this, and alternative results for the lowest eigenvalue, on the basis of different models of the correlation and compare with the results of accurate numerical calculations. A more extensive study of all n eigenvalues and, therefore, the dependence of $1/r_{12}$ on i , will be reported elsewhere.

As a first model for angular correlations between the electrons, we note that several studies of high-lying doubly-excited states and the vicinity of the double ionization limit have emphasized that the two electrons lie on opposite sides of the positively charged core. This is immediately plausible because the electron-electron repulsion between two slow electrons can be expected to drive them to such a configuration. In the limit of a delta function distribution, $\delta(\pi - \theta_{12})$, where θ_{12} is the angle between the radius vectors, the various angular momentum states are equally likely so that the weight W_ℓ , or the probability of each $(n\ell)^2$ state, is given by

$$W_\ell^{(\delta)} = (2\ell + 1)/n^2. \quad (3)$$

The superscript δ denotes that this is the probability for a delta function peaking at $\theta_{12} = \pi$ and will distinguish $W_\ell^{(\delta)}$ from the alternative W_ℓ considered below. With the

weights in (3) we have, therefore,

$$\langle r_{12}^2 \rangle^{(g)} = \sum_{\ell=0}^{n-1} W_{\ell}^{(g)} \langle r_1^2 + r_2^2 + 2r_1 r_2 \rangle. \quad (4)$$

Upon substituting on the right side the values of $\langle r_j^2 \rangle$ and $\langle r_j \rangle$ appropriate to hydrogenic orbitals (Landau and Lifshitz 1977, equation (36.16)) and carrying out the summations, we get

$$\langle r_{12}^2 \rangle^{(g)} = (40n^4 + 22n^2 + 1)/6. \quad (5)$$

Another picture of angular correlations, closely linked to the above in that the electrons are at a mutual angle of $\theta_{12} = \pi$ exactly at the double ionization limit, but different in that at energies away from this limit there are departures from such a sharp peaking, is provided by the Wannier theory for double ionization near threshold. Both experimentally (Cvejanovic and Read 1974) and theoretically (Rau 1976), it has been noted that the distribution around $\theta_{12} = \pi$ is of a Gaussian shape with a width proportional to $E^{1/4}$, where E is the energy measured from the threshold. It has been shown more recently that although several ℓ values are mixed as before, the $E^{1/4}$ dependence of the width in angles implies that the dominant mixing stretches only to values of $\ell \sim E^{-1/4}$. Further, this result has been connected to the picture of SO_4 symmetry by showing that the mixing coefficients for $(n\ell)^2$ provided by SO_4 have this dependence of ℓ values that scale as $n^{1/2}$. For the lowest eigenvalue, the weight of each $(n\ell)^2$ is given by (Rau 1984)

$$W_{\ell}^{(SO_4)} = (2\ell + 1)(2n - 1) [(n - 1)!]^4 [(n + \ell)!(n - \ell - 1)!]^{-2}. \quad (6)$$

To obtain an expression for r_{12}^2 with these weights, we evaluate (4) again but with $W_{\ell}^{(SO_4)}$ instead of $W_{\ell}^{(g)}$. A simpler expression in place of (6), namely (Rau 1984),

$$W_{\ell}^{(SO_4)} \simeq [2(2\ell + 1)/n] \exp[-2\ell(\ell + 1)/n], \quad (7)$$

which is a very good approximation at large n particularly over the range of values where (6) is appreciable, proves more convenient. Together with approximating certain sums by integrals, we now obtain

$$\langle r_{12}^2 \rangle^{(SO_4)} \simeq (n^2/2)(19n^2 - 6n + 5/2). \quad (8)$$

Considering the approximations made in its evaluation, (8) is in good agreement with (2). In particular, both have the dominant dependence $(19n^4/2)$ to be contrasted with the $(20n^4/3)$ of $\langle r_{12}^2 \rangle^{(g)}$ in (5). The above derivation of $\langle r_{12}^2 \rangle^{(SO_4)}$ exemplifies that the nature of the angular correlations in the lowest state as described by the SO_4 scheme corresponds to the distribution of $(n\ell)^2$ values according to (6).

The energy of the lowest 1S state in each n manifold of H^- can now be written down as

$$E_n = -(1/n^2) + 1/\langle r_{12}^2 \rangle^{1/2}, \quad (9)$$

where E_n is the energy measured from the double ionization limit. Table 1 contrasts the results obtained upon using (2) and (5) in (9) with numerical calculations of E_n within the n -manifold. In these numerical calculations, labelled "S.I." in the table, all the relevant Slater integrals were calculated with hydrogenic functions and then the matrix of $1/r_{12}$ between the $(n\ell)^2$ states diagonalized to determine the eigenvalues.* Although

* I am indebted to Prof. R J W Henry for these numerical results for $n = 1-10$ and to Dr Charles W Clark for the results for $n = 18$.

Table 1. Binding energies $-E_n$ (in eV) of the lowest 1S state of H^- within each n manifold. The columns labelled δ and SO_4 are the results obtained with the electron-electron interaction taken from (5) and (2) respectively. They are compared with results in the third column obtained through a full numerical diagonalization of the states within the manifold, the basis states for $(n\ell)^2$ being chosen to be products of hydrogenic functions.

n	(δ)	(SO_4)	(S.I.)
2	4.34	3.60	3.46
3	1.886	1.728	1.681
4	1.053	1.017	0.986
5	0.672	0.668	0.649
6	0.465	0.473	0.454
7	0.342	0.351	0.337
8	0.261	0.272	0.260
10	0.167	0.176	0.168
18	0.052	0.055	0.053

superficially the $E_n^{(\delta)}$ values for larger n seem closer to $E_n^{(SI)}$ than $E_n^{(SO_4)}$, this could be misleading. Note that the entries for $E_n^{(\delta)}$ cross those for $E_n^{(SI)}$ around $n = 10$. In terms of the n -dependence, therefore, our conclusion is that $E_n^{(SO_4)}$ provides a better description. In any case, by the time we approach these larger n values, $n > 20$, all the entries in table 1 become deficient because the restriction to states within the same n -manifold, which amounts to ignoring radial correlation, can be expected to break down. In the next section, we will look at an alternative picture of two-electron states which does not neglect radial correlation.

3. Rydberg series of levels

We have considered so far each n -manifold individually. In this paper, we have looked only at the lowest 1S state within each manifold but other studies, particularly on the basis of SO_4 symmetry, have also similarly restricted themselves to one n -manifold at a time even when they have looked at all the n 1S states with $i = 0, 1, \dots, n-1$. These studies (Herrick *et al* 1980) have considered systematics of the states *within* a manifold; for instance, the n 1S states from a pattern of a one-dimensional vibrator, with $(n-1-i)$ serving as a vibrational quantum number. We consider instead in this section a different kind of systematics, namely that *across* in n .

A recent study (Rau 1983) showed that highly correlated doubly excited states form a novel Rydberg progression in which the pair is viewed as a single entity in the six-dimensional space of coordinates relevant to its description. The energies of the states fit a six-dimensional Bohr-Rydberg formula and converge to the double ionization limit:

$$E_n = -4 \left(Z - \frac{1}{4} - \sigma \right)^2 / \left(n + \frac{3}{2} - \mu \right)^2, \quad n = 1, 2, \dots; \quad (10)$$

Z is the nuclear charge and σ and μ are constants. The only experimental evidence for high doubly-excited states is in the He^- system (Buckman *et al* 1983) and the observed states were in fact shown to conform to (10) (Rau 1983). There is no similar experimental information in either H^- or He but accurate numerical calculations are available for 1S states in these atoms for $n \leq 5$ (Herrick *et al* 1980, Lipsky *et al* 1977; Oberoi 1972). We draw upon these except for the $n = 2$ state where experimental data are available (Schultz 1973).

Table 2 gives the lowest 1S states for each n as described by the six-dimensional formula (10) and compares with the essentially "exact" numerical values available for $n \leq 5$. The results of SO_4 theory and the Slater integral calculation of §2 are repeated from table 1 for purposes of comparison. As in the previous study for He^- (Rau 1983), the six-dimensional formula gives a very good description of the pattern across in n . The difference between it and the results in the SO_4 and S.I. columns can be taken as an index of the radial correlation which is absent in these models which work within an n manifold.

The values of the "correlation constant" σ and the quantum defect μ in (10) were fixed by a study of the numerical calculations (Lipsky *et al* 1977) of doubly-excited states in the two-electron isoelectronic sequence with $Z \leq 5$:

$$\sigma = \frac{1}{2}Z - 0.164, \quad (11a)$$

$$\mu = (3/2)[1 - (1/10Z)]. \quad (11b)$$

In table 3 we compare the results of the six-dimensional formula (10) for the four states in He where accurate numerical calculations are available with the results obtained from the SO_4 expression in (2), suitably scaled by $(1/Z^2) = 1/4$.

Finally, it is of interest to examine the dependence of the various results for asymptotically large Z and for the lowest state ($n = 1$) of the two-electron system. In this limit, when correlations become negligible, we should expect to recover the well-

Table 2. Binding energies $-E_n$ (in eV) of the lowest 1S states of H^- as obtained by the SO_4 and Slater integral calculations (same as in table 1) which are restricted to an n manifold compared with results from the six-dimensional Rydberg formula in (10) and (11). The last column gives accurate results available from experiment or detailed numerical calculations.

n	SO_4	S.I.	Equation (10)	"Exact"
2	3.60	3.46	4.042	4.04
3	1.728	1.681	1.883	1.886
4	1.017	0.986	1.085	1.085
5	0.668	0.649	0.705	0.704
6	0.473	0.454	0.494	
7	0.351	0.337	0.366	
8	0.272	0.260	0.281	
10	0.176	0.168	0.181	
18	0.055	0.053	0.057	

Table 3. Similar to table 2 but for the lowest 1S states of He .

n	(SO_4)	Equation (10)	"Exact"
2	20.8	21.12	21.11
3	9.50	9.62	9.61
4	5.44	5.48	5.49
5	3.51	3.53	3.54

known result of a screened charge ($Z - 5/16$), that is,

$$E_1 = -(Z - 5/16)^2 \simeq -Z^2 + (0.625)Z.$$

The six-dimensional formula in (10) and (11) gives the closely related

$$E_1 = -Z^2 + (0.644)Z,$$

whereas the SO_4 result in (2) gives

$$E_1 = -Z^2 + (0.408)Z.$$

In the limit of large n and again asymptotically large Z , the two expressions become very similar, the six-dimensional formula giving

$$E_n = -Z^2 + (0.344)Z,$$

and (2) leading to

$$E_n = -Z^2 + (0.324)Z.$$

4. Conclusions

By looking at the most tightly bound 1S state in each n -manifold, with both electrons having principal quantum number n , we have shown that angular correlations between the electrons as described by the $(n\ell)^2$ distribution given in (6) accounts for the representation of $1/r_{12}$ for such states developed on the basis of SO_4 group symmetry. On the other hand, these lowest states with differing n are also organized into a different pattern, namely, a Bohr-Rydberg series converging to the double ionization limit. The relevant Rydberg formula in (10) also incorporates the radial correlation between the two electrons and is in conformity with the Wannier theory for two-electron states in the vicinity of the double ionization limit.

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