Group-Theoretic Approach to Two-Electron Correlations in Atoms

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We suggest that group-theoretic techniques may be useful for studying two-electron correlations in atoms. We show that matrix elements of the Coulomb interaction for doubly excited states of the ^1S configuration can be approximated by a constant plus a pairing term. The latter gives rise to a highly correlated state similar to a Cooper pair in the electron gas. It may be identified with the state that leads to the Wannier threshold law for the escape of two electrons from a Coulomb core.

Several phenomena in atomic physics appear to be dominated by two-electron correlations. Among others, we mention the properties of the ground states of negative ions and of doubly excited states in atoms and ions.[1] With one major exception,[2] the traditional route for calculating properties of such states has been through the use of a single-particle basis, within which matrix elements of the residual Coulomb interaction e^2/r_{12} are calculated. For strongly correlated states, this route leads to large configuration mixing calculations. The purpose of this note is to suggest an alternative approach, based on group-theoretic techniques. Although the mathematical aspects of our approach are different from that of Ref. 2, which uses hyperspherical coordinates, the physical motivation of focusing on the joint motion of the two electrons is similar. As a result, our work provides a complementary algebraic description to the geometrical one using hyperspherical coordinates; our correlated state shares many properties with that obtained in Ref. 2.

Group-theoretic techniques are not new in atomic physics. Racah[3] used them to analyze states of the $(nl)^N$ configurations. His calculations were extended by Jahn, Flowers, and others and are

well summarized by Judd.[4] More recently, the group O(4) has been used for classifying doubly excited states[5-7]. The approach we suggest here is closer in spirit to Racah's than to that of Refs. 5, 6, and 7, since we do not emphasize, at this stage, possible symmetries of the electron-electron interaction, but rather present a scheme for performing calculations in a way more economical than the conventional one in terms of Slater integrals.

In order to introduce our technique, we begin by considering the problem of two electrons in hydrogenic levels with principal quantum number n and coupled to total spin (S) and angular momentum (L) equal to zero, i.e., ^1S states. In the conventional approach, one introduces a hydrogenic basis $|nl\rangle$, expands the Coulomb interaction as

$$\frac{e^2}{r_{12}} = \frac{e^2}{r_>} \sum_{k=0}^{\infty} \left(\frac{r_<}{r_>}\right)^k P_k(\cos\theta_{12}), \qquad (1)$$

where $r_<$ ($r_>$) is the lesser (greater) of r_1 and r_2 and θ_{12} is the angle between the two radius vectors, and evaluates matrix elements of Eq. (1) in the basis $|(nl)^2 \, ^1S\rangle$. This evaluation involves some Racah algebra and the Slater integrals, $R^k(ll, l'l')$. With hydrogenic wave functions, the integrals R^k can be evaluated in closed form and tables exist[8] for $n \leq 4$. The final result is

$$\langle (nl)^2 \, ^1S | r_{12}^{-1} | (nl')^2 \, ^1S \rangle = R^0(ll, ll)\delta_{ll'} + (-)^{l+l'}[(2l+1)(2l'+1)]^{1/2} \sum_{k \neq 0} \begin{pmatrix} k & l & l' \\ 0 & 0 & 0 \end{pmatrix}^2 R^k(ll, l'l') . \qquad (2)$$

Matrix elements evaluated in this way for $n = 2$–4 are shown in Table I, column 3. At any n, there are $n(n+1)/2$ matrix elements and, in their determination, one needs $n(n+1)(n+2)/6$ independent Slater integrals. It is clear that the bookkeeping involved in these calculations grows explosively with increasing n.

Consider instead the group-theoretic approach to the same problem. Since the n^2 components of the hydrogenic basis $|nl\rangle$, $l = n-1, n-2, \ldots, 1, 0$ span an n^2 dimensional space, the group structure

TABLE I. Matrix elements of $\langle(nl)^2{}^1S|e^2/r_{12}|(nl')^2{}^1S\rangle$ in atomic units (27.21 eV), calculated with a product of hydrogenic functions. The last column is the prediction within the $O(n^2)$ expansion in Eq. (7); in each case, the first two entries are fitted to determine A and B in this equation.

n	l, l'	Calculated	$O(n^2)$ scheme
2	0,0	0.3008	0.3008
	1,1	0.4366	0.4366
	0,1	−0.1016	−0.1150
3	0,0	0.1328	0.1328
	1,1	0.1726	0.1726
	2,2	0.2150	0.2124
	0,1	−0.0488	−0.0346
	0,2	0.0204	0.0472
	1,2	−0.0512	−0.0774
4	0,0	0.0746	0.0746
	1,1	0.0938	0.0938
	2,2	0.1062	0.1130
	3,3	0.1288	0.1321
	0,1	−0.0282	−0.0166
	0,2	0.0138	0.0214
	0,3	−0.0062	−0.0254
	1,2	−0.0324	−0.0372
	1,3	0.0132	0.0440
	2,3	−0.0286	−0.0568

of the problem is[4] $U(n^2) \times U_S(2)$, where $U_S(2)$ refers to the spin. Since we consider, for the moment, only states with $S = 0$ we shall neglect the spin part, $U_S(2)$, altogether and concentrate our attention on the orbital part, $U(n^2)$. A technique which has found useful applications in other fields of physics where similar problems arise is that of expanding the interaction, in this case $1/r_{12}$, in terms of invariant operators (Casimir operators) of all the group chains which start from $U(n^2)$ (the head group) and end with the rotation group $O(3)$ (the tail group).[9,10] If all operators are retained, then this is only a different way of recasting the expansion (2). The importance of this technique lies in the fact that often a few terms in the expansion are sufficient to describe the interaction well. For the problem at hand, we consider the group chain $U(n^2) \supset O(n^2) \supset \ldots$ $\supset O(3)$ [where the dots indicate all possible ways of breaking $O(n^2)$ down to $O(3)$], and retain only two terms in the expansion,

$$e^2/r_{12} = A\underline{1} + B\underline{P}_{n2} + \cdots . \tag{3}$$

Here $\underline{1}$ is the unit operator and $\underline{P}_{n2}$ is the pairing operator of $O(n^2)$. This operator is, apart from

a constant, equal to the quadratic Casimir operator of $O(n^2)$, $\underline{C}_2(O_{n2})$.[11] The pairing operator $\underline{P}_{n2}$ can be written explicitly in terms of creation and annihilation operators for electrons. Introducing the operators

$$Q_+ = \tfrac{1}{2}\sum_l (-)^l (a_{l,1/2}{}^\dagger \cdot a_{l,1/2}{}^\dagger) ,$$

$$Q_- = \tfrac{1}{2}\sum_l (-)^l (\tilde{a}_{l,1/2} \cdot \tilde{a}_{l,1/2}) , \tag{4}$$

one has

$$\underline{P}_{n2} = 2Q_+ Q_- , \tag{5}$$

In Eq. (4), the dot is a shorthand notation for contraction both with respect to spin and to orbital angular momentum[4] and $\tilde{a}_{l,1/2,m_l,m_s} = (-)^{l-m_l+1/2-m_s} \times a_{l,1/2,-m_l,-m_s}$. With the appropriate normalization, the matrix elements of the operator $\underline{P}_{n2}$ are given by

$$\langle(nl)^2{}^1S|\underline{P}_{n2}|(nl')^2{}^1S\rangle$$
$$= (-)^{l+l'}[(2l+1)(2l'+1)]^{1/2} . \tag{6}$$

For a single configuration, the operators Q_+ and Q_- are identical to the quasispin operators.[4] The introduction of Q_+ (Q_-) in Eq. (4) can be viewed as a generalization of quasispin to mixed configurations.[12] An important point in the definition in Eq. (4) is the alternating phase $(-)^l$. It is well known from the structure of Lie groups that quasispin operators for mixed configurations can be defined with or without this phase. The physical problem at hand dictates which choice must be made and it is clear from Table I that the appropriate choice here is that given in Eq. (4). The role of such a $(-)^l$ factor in the early attempts to get a O(4) classification for doubly excited states was noted in Ref. 5.

Combining Eqs. (3) and (6) we have

$$\left\langle(nl)^2{}^1S\left|\frac{e^2}{r_{12}}\right|(nl')^2{}^1S\right\rangle$$
$$= A\delta_{ll'} + B(-)^{l+l'}[(2l+1)(2l'+1)]^{1/2} . \tag{7}$$

In column 4 of Table I we show the values of the matrix elements calculated using Eq. (7). In each case, the first two matrix elements are fitted to extract A and B and then all others are predicted by Eq. (7). Even though there are discrepancies in some of the off-diagonal matrix elements (which are small) by as much as a factor of 4, the results are, nevertheless, striking, considering that at any n only two parameters have been adjusted to obtain the entire set of numbers. In fact, they indicate that the two

terms in Eq. (3) describe the bulk of the interaction. Deferring to a later paper improvements in the fit by including more terms in the expansion (3), we now turn to examine some implications of the results of Table I.

The structure of Eq. (3), a constant plus a pairing term, appears in many fields of physics and it is responsible for the occurrence of collective pair states. One tightly correlated state splits off from the remaining ones ("plasma mode"). In nuclear physics, where the residual interaction is attractive, the correlated pair state moves down in energy and it becomes the ground state.[13] This state is the analog of a Cooper pair in the electron gas. Here, where the residual interaction is repulsive, we expect the correlated state to move up in energy. This is shown in Table II. The actual eigenvalues obtained by diagonalizing the exact Coulomb matrix are shown in column 2. In column 3 we show the results obtained in the $O(n^2)$ scheme. Here all but one state remain at energy A. The collective pair state moves to energy $A + B\sum_l (2l+1) = A + Bn^2$. Although the $O(n^2)$ scheme overestimates the energy shift, it is clear from Table II that a collective mode is formed, since the spacing between the highest eigenvalue and the one below it is comparable to the entire spread of all but the highest state. It is very intriguing to suggest that the state which peels off from the rest is related to the state that dominates the threshold process of double electron emission,[14-16] which we call the Wannier state.[17] If that is so, the way in which the Wannier state will evolve will depend only on the behavior of the coefficients A and B with increasing n. From the general ideas of quantum-defect theory, we expect these coefficients to have an expansion in $1/n$, starting

with $1/n^2$. The calculated values of A for $n = 2-4$ seem to be described well by a $1/n^2$ scaling. Given the limited set of numbers it is less clear whether the coefficient B starts with $1/n^2$ or $1/n^3$. Our emphasis on A and B and their n dependence stems from the fact that, physically, the most correlated two-electron state is the one near threshold. The group-theoretic analysis of the electrons as a pair should, therefore, be most suited to describing this state which will exhibit the highest symmetry. Looking down the rest of the family of doubly excited states with decreasing n, there will be a gradual weakening of this symmetry with more terms in the expansion (3) being required for their accurate description. We also note that the configuration mixing involved in describing a ^1S doubly excited state stretches to include different n values for the electrons: However, the mixings are strongest within the same n because they are diagonal in the energy. This motivates why we concentrate on this situation and our belief that symmetries will then be most easily uncovered.

The technique presented here for ^1S states can be extended to include other states. In a study of the experimental data available on $n = 2$ and $n = 3$ doubly excited states of the He isoelectronic sequence, a rotorlike spectrum for states of different L has been noted.[7] Within the framework discussed here this spectrum would arise, for example, by including in addition to the quadratic Casimir operator of $O(n^2)$, the quadratic Casimir operator of $O(3)$, i.e.,

$$e^2/r_{12} = A\underline{1} + B\underline{P}_{n^2} + C\underline{C}_2(O_3), \qquad (8)$$

where $\langle \underline{C}_2(O_3) \rangle = L(L+1)$. The behavior of the coefficient C with n will provide some interesting insight into the way in which the rotorlike structure evolves for large n. Our results, to be presented elsewhere, show that C has a $1/n^3$ dependence. This conforms to the understanding that L is relatively unimportant for the Wannier state.[14,17]

In conclusion, we have presented here a group-theoretic technique based on the expansion of the interaction into invariant operators. The virtue of this technique is that the expansion may be rapidly converging, thus giving rise to major simplifications in the calculations. These simplifications are particularly important when many configurations must be admixed (n large). Although we have applied here this technique only to the study of correlations in two-electron configurations, $(nl)^2$, it is clear that the same tech-

TABLE II. Eigenvalues in atomic units of the Coulomb matrices of Table I. The third column is the prediction of the $O(n^2)$ scheme.

n	Calculated	$O(n^2)$ scheme
2	0.4894	0.5000
	0.2460	0.2344
3	0.2648	0.2928
	0.1570	0.1128
	0.0986	0.1128
4	0.1686	0.2186
	0.1086	0.0650
	0.0738	0.0650
	0.0526	0.0650

nique can also be used for studying correlations in multielectron configurations. For example, matrix elements of the pairing operator P_{n2} can be easily constructed[11] for configurations of the type $(nl)^N$, $N > 2$. This may lead to considerable simplifications in the calculation of the structure of complex atoms.

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